

The Chemistry of Unsaturated Ethylene-Propylene-Based Terpolymers

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I. INTRODUCTION

A. The Evolution of α -Olefins Elastomers

The study of Ziegler-Natta catalysts has shown their versatility of application with several monomers, thus for the first time, the synthesis of new polymers having new properties has been possible (Natta et al., 1955; Natta 1964).

In the case of α -olefins, crystalline polymers having a stereoregular structure have been largely investigated (Natta, 1959), but amorphous polymers, having a prevalent regular head-to-tail enchainment, have also been obtained (Natta et al., 1965a). The latter polymers, charac-

terized by an aspecific structure, i.e., by the presence in the chain of sequences of a mmrrmr type *, show an elastomeric behavior which can be compared with the performance of other hydrocarbon elastomers, for instance, polyisobutylene, the α -olefin elastomer well-known at the time of the early work on coordination polymerization. Notwithstanding the presence of only one alkyl group in the α -olefin monomeric unit, which would favor the mobility of the chain segments and hence the flexibility of the whole chain, the dynamic properties of amorphous poly- α -olefins are not satisfactory because their second order transition is too high (-20°C in the case of amorphous polypropylene and -65°C in the case of polyisobutylene).

On the other hand, the use of more flexible polymer chains as the polyethylenic one for producing elastomers finds a sharp limit in the high tendency of polyethylene to crystallize. To overcome this disadvantage, the introduction of irregularities in the chains was attempted through chlorination, sulfur-chlorination and chlorophosphonation (Bruzzone and Crespi, 1960; Crespi and Bruzzone, 1961a,b; Natta et al., 1960a; Portyanskii and Naiberg, 1968; Leonard et al., 1961). Unfortunately, in order to destroy the high crystallinity of polyethylene, a high content of chlorine in the macromolecules (about 30 wt%) is necessary. The resulting elastomers show good behavior only under slow deformations. Furthermore, they have a high density, low flexibility, and the polar groups of different chains tend to associate, hence the dynamic properties are not excellent.

The facile synthesis of random ethylene- α -olefins copolymers by means of Ziegler-Natta catalysts (Natta et al., 1963b) is equivalent to substituting, statistically, hydrogen atoms of the polyethylene chains with alkyl groups. When the content of α -olefin in copolymer is close to 25 mole %, and the distribution of methyl groups is random, polyethylene crystallinity is practically absent and the resulting amorphous copolymer shows very interesting dynamic properties. In fact, fast cycles of deformation are accompanied by low dissipation of mechanic energy. Such behavior can be attributed to the presence of methylenic sequences which allow a higher mobility of the chains than in amorphous poly- α -olefins; moreover, the glass transition temperature is low, even though dependent on the copolymer composition (Natta and Crespi, 1960).

*We prefer the stereochemical notation proposed by Frisch et al. (1966) as unambiguous and more concise instead of the classical method using the conventional symbols, i.e., *ddd* or *lll*, *ddl* or *lld* and *dld* or *ldl* for, respectively, isotactic, heterotactic and syndiotactic triads (Zambelli et al., 1967).

The very interesting properties of ethylene-propylene copolymers coexist with the virtual absence of unsaturation in the chains. Therefore, before their utilization (vulcanization) of these materials the crosslinking process must be carried out in an unconventional way, for instance with peroxides (Crespi and Bruzzone, 1959; Natta et al., 1961a; Di Giulio and Ballini, 1962; Rabinson et al., 1962).

The traditional processes of vulcanization can be used when a limited amount of unsaturation is present in the ethylene-propylene chains. Initially this target was pursued through controlled chlorination of the copolymer, followed by dehydrochlorination (Crespi and Bruzzone, 1961b).

Successively it was shown that the more convenient way to unsaturated ethylene-propylene-based elastomers is the synthesis of terpolymers which utilize, as third monomer, dienes (or, more generally, polyenes) which are able to enter the ethylene-propylene backbone and to cross-link under usual vulcanization processes with sulfur and accelerators.

Since, for the most part, the termonomers initially employed were dienes, the abbreviation EPDM (American Society for Testing and Materials, 1970) was introduced (Ethylene-Propylene-Diene-Monomers) to distinguish this new class of rubbers from other elastomeric products based on α -olefins, for instance EPM, the ethylene-propylene copolymer. Obviously the term is not correct when used to describe ethylene-propylene-based terpolymers having, as termonomer, a molecule with more than two unsaturations or functionality other than ethylenic. However, the abbreviation is wide-spread and it will be used also in this review.

The broad interest in EPDM's is documented by an enormous number of patents (Magovern, 1970; Ranney, 1970) which deal mainly with termonomers, catalyst systems, polymerization conditions, finishing operations, processes, and applications. The scientific literature contains many papers related, prevailingly, to the study of physical and technological properties of EPDM's, before and after vulcanization, whereas, relatively little attention has been devoted to the synthesis of these elastomers. Recently some reviews have been published on the synthesis and general properties of ethylene-propylene copolymers (Crespi et al., 1964; Natta et al., 1969; Pasquon et al., 1967; Phung et al., 1967; Valvassori and Cameli, 1969) and they contain also some concise information on particular EPDM's.

The purpose of the present review is to supply a survey of the work carried out up to the end of 1973 and devoted to the synthesis and physicochemical characterization of EPDM's. The survey will be sup-

plemented by recent results (Arrighetti et al., 1971; Cesca et al., 1973, 1974a, b, c) obtained in the author's laboratory, on the mechanism of EPDM synthesis and on new classes of terpolymers which contain a system of conjugated double bonds.*

B. Early Researches and General Characteristics of Termonomers and EPDM's

The early syntheses of EPDM's were carried out at the time of the first work on ethylene-propylene copolymerization (Belg. Pat. 1957, 1959, 1960; Brit. Pat. 1955a, 1956b). The possibility of terpolymerizing ethylene, an α -olefin, and a third unsaturated monomer was assumed to be valid also for comonomers containing more than one center of unsaturation. Unfortunately, the choice of the third monomer was made having little knowledge of the behavior of dienes (in particular conjugated dienes) during α -olefins copolymerization. Furthermore, at that time, the same copolymerization process began only to be studied and little information was available on the general properties of the elastomer obtained.

It was evident during the investigation that, in order to guarantee a good elastomeric behavior from the resulting terpolymer, the third monomer of EPDM had to copolymerize homogeneously (i.e., avoiding the formation of homopolymers and binary copolymers) and statistically (i.e., avoiding the presence of long sequences of any monomer).

Successively it was shown that these fundamental points could be accomplished when suitable termonomers, such as dicyclopentadiene (Brit. Pat. 1956c, 1957a, 1957b) or 1,4-hexadiene (Brit. Pat. 1955c, 1956a), were used. As general rule, a good termonomer should have two double

*When the manuscript of this work had been completed, an exhaustive review on EPDM's appeared (Baldwin and Ver Strate, 1972). The publication is mainly concerned with the characterization and technological evaluation of both EPM and EPDM materials. In fact, vulcanization, vulcanizate analysis, compounding and processing, vulcanizate properties, applications, and specific compounding, are the titles of some chapters. By contrast, our work is mainly devoted to the chemistry of EPDM's and restricted, when possible, to ethylene-propylene-based terpolymers.

However, we have been able to insert in our own text some new results presented in the aforesaid work and concerning our arguments.

More recently another review on EPDM has been published (Stelianu, 1971). The article is rather generic and quite short to adequately treat the general characteristics, synthesis, properties, and vulcanization of EPDM's. The paper is based on 14 references (articles and patents) which appeared before 1967.

bonds of different reactivity, the former being very reactive toward Ziegler-Natta catalysts to ensure a ready incorporation of the third monomer into the terpolymer chains, the latter being as unreactive as possible during the terpolymerization reaction.

In practice, an appropriate choice of the third monomer reduces slightly the rate of terpolymerization with respect to the copolymerization rate, has little effect on the MW of EPDM, and modifies slightly the reactivity of the principal comonomers. Other important features of a satisfactory termonomer are: high levels of utilization in the polymerization stage; no polymerization activity of the residual unsaturation (to avoid branching and gel), but good reactivity toward the vulcanizing agents.

Obviously every termonomer possesses to a different degree the general requirements specified above. However, several compounds are known which can furnish EPDM's having the fundamental properties of ethylene-propylene copolymers. This conclusion might seem quite obvious because EPDM's contain not very high amounts of unsaturation, generally less than 10 wt % of third monomer. Actually, such a level of a third component influences some properties of the resulting EPDM (e.g., T_g see Fig. 1). It will be seen in Section III B 7, that by employing termonomers which show very high reactivity in the residual unsaturation, low levels (ca. 1 wt %) of third monomer introduce a sufficient reactivity for the curing process. At the same time, low contents of termonomer modify minimally the excellent physical and chemical properties of the ethylene-propylene copolymer chains.

The principal termonomers so far described will be examined in detail in successive sections. It is useful to summarize here the fundamental properties of ethylene-propylene-based elastomers (Natta et al., 1963b): low density; excellent resistance to oxidation, ozone, heating and chemical agents; low permeability to vapors and permeability to gases; good electric properties; a very low brittle point. Also their mechanical properties, stress relaxation, and viscoelastic behavior are excellent. In Table I some properties of six vulcanized terpolymers are compared with typical diene-based rubbers. The inherent low cost of the olefinic monomers and the large growing potential market for these elastomers contribute in classifying EPDM's among the more interesting synthetic rubbers obtained so far (Chem. Eng. News et al., 1973).

Despite the good general properties of EPDM now stressed, it should be emphasized that, more recently, new types of EPDM have been developed for use in new areas, in particular in the field of covulcanization with highly unsaturated elastomers (Blümbel, 1968; Filburn and

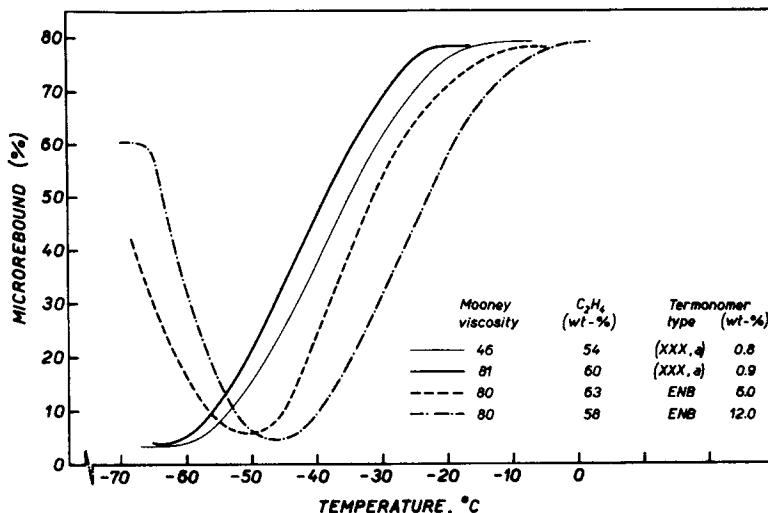


Fig. 1. Microrebound vs. temperature curves for some EPDM's and EPTM's. Symbols as in Table I.

Spenadel, 1970; Kerrutt et al., 1969; Samuels and Wirth, 1967 a,b; Satake et al., 1971a; Schroeder, 1971). The type of unsaturation introduced in EPDM chains by the third monomer is decisive in influencing the cross-linking process, but the concentration of unsaturation also plays an important role. Therefore, by choosing a suitable type and concentration of termonomer it is possible to synthesize EPDM's having a high rate of vulcanization (Ghetti et al., 1969; Shaw, 1968; Stemmer, 1966, 1968; Morgan, 1968) and good behavior in covulcanization with *cis*-1,4-polyisoprene, *cis*-1,4-polybutadiene or styrene-butadiene copolymer.

II. GENERAL PROBLEMS RELATED TO THE SYNTHESIS AND CHARACTERIZATION OF EPDM'S

Apart from the industrial processes of EPDM's which will be reviewed in another section (cf. Section VII), it is important to examine some general problems connected with the synthesis and the characterization of ethylene-propylene-based terpolymers obtained on a laboratory scale. Such problems are, in part, common to the synthesis of ethylene-propylene copolymers because they are due to the gaseous nature of olefinic

TABLE I
Comparison of Some Properties of Vulcanizates Obtained from EPDM's^a, EPTM's^b and Other Typical Dienic Rubbers^c

Type of termonomer ^d	1,4-HD	DCP	EPDM ^d	EPTM ^d	DMPNB	MCNM	NR ^e	SBR ^f	BR ^g
Termonomer content (mole/kg)	0.35	0.40	0.35	0.40	0.26	0.10	—	—	—
C ₈ H ₆ (wt %)	38	32	35	45	38	50	—	—	—
Mooney viscosity (1 + 4 at 100°C)	82	80	95	80	46	70	—	—	—
Tensile strength (kg/cm ²)	248	264	235	270	229	230	268	245	193
Elongation at break (%)	460	420	360	485	510	375	520	540	540
300% Modulus (kg/cm ²)	130	170	194	124	113	180	126	108	81
Hardness, Shore A	70	73	75	65	70	67	62	62	61

^aAfter Valvassori and Cameli, 1969.

^bCf. Section III B.

^cBasic compound: rubber 100; HAF black 50; naphthenic oil 5; AO 1.

^dRecipe: ZnO 5; TMTMS 1.5; sulfur 1.5; stearic acid 1; MBT 0.5; vulcanization time 60 min; T = 153°C.

^eRecipe: stearic acid 3; ZnO 3; sulfur 2; Nobs Special 0.5; time 30 min; T = 153°C.

^fRecipe: ZnO 3; stearic acid 2; sulfur 1.75; Santocure 1.2; other conditions as in ^e.

^gRecipe: as in ^e, except Nobs Special 0.9 instead of Santocure

1,4-HD = 1,4-hexadiene; DCP = dicyclopentadiene; MTHI = 6- and 7-methyl-4,5,8,9-tetrahydroindene; IPTHI = 1-isopropylidene-3a,4,7,7a-tetrahydroindene; DMPNB = dimethyl-5-pentadienyl- or 5-pentenyl-2-norbornene derivatives, i.e., compounds (XXXIII-XXXIV) of Section III B 6; MCNM = methylcyclopentadienyl-5-norborn-2-enyl-methane, i.e., compound (XXX, a) of Section III B 5.

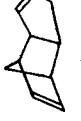
monomers and to the particular behavior of the catalyst systems employed. However in the case of EPDM's, some relevant complications arise, due to the presence of termonomer and its reactivity, both during the polymerization and during the finishing or analytical stages.

From a general point of view, terpolymerization studies should establish a quantitative correlation between the terpolymer composition and the concentration of monomers in the feed by means of the terpolymerization equations, in order to deduce, on a quantitative basis, the indexes of reactivity (reactivity ratios). The terpolymerization equations have been theoretically derived for radical terpolymerization, omitting the assumption of the steady state (Ham, 1964) and in a limited number of cases they have been experimentally verified.

In ionic terpolymerization some reasonable assumptions have been proposed (Valvassori and Sartori, 1967) in order to simplify the complicated theoretical equations, but these relationships have not been utilized yet in the case of EPDM's. Only in a recent paper (Christman and Keim, 1968) was an attempt made to relate the reactivity of several termonomers to propylene reactivity. An order of relative reactivity between different dienes was obtained (see Table II). However, it should be noted that the results of Table II were obtained on the basis of four main assumptions, namely:

1. Ethylene and propylene behave ideally, i.e., the rate of addition of a monomer to a growing chain is independent of the last unit incorporated. This means that $r_{C_2H_4} r_{C_3H_6} = 1$, but the assumption is an approximation because other results (Natta et al., 1969) indicate that for several vanadium-based catalysts $r_{C_2H_4} r_{C_3H_6} < 1$.
2. Dienes react equally well with ethylene or propylene. This assumption does not find support in the evidence that most of the initiation occurs with ethylene, both in the case of EPM (Valvassori et al., 1962) and EPTM (Cesca et al., 1968a), and on some preliminary values of individual rate constants in regard to the addition of propylene to growing chains ending in different monomeric units (Baldwin and Ver Strate, 1972).
3. The relative reactivity of propylene to ethylene is not influenced by the presence of the third monomer. Even this assumption disagrees with several experimental observations (see Section IV) according to which the ratio of ethylene to propylene in the polymer changes when the diene is present. In the absence of precise data (see Section II A) it seems unlikely to attribute the observed changes to the variation of monomer concentration in the feed, due to the (general-

TABLE II
Value of Reactivity Ratio for Various Dienes^a

Compound ^b	Name	Abbreviation	Reactivity ratio ^{c,d}			
			A	B	C	D
	<i>endo</i> -dicyclopentadiene	<i>endo</i> -DCP	7.6	7.3		
	<i>exo</i> -dicyclopentadiene	<i>exo</i> -DCP	14.4			
	1,2- <i>endo</i> -dihydrodicyclopentadiene	DHDCP		6.8 ^e		
RH	2-norbornene	NB		16.5 ^e		
RCH=CH₂	5-vinyl-2-norbornene	VNB	5.8	5.1		
RCCI=CH₂	5-(chlorovinyl)-2-norbornene	CVNB	<2.0			
RC(CH₃)=CH₂	5-isopropenyl-2-norbornene	IPNB		13.6		
RCH₂CH₂CH=CH₂	5-(3'-butenyl)-2-norbornene	3-BNB	8.8			
RCH₂CH=CHCH₃	5-(<i>cis</i> -2'-butenyl)-2-norbornene	<i>cis</i> -2-BNB	7.2	7.7		
RCH₂(CH₃)C=CHCH₃ + RCH₂CH=C(CH₃)₂	5-(2'- or 3'-methyl-2'-butenyl)-2-norbornene	MBBNB ^f	9.5	10.3		
RCH(CH₃)CH=CHCH₃	norbornene					
	5-(1'-methyl-2'-butenyl)-2-norbornene	1-MBNB				
	5-(1'-methyl-2'-butenyl)-2-norbornene	1-MBNB	10.1			

	CHNB	11.9
	MNB	5.6
	ENB	16.0
	ENBD	7.2
	THI	0.9e
	MTHI	0.9e
<i>cis</i> -CH ₂ =CHCH ₂ CH=CHCH ₃	<i>cis</i> -1,4-HD	0.66
<i>trans</i> -CH ₂ =CHCH ₂ CH=CHCH ₃	<i>trans</i> -1,4-HD	0.67
CH ₂ =CHCH ₂ CH ₂ CH(CH ₃)CH=C(CH ₃) ₂	5,7-dimethyl-1,6-octadiene	0.69
CH ₂ =CHCH(CH ₃)CH ₂ CH ₂ CH=C(CH ₃) ₂	3,7-dimethyl-1,6-octadiene	1.1 ^e
CH ₂ =CH(CH ₃) ₂ CH=CH(CH ₂) ₇ CH ₃	1,9-octadecadiene	0.77e
CH ₂ =CH(CH ₂) ₇ CH=C(CH ₃) ₂	11-methyl)dodecadiene-1,10	ODD
	MDDD	1.4
		1.4

^aReprinted from Christman and Keim, 1968 with the permission of the American Chemical Society, Washington, D.C.



^cWith respect to propylene.

^dCatalyst: A, VO(O-*t*-Bu)₅-Et₃Al₂Cl₃; B, VOCl₃-Et₃Al₂Cl₃; C, VCl₄-(*t*Bu)₃Al; D, VCl₄-Et₃AlCl.

^eSingle determinations.

12-MBNB/3-MBNB = 2/1

ly) low concentration of diene introduced, instead of the variation in the reactivity ratios.

The latter explanation rests on the possibility that termonomer interacts with catalytic centers to yield some species different from those existing when EPM is formed (see Section II A).

As it has been recently pointed out (Baldwin and Ver Strate, 1972) an exact answer would require that ethylene-propylene reactivity ratios be determined in the presence of the diene (see Section II C). Indeed such results have recently been obtained (Askerov et al., 1973) and confirm the conclusions (see below) obtained from previous semiquantitative data.

However, the relative reactivities in Table II were obtained for a narrow range of ethylene to propylene ratios.

4. The method is based on the withdrawal from the reaction solution of samples which are analyzed for the concentration of unreacted diene. This approach has been tested as reliable in the case of ENB (Levine and Haines, 1970; Tosi et al., 1972) but in general, the possibility of the existence of side reactions (see Section II D) which might consume additional amounts of termonomer, should be taken into account. However, these introductory remarks would be incomplete without citing two recent papers (Askerov et al., 1973; Podolny and Kissin, 1974) which are interesting contributions in establishing a quantitative basis to investigations concerning EPDM synthesis.

Since the difficulties encountered in fitting terpolymerization equations with sufficiently accurate experimental data are well known, Askerov et al. (1973) have attempted to simplify the general equations by making some assumptions which are justified by previous analyses carried out on a terpolymer based on three α -olefins (Valvassori and Sartori, 1967) and obtained with Ziegler-Natta catalysts. By assuming $r_{132}r_{123} = 1$, $r_{231}r_{213} = 1$, $r_{312}r_{321} = 1$ and $r_{231}r_{312}r_{123} = r_{132}r_{321}r_{213}$ (index 1, 2, and 3 refers, respectively, to ethylene, propylene, and termonomer), the terpolymerization equations assume forms which are suitable for a non-linear interpolation method (Tidwell and Mortimer, 1965) and with the aid of a computer, several reactivity ratios can be obtained. When the termonomer was 5-ethylidene-2-norbornene and the catalyst system $\text{VOCl}_3\text{-Et}_3\text{Al}_2\text{Cl}_3$, the following constants were calculated: $r_{112} = 33.0$, $r_{132} = 37.78$, $r_{221} = 0.022$, $r_{231} = 0.211$, $r_{223} = 0.23$, $r_{332} = 15.14$, $r_{331} = 1.42$, and $r_{113} = 7.4$. Good agreement was found between determined and calculated values of EPDM composition.

For the investigated system (Askerov et al., 1973) the value of the ratio of the rate constants K_{113}/K_{112} is 4.5, i.e., rather different from the value

of K_{13}/K_{12} reported in Table II and obtained from another simplified version of the terpolymerization equations. Evidently, different simplifications affect the final results to a different degree. Analogously, Podolnyu and Kissin (1974) have derived another simplified terpolymerization equation:

$m_1 : m_2 : m_3 = M_1(M_1 + M_2/r_{12} + M_3/r_{13}) : M_2(M_1 + RM_3)/r_{12} : M_2M_3R^1/r_{13}$ where $R = K_{23}/K_{21}$ and $R^1 = K_{32}/K_{31}$. For the ENB-EPDM produced with the system $\text{VOCl}_3\text{-Et}_3\text{Al}_2\text{Cl}_3$ and within the limits of the assumptions made and of the analytical methods used, the following been obtained:

$r_{12} = 6.7 \pm 0.3$; $r_{13} = 0.067 \pm 0.005$; $R = 3.5 \pm 0.5$; $R^1 = 0.014 \pm 0.002$, from which $r_{12}/r_{13} = K_{13}/K_{12} \approx 100$, i.e., a value different from those of Askerov and Christman (see below).

It is worth noting that in the absence of termonomer, r_{12} and r_{21} assume, respectively, the value of 14.5 and 0.024 (cf. the values of r_{112} and r_{221} given above). This means that the presence of termonomer greatly enhances the ethylene reactivity, whereas it reduces slightly the reactivity of propylene. As a consequence, the tendency to alternation of the olefin units decreases as the value of $r_{12}r_{21}$ increases (see Table III).

The mechanistic implications of this result, which agrees with a number of experimental evidences (see Sections III and IV), will be discussed in Section V A in the light of an enhanced coordinative ability attributable to termonomer (a diene having, generally, a norbornenic double bond characterized by a reactivity higher than that of lower α -olefins) with respect to a more hindered mono-olefin.

Obviously, the diagnostic power of the relationships deduced from the statistics applied to the theory of multicomponent polymeric systems will be fully displayed when analytical methods capable of yielding accurate compositional data will be available (see Section II H).

Very recently the results of Christman and Keim (1968) have been re-examined (Baldwin and Ver Strate, 1972) applying the terpolymerization equation in a simplified version. When the reaction of diene with itself or with propylene can be neglected, in comparison with ethylene, and the catalyst is formed by only one active species, then the simplified treatment gives:

$$(dM_3/dt)/(dM_2/dt) = (K_{13}/K_{12})(1 + r_{21}/M_2)^{-1}(M_3/M_2)$$

where the indexes 1, 2, 3 refer, respectively, to ethylene, propylene, and diene. The relative reactivity r_c of Table II becomes:

$$r_c = (K_{13}/K_{12})(1 + r_{21}/M_2)^{-1}$$

TABLE III
Reactivity Ratios Determined for Ethylene and Propylene in the Presence of Different Catalyst Systems

Catalyst system	Molar ratio cat./cocat.	Solvent (type)	Tempera- ture (°C)	$r_{C_2H_4}$	$r_{C_3H_6}$	$r_{C_2H_4} \times r_{C_3H_6}$	Remarks ^a	Ref. ^b
$VOCl_3-(n-C_6H_5)_3Al$	1:3	<i>n</i> -heptane	25	17.95 ± 0.27	0.065 ± 0.002	1.17	A,E,H,K	Mazzanti et al., 1957 ^a
	1:3	<i>n</i> -heptane	25	17.85 ± 1.16	0.065 ± 0.006	1.18 ± 0.13	b(i)	
	1:3	<i>n</i> -heptane	25	17.55 ± 2.37	0.065 ± 0.005	1.14 ± 0.18	b(ii)	
$VOCl_3-(iBu)_2AlCl$	—	<i>n</i> -heptane	33	14.80	0.037	0.55	A,F,E,M	Bushick, 1965
—	—	<i>n</i> -heptane	33	13.19 ± 3.15	0.028 ± 0.019	0.37 ± 0.26	b(i)	
—	—	<i>n</i> -heptane	33	13.20 ± 6.24	0.033 ± 0.012	0.43 ± 0.26	b(ii)	
$VOCl_3-(iBu)_2AlCl$	—	<i>n</i> -heptane	26	20.3 (21.8-19.2) ^c	0.022 (0.024-0.021) ^c	0.45 ± 0.04	B,F,J,L	Cozewith and Ver Strate, 1971
$VOCl_3-Et_2AlCl$	—	<i>n</i> -heptane	26	12.1(13.4-11.1) ^c	0.018(0.021-0.017) ^c	0.22 ± 0.04	B,F,J,L	Cozewith and Ver Strate, 1971
$VOCl_3-Et_2AlCl$	1:50	<i>n</i> -heptane	20	19.6 ± 0.3	0.029 ± 0.003	—	A,F,-M	Karasev and Minsker, 1973
	1:50	<i>n</i> -heptane	20	18.3 ± 3.2	0.023 ± 0.012	0.428 ± 0.077	b(i)	
	1:50	<i>n</i> -heptane	20	27.7 ± 8.5	0.037 ± 0.008	1.034 ± 0.386	b(ii)	
$VOCl_3-Et_2AlCl$	>100	liq. C_3H_6	20	18.6 ± 0.9	0.050 ± 0.009	0.93	D,F,C,M	Thomala, 1972
$VOCl_3-Et_2AlCl_3$	—	<i>n</i> -heptane	26	10.1(10.8-9.7) ^c	0.025(0.027-0.023) ^c	0.25 ± 0.03	B,F,J,L,	Cozewith and Ver Strate 1971
$VOCl_3-EtAlCl_3$	1:50	<i>n</i> -heptane	20	18.6 ± 0.3	0.050 ± 0.003	—	A,F,-M	Karasev and Minsker, 1973
	1:50	<i>n</i> -heptane	20	18.3 ± 3.3	0.049 ± 0.020	0.89 ± 0.40	(i)	
	1:50	<i>n</i> -heptane	20	19.8 ± 4.8	0.052 ± 0.006	1.03 ± 0.27	(ii)	
—	—	—	14.5	0.024	0.348	i	Askerov et al., 1973	
	—	—	33.0	0.022	0.726	i,j	Askerov et al., 1973	
$VOCl_3-(iBu)_2Al$	1:10-100	cyclohexane	70	28	—	—	D,F,-M, Karol and Carrick, 1961	
$VOCl_3-(iBu)_2AlCl$	1:116	<i>n</i> -heptane	30	16.8	0.052	0.87	D,F,-M	Firsov et al., 1966
	1:116	<i>n</i> -heptane	30	16.57 + 1.93	0.050 + 0.009	0.83 ± 0.18	b(i)	
	1:116	<i>n</i> -heptane	30	19.59 ± 4.57	0.056 ± 0.005	1.10 ± 0.27	b(ii)	

$\text{VOCl}_3\text{-}(i\text{Bu})_2\text{AlCl}$	—	—	—	35.3	0.027	0.95	—	Seidov et al., 1969
$\text{VOCl}_3\text{-Et}_2\text{AlCl}$	—	—	—	—	—	0.37	—	Bier, 1961
$\text{VCl}_4\text{-}(n\text{-C}_6\text{H}_{13})_3\text{Al}$	1.3	<i>n</i> -heptane	25	7.08 ± 0.20	0.088 ± 0.003	0.62	A,E,H,K	Mazzanti et al., 1957b
	1.3	<i>n</i> -heptane	25	7.35 ± 0.48	0.092 ± 0.002	0.67 ± 0.05	b(i)	
	1.3	<i>n</i> -heptane	25	7.46 ± 1.13	0.092 ± 0.003	0.69 ± 0.10	b(ii)	
$\text{VCl}_4\text{-HCl}_2\text{Al}\text{-OEt}_2$	1.2, 5	benzene	25	10.7	0.022	0.24	A,E,G,L	Marconi et al., 1964b
	1.2, 5	benzene	25	10.53 ± 0.26	0.021 ± 0.002	0.22 ± 0.02	b(i)	
	1.2, 5	benzene	25	10.75 ± 1.13	0.023 ± 0.002	0.25 ± 0.02	b(ii)	
$\text{VCl}_4\text{-Et}_2\text{AlCl}$	1.6	<i>n</i> -heptane	—20	16.24	0.024	0.39	A,F,J,L	Cesca et al., 1968a
	1.6	<i>n</i> -heptane	—20	16.57 ± 1.75	0.020 ± 0.01	0.33 ± 0.17	b(i)	
	1.6	<i>n</i> -heptane	—20	17.12 ± 7.34	0.025 ± 0.005	0.43 ± 0.20	b(ii)	
$\text{VCl}_4\text{-Et}_3\text{Al}$	—	<i>n</i> -heptane	26	10.3(12.6–8.6) ^c	0.025(0.030–0.021) ^c	0.25 ± 0.11	B,F, ^{-,L}	Cozewith and VerStrate, 1971
$\text{VCl}_4\text{-}(i\text{Bu})_3\text{Al}$	—	<i>n</i> -heptane	26	11.0(11.5–10.7) ^c	0.028(0.030–0.027) ^c	0.30 ± 0.07	B,F, ^{-,L}	Cozewith and VerStrate, 1971
$\text{VCl}_4\text{-Et}_2\text{AlCl}$	—	<i>n</i> -heptane	26	5.9(5.6–4.5) ^c	0.029(0.031–0.029) ^c	0.17 ± 0.02	B,F, ^{-,L}	Cozewith and VerStrate, 1971
$\text{VCl}_4\text{-Et}_3\text{Al}_2\text{Cl}_3$	—	<i>n</i> -heptane	26	9.1(9.6–8.9) ^c	0.031(0.033–0.030) ^c	0.28 ± 0.02	B,F, ^{-,L}	Cozewith and VerStrate, 1971
$\text{VCl}_4\text{-Et}_2\text{AlCl}$	1:5-10	in bulk	—78	—	—	0.26 ± 0.01	A,F,J,K	Zambelli et al., 1968a
$\text{VCl}_4\text{-Et}_2\text{AlCl-anisole}$	1:5:1	in bulk	—78	—	—	0.28 ± 0.02	A,F,J,K	Zambelli et al., 1968a
$\text{VCl}_4\text{-Et}_3\text{Al}$	1:5:10	in bulk	—78	—	—	1.00 ± 0.04	A,F,J,K	Zambelli et al., 1968a
$\text{VCl}_4\text{-Et}_3\text{Ga}$	<1/2	in bulk	—78	—	—	1.14 ± 0.03	A,F,J,K	Zambelli et al., 1968a
$\text{VCl}_4\text{-Et}_2\text{AlCl}$	1:3,5	<i>n</i> -heptane	—10	13.7	0.021	0.29	A,F,J,M	Giachetti et al., 1966
	1:3,5	<i>n</i> -heptane	—10	13.15 ± 3.61	0.021 ± 0.003	0.28 ± 0.08	b(i)	
	1:3,5	<i>n</i> -heptane	—10	12.42 ± 5.77	0.021 ± 0.004	0.26 ± 0.13	b(ii)	
$\text{VCl}_4\text{-Et}_2\text{AlCl}$	1:2	<i>n</i> -heptane	21	3.0	0.073	0.22	D,F, ^{-,M}	Firsov et al., 1966
	1:2	<i>n</i> -heptane	21	2.16 ± 3.72	0.070 ± 0.005	0.15 ± 0.26	b(i)	
$\text{VCl}_4\text{-}(i\text{Bu})_2\text{AlCl}$	—	—	20.0	0.023	0.46	—	Seidov et al., 1969	

(Continued)

TABLE III (Continued)

Catalyst	Molar ratio catal./cocat	Solvent (type)	Tempera- ture(°C)	$r_{C_2H_4}$	$r_{C_3H_6}$	$r_{C_2H_4} \times r_{C_3H_6}$	Remarks ^a	Ref. ^b
VCl ₄ -(iBu) ₂ AlCl	—	in bulk	-20/50	20.5	0.025	0.51	D,F,-,M	Seidov et al., 1966
VCl ₄ -Et ₃ Al ₁	—	—	—	—	—	1.07	—	Tosi et al., 1969a
VCl ₄ -Et ₃ AlCl	—	—	—	—	—	0.26	—	Tosi et al., 1969a
VCl ₄ -(iBu) ₃ Al	—	cyclohexane	70	16	—	—	D,F,-,M,K	Karol and Carrick, 1961
VCl ₄ -AlBr ₃ -Sn (C ₆ H ₅) ₄	—	cyclohexane	70	16	~0, 1	—	D,F,J,M,K	Karol and Carrick, 1961
VCl ₃ -(n-C ₆ H ₁₃) ₃ Al	1:2	cyclohexane	70	9.53 ± 3.77	0.79 ± 0.63	0.53 ± 0.097	v(i)	
	1:2	n-heptane	75	5.61 ± 0.20	0.145 ± 0.007	0.81	A,E,G,K	Natta et al., 1958
	1:2	n-heptane	75	5.28 ± 0.40	0.134 ± 0.024	0.71 ± 0.14	v(i)	
	1:2	n-heptane	75	6.54 ± 1.09	0.172 ± 0.015	1.11 ± 0.21	v(ii)	
	1:2.5	benzene	70	9.4	0.056	0.53	A,F,G,L	Marconi and Cesca, 1965
VAcac ₃ -Et ₂ AlCl	1:2.5	benzene	70	9.44 ± 2.19	0.055 ± 0.019	0.52 ± 0.22	v(i)	
	1:2.5	benzene	70	9.41 ± 0.69	0.054 ± 0.005	0.51 ± 0.06	v(ii)	
	1.5	n-heptane	-20	15.0	0.04	0.60	A,E,J,K	Natta et al., 1961d
	1.5	n-heptane	-20	13.49 ± 2.26	0.039 ± 0.003	0.53 ± 0.09	v(i)	
	1.5	n-heptane	-20	13.42 ± 3.98	0.039 ± 0.005	0.52 ± 0.17	v(ii)	
VAcac ₃ -Et ₂ AlCl	—	n-hexane	-10	—	—	0.40-0.45	d	Carman and Wilkes, 1971
	—	n-hexane	-10	—	—	1.16-0.85	d	Wilkes et al., 1973
VAcac ₃ -Et ₃ Al ₂ Cl ₃	1:8	—	25	—	—	1.10	d, e, g	Wilkes et al., 1973
VAcac ₃ -Et ₂ AlCl ₃	1:32	—	0	—	—	1.03	d, e, f	Wilkes et al., 1973
VAcac ₃ -(iBu) ₂ AlCl	—	—	—	16.0	0.04	0.64	—	Seidov et al., 1969
VAcac ₃ -(iBu) ₂ Bu ₂ AlCl	1:10	—	-10	—	—	0.91-1.50	—	Wilkes et al., 1973
	—	liq. C ₃ H ₆	0/20	14.95	0.0242	0.362	h	Seidov et al., 1973
	—	liq. C ₃ H ₆	0/20	18.2	0.0052	0.095	g, h	Seidov et al., 1973
VAcac ₃ -Et ₂ AlCl	—	—	—	—	—	0.35	—	Tosi et al., 1969a

VO(O- <i>n</i> -Bu) ₃ - (<i>i</i> Bu) ₂ AlCl	—	<i>n</i> -heptane	33	22.00	0.046	1.01	A,F,J,M	Bushick, 1965
		<i>n</i> -heptane	33	23.71 ± 1.31	0.054 ± 0.008	1.28 ± 0.19	b(i)	
		<i>n</i> -heptane	33	23.28 ± 1.48	0.050 ± 0.005	1.16 ± 0.14	b(ii)	
		<i>n</i> -heptane	33	15.00	0.070	1.04	A,F,J,M	Bushick, 1965
VO(OEt) ₃ - (<i>i</i> Bu) ₂ AlCl	—	<i>n</i> -heptane	33	15.97 ± 5.98	0.072 ± 0.071	1.15 ± 1.21	b(i)	
		<i>n</i> -heptane	33	15.43 ± 3.02	0.074 ± 0.022	1.14 ± 0.41	b(ii)	
		<i>n</i> -heptane	26	16.8(18.4-15.8) ^c	0.019(0.022-0.017) ^c	0.32 ± 0.06	B,F,J,L	Cozewith and Ver Strate, 1971
VO(O- <i>n</i> -Bu) ₃ - Et ₂ AlCl	—	chlorobenzene	30	19.8(21.0-19.1) ^c	0.012(0.014-0.011) ^c	0.24 ± 0.04	B,F,J,L	Cozewith and Ver Strate, 1971
VO(OEt) ₃ -Et ₂ AlCl	—	chlorobenzene	30	26.0	0.039	1.02	C,F,J,-	Lukach and Spurin, 1964
VO(OR) ₃ -R ₂ AlCl	—	chlorobenzene	30	24.4	0.041	1.00	C,F,J,-	Lukach, and Spurin, 1964
VOCl(OEt) ₂ - (<i>i</i> Bu) ₂ AlCl	—	<i>n</i> -heptane	33	18.90	0.056	1.06	A,F,J,M	Bushick, 1965
VO(OC ₈ H ₁₇) ₂ -Cl _{1.3-} >100	liq. C ₈ H ₆	20	10.2 ± 0.5	0.037 ± 0.005	0.38	D,F,J,M	Thomalla, 1972	
VOCl ₂ (OEt)- (<i>i</i> Bu) ₂ AlCl	—	<i>n</i> -heptane	33	20.33 ± 2.89	0.066 ± 0.024	1.34 ± 0.52	b(i)	
		<i>n</i> -heptane	33	20.20 ± 3.04	0.067 ± 0.013	1.35 ± 0.33	b(ii)	
		<i>n</i> -heptane	33	16.80	0.055	0.93	A,F,J,M	Bushick, 1965
VOCl ₂ (OR)-EtAlCl ₂	—	<i>n</i> -heptane	33	19.03 ± 3.35	0.070 ± 0.024	1.33 ± 0.51	b(i)	
		<i>n</i> -heptane	33	19.00 ± 1.79	0.070 ± 0.0098	1.33 ± 0.22	b(ii)	
VO(Acac) ₂ -Et ₂ AlCl	—	—	—	—	—	—	A,F,J,M	Bier, 1961
VO(C ₈ H ₇ O ₂) ₃ - Et ₂ AlCl	>100	liq. C ₈ H ₆	20	7.6 ± 0.5	0.047 ± 0.005	0.36	D,F,J,M	Cozewith and Ver Strate, 1971
								Thomalla, 1972

(Continued)

TABLE III (Continued)

Catalyst	Molar ratio catal./cocat	Solvent (type)	Tempera- ture(°C)	$r_{\text{C}_2\text{H}_4}$	$r_{\text{C}_3\text{H}_6}$	$r_{\text{C}_2\text{H}_4} \times r_{\text{C}_3\text{H}_6}$	Remarks ^a	Ref. ^b
VO(Acac) ₃ Cl- Et ₂ AlCl	—	n-heptane	26	16.4(17.0-15.9) ^c	0.018(0.019-0.017) ^c	0.30 ± 0.02	B,F,J,L	Cozewith and Ver Strate, 1971
VO(Acac)Cl ₂ - Et ₂ AlCl	—	n-heptane	26	16.5(17.4-15.8) ^c	0.012(0.013-0.011) ^c	0.20 ± 0.03	B,F,J,L	Cozewith and Ver Strate, 1971
V(NEt ₂) ₄ -Et ₂ AlCl ₂	1.5	n-heptane	15	20.73	0.012	0.25	A,F,J,L	Cucinella and Mazzei, 1971a
	1.5	n-heptane	15	26.56 ± 4.56	0.019 ± 0.0012	0.50 ± 0.09		b(i)
	1.5	n-heptane	15	22.35 ± 6.39	0.0071 ± 0.0022	0.16 ± 0.47		b(ii)
	1.6-9	n-heptane	15	15.95	0.0011	0.18	A,F,J,L	Cucinella and Mazzei, 1971a
TiCl ₄ -(n-C ₈ H ₁₃) ₃ Al	1.6-9	n-heptane	15	15.93 ± 1.25	0.012 ± 0.012	0.19 ± 0.19		b(i)
	1.6-9	n-heptane	15	16.01 ± 2.66	0.0084 ± 0.0013	0.13 ± 0.21		b(ii)
	1.3	n-heptane	25	33.36 ± 1.32	0.032 ± 0.001	1.07	A,E,H,K	Natta et al., 1958
	1.3	n-heptane	25	36.22 ± 4.49	0.035 ± 0.003	1.27 ± 0.19		b(i)
	1.3	n-heptane	25	40.15 ± 6.09	0.037 ± 0.003	1.48 ± 0.25		b(ii)
TiCl ₄ -HCl ₃ Al.OEt ₂	1:1.5	toluene	5	15.9	0.013	0.21	A,F,H,I	Marconi et al., 1964c
	1:1.5	toluene	5	15.79 ± 0.73	0.013 ± 0.002	0.20 ± 0.03		b(i)
	1:1.5	toluene	5	15.63 ± 3.99	0.013 ± 0.002	0.20 ± 0.06		b(ii)
TiCl ₄ -(iBu) ₃ Al	—	cyclohexane	70	37	—	—	D,F,-,M,K	Karol and Carrick, 1961
α -TiCl ₃ -(n-C ₆ H ₁₃) ₃ Al	1.2	n-heptane	75	15.72 ± 0.44	0.110 ± 0.003	1.73	A,E,G,K	Natta et al., 1958
	1.2	n-heptane	75	15.82 ± 1.75	0.111 ± 0.012	1.76 ± 0.27		b(i)
	1.2	n-heptane	75	15.63 ± 1.52	0.111 ± 0.008	1.73 ± 0.21		b(ii)
α -TiCl ₃ -Et ₃ Al	1.5	n-heptane	70	—	—	1.9 ± 0.3	-F,C,M	Goldenberg and Pilipovskii, 1973

α -TiCl ₃ -Et ₂ Al-pyridine	1:5:1	n-heptane	70	—	—	—	1.5 ± 0.2	—F,C,M
β -TiCl ₃ -Et ₂ Al	1:2	n-heptane	70	—	—	—	2.3 ± 0.3	—F,C,M
TiCl ₂ (n-C ₆ H ₁₃) ₃ Al	—	n-heptane	75	15.72	0.110	1.73	2.04 ± 1.25	A,E,G,K
—	—	n-heptane	75	17.33 ± 6.68	0.118 ± 0.056	—	1.14 ± 0.43	^{b(i)}
—	—	n-heptane	75	12.94 ± 3.82	0.088 ± 0.021	—	—	^{b(ii)}
ZrCl ₄ (iBu) ₃ Al	—	cyclohexane	70	61	—	—	D,F,-M,K	Karol and Carrick, 1961
HfCl ₄ (iBu) ₃ Al	—	cyclohexane	70	76	—	—	D,F,-M,K	Karol and Carrick, 1961
Cr(C ₆ H ₅) ₂ -SiO ₂	—	n-hexane	90	72	—	—	D,F,C,M,K	Karol et al., 1972

^aA = "Semiflow technique" (cf. Section II E); B = "continuous technique"; C = "closed technique"; D = Batch technique; E = aged catalyst; F = unaged catalyst; G = physically heterogeneous catalyst; H = highly dispersed catalyst; J = soluble catalyst; K = radiochemical analysis of copolymer; L = IR analysis as referred to radiochemical standards; M = IR analysis referred to homopolymers.

^b(i) This work, linear interpolation of experimental data according to Fineman-Ross equation. Error limits of the reactivity ratios as confidence limits within 95%. (ii) This work, nonlinear interpolation of experimental data according to a variation (Ragazzini et al., 1970) of the method proposed by Behnken (1964), Tidwell and Mortimer (1965). Confidence limits within 95%. Thanks are due to Spallanzani and Doccì for the preparation of the computer program.

^cThrough ¹³C-NMR data.

^dCarried out in the presence of 5-ethylidene-2-norbornene (ca. 1 mole % in the final EPDM).

^eCarried out in the presence of ZnEt₂.

^fCarried out in the presence of H₂.

^gCopolymer separates in the reaction mixture.

^hCopolymerization carried out in a semi-industrial apparatus.

Reactivity ratios obtained by solving simplified terpolymerization equations; the values of other reactivity ratios have been obtained (cf. the text, pp. 12-13).

ⁱBy assuming $r_1 \times r_2 = 1$.

from which the ratio K_{13}/K_{12} can be calculated as about 0.5 for linear dienes and about 20 for dienes containing the norbornene unsaturation. The results agree with the previous order of reactivity deduced on a qualitative basis for some termonomers (Gladding et al., 1962; German et al., 1966).

The difficulty in applying the terpolymerization equations to EPDM's shows the existence of relevant complications encountered by several authors and about which little has been said. Some other problems will be discussed in the following sections.

A. Interaction of the Third Monomer with Catalyst Centers

The catalyst is modified by the presence of the third monomer; in fact, its polyenic character and the presence of a double bond having enhanced reactivity increase the possibility of coordination and reaction with the initiating species. Actually, it has been found that, generally, the reactivity of propylene is lowered in the presence of termonomer and this result disagrees with what happens when the termonomer is an α -olefin, e.g., 1-butene (Natta et al., 1963a). Also the total number of active centers is lowered according to conversion data (see Section IV). However in some cases, the presence of the third monomer gives a certain degree of homogeneity to the catalytic species (see also Section II G).

These experimental observations might be explained on the basis of a selected and more stable coordination to catalyst centers (See Section II D) by the termonomer which is in competition with other ligands, in particular with the more bulky ligands (see below).

The problem could have a quantitative answer when reliable kinetic schemes would find experimental confirmations through the determination of the rate constants which would describe the reactivity of the chemical species involved in the terpolymerization process (see the previous section and Section II C).

However, according to more recent results (Takegami and Suzuki, 1969; Suzuki and Takegami, 1970; Takegami et al., 1972), when a bulky monolefin is present in the polymerization medium, it is able to hinder the vanadium-carbon bond of the catalyst centers and, hence, no further insertion of bulky monomer can occur. After the insertion of a bulk monomer, the introduction of an ethylene unit becomes the most probable event. Furthermore, the possible alteration of the "normal" pathway of propylene insertion (essentially propylene inversion; see Section II H 3) can also take place. Some stereochemical events recently reviewed (Zambelli and Tosi, 1974) have shown this.

Therefore, the influence of any termonomer on the activity of catalyst could take place either through preferential coordination of the efficient electron donor molecule of termonomer, or/and through steric effects, since every termonomer is, generally, much more bulky than 1-pentene (Takegami and Suzuki, 1969) or propylene (Zambelli et al., 1972).

B. Intrinsic Heterogeneity of Catalysts Used in EPDM Synthesis

Recently (Cozewith and Ver Strate, 1971) it has been shown, through a detailed investigation by fractionation and analysis of the composition and MWD of ethylene-propylene copolymers fractions, that typical Ziegler-Natta catalysts furnish more than one type of active centers, analogously to what happens with other ionic catalysts (Masuda and Higashimura, 1971).

In the past this situation was partly recognized (Lukach and Spurlin, 1964; Baker and Tait, 1967) for catalyst systems having physical heterogeneity (e.g., VCl_3-AlEt_3) in comparison with homogeneous ones (e.g., $VAc_3-Al-iBu_2Cl$). The former yielded (Fig. 2) broad distributions of composition and MW, whereas, the latter gave quite narrow results, but, in many cases, it is difficult to distinguish between a colloidal dispersion and a true solution. However, when catalyst heterogeneity is ascertained, the common reactivity ratios should be considered as average indexes of elementary reactivity ratios pertaining to different individual catalytic species. When this conclusion is accepted, the canonical

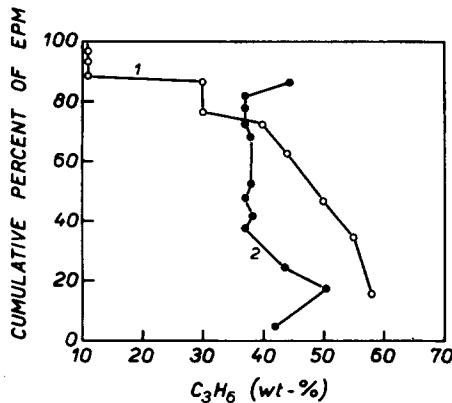


Fig. 2. Fractionation data with solvent gradient technique of EPM's prepared with a physically heterogeneous (1) and homogeneous (2) catalyst system. 1— VCl_3-Et_3Al and 2— $VAcac_3-(iBu)_2AlCl$. (Vizen and Kissin, 1969).

copolymerization equation becomes modified and it is reduced to the classical form only when a single type of active species is involved (Cozewith and Ver Strate, 1971).

Furthermore, the product of reactivity ratios, being the product of complex averages, cannot be utilized to obtain the copolymer sequence distribution directly when the average composition is specified, as in the case of catalysts assumed to be formed by a single species (Natta et al., 1960b; Veerkamp and Veermans, 1961). In fact, it can be verified that broad variations in the individual reactivity ratio products are possible for a given set of average reactivity ratios, even when a defined composition of the polymer is assumed.

The influence of a third monomer has not been examined in this context of catalyst heterogeneity, but it is likely that the same complicated situation arises in the synthesis of EPDM's because the catalyst used is the same one involved in EPM synthesis (see Section II G).

From a mechanistic point of view it is interesting to observe (Table IV) that the aforesited studies (Cozewith and Ver Strate, 1971) have indicated the minimum number of active species present in the catalysts investigated.

The elevated interest in this kind of result suggests that it would be advisable to have similar data for other catalyst systems, operating also under different conditions. The necessity of accurate experimental procedures must be taken into account since the problems inherent in fractionation operations (Myagchenkov and Frenkel, 1968; Koenningveld and Staverman, 1968) may yield misleading results (see Section II H 4).

TABLE IV

Product of Reactivity Ratios of Ethylene and Propylene Obtained with Some Catalyst Systems and Minimal Number of Active Species Present in Them^a

Catalyst system	$r_{C_2H_4} \times r_{C_3H_6}$	Number of active species ^b
VCl ₄ -Et ₂ AlCl	0.14 ± 0.02	2
VCl ₄ -Et ₃ Al ₂ Cl ₃	0.28 ± 0.02	1
VOCl ₃ -Et ₂ AlCl	0.22 ± 0.04	3
VOCl ₃ -Et ₃ Al ₂ Cl ₃	0.25 ± 0.03	1
VO(OBu) ₃ -Et ₂ AlCl	0.32 ± 0.06	2
VO(Acac) ₂ -Et ₂ AlCl	0.13 ± 0.03	2
VO(Acac) ₂ Cl-Et ₂ AlCl	0.30 ± 0.02	2
VO(Acac)Cl ₂ -Et ₂ AlCl	0.20 ± 0.03	2

^aReprinted from Cozewith and Ver Strate, 1971 with permission of the Division of Rubber Chemistry Inc., A. C. Akron, Ohio.

^bObtained from catalyst system used in a continuous-stirred tank-reactor. Polymerization solvent: *n*-heptane; T = 26°C.

C. Kinetic Investigations

The possibility that the third monomer, besides inserting into EPDM chains, interferes with the chain propagation step, has been shown in many cases (see Section II A and III B 4). It would be very useful to put on quantitative basis the principal side reactions (chain termination, transfer, etc.) attributable to the third monomer. This would mean it would have to be possible to carry out detailed kinetic investigations under opportune conditions in order to distinguish between single contributions to the overall kinetics. So far successful kinetic analyses have not been performed because of the elevated number of single steps; in fact, just the propagation stage alone is based on 9 elementary steps (Valvassori and Sartori, 1967). Other individual steps should take into account the interference of the third monomer and of the catalyst components with the active species, their influence on MW and MWD etc., based on reliable expressions describing the individual rates.

Only very recently (Baldwin and Ver Strate, 1972) a kinetic scheme has been proposed, quite general in its formal statement, based on six stages: initiation, catalyst deactivation, propagation, chain termination, transfer and branching.

Aside from the propagation step, represented in the scheme by a single general equation which, actually, should be expanded beyond the nine equations normally considered for terpolymerization if propylene and the termonomer should react in two or more ways (see Section II H 3), the whole scheme includes thirteen general equations. On the basis of some literature data, equations for the single general reaction rates are put forward; in some cases the reaction orders are undefined (e.g., catalyst deactivation or termination). The influences of products formed during the aging of catalyst or as the result of possible reactions occurring in the reacting medium are assumed to be small.

Also the addition of transfer agents (e.g., H_2) is assumed to have no effect on catalyst efficiency, in contrast with earlier data referring to Ti-based catalysts (Natta et al., 1959; Cesca et al., 1974a) or with more recent results observed in EPDM synthesis.

The possibility of solution of such a system of equations has been verified for a continuous-stirred tank-reactor (see Section II F); conversion, composition, and MWD can be obtained elaborating on the relationships previously put forward.

It is worth noting that some answers to questions encountered in these kind of problems are in part offered by the literature (Baldwin and Ver Strate, 1972). For instance the influence of statistical fluctuations or of

various rate constants on the polymer composition have been previously presented. Also the case of catalysts having multiple species, or of polymer with complex MWD, or the general effect of branching has been treated. References dealing with the less favorable case of batch reactors can also be found.

By using an iterative procedure, which probably utilizes computer programs and values for composition, conversion, MW, residence time, total concentration of active centers, etc., deduced from the study of a terpolymerizing system in a continuous reactor, preliminary data have been obtained for some individual rate constants involved in the overall kinetic scheme. Their values, however, have to be considered as indicative and for some reactions (e.g., branching) no data are given, but the system furnishes chain lifetimes on the order of minutes (at 23°C) for $DP = 10^4$, while the randomness of the polymer increases when the temperature increases. However, the assumption that the reactivity of the terminal unsaturation of the macromolecules involved is comparable to that of the terminal bond of C_6-C_{12} α -olefins, seems an overestimation. Probably the amount of branching that results (on the order of one branch for one macromolecule formed under typical conditions) is excessive (see also Section II J).

Other results of this kinetic approach, in regard to a catalyst containing only a single active species and to the use of 5-ethylidene-2-norbornene, are, in absence of branching: (a) a most probable MWD; (b) little influence due to statistical fluctuations, on the order of $\pm 2\%$ (95% confidence limits); (c) the reactivity ratios product is of the order of the literature values; (d) MW regulators have no effect on MWD.

It may be worthwhile to note that the ratio of the sum of the rate constants of the individual stages of propagation to the sum of the rate constants of the chain breaking processes (namely, chain termination by the termonomer and chain transfer to alkyl Al derivative), is of the same order, i.e., 10^{-2} , as the value obtained (Cesca et al. 1968c) according to a much more simplified kinetic scheme for the same ratio with a different termonomer (see Section III B 4).

The agreement at this stage of investigations has, probably, very limited value because the experimental conditions are different. However, aside from the value of studying the complicated process of terpolymerization as an unit process, the observed concordance and an overall examination of the results obtained so far seem to indicate that a detailed kinetic scheme requires an exact knowledge of the parameters and of the relationships involved. This is necessary in order to reach significant values for the kinetic constants under investigation. Sometimes more precise results can be obtained by carrying out separate experiments,

under simplified conditions, with the aim of obtaining separate data on some individual variables. For instance the evaluation of reactivity ratios in a three component system can be obtained from single binary systems (Pasquon et al., 1967, p. 411) and, analogously, the determination of chain growing lifetimes (Pasquon et al., 1961, p. 411; Grievson, 1965), concentration of active centers (Pasquon et al., 1967, p. 411), individual rate constants (Natta et al., 1961b), or the influence of MW regulators, the dependence of MW or of catalyst activity on the polymerization time, etc. can be derived from homopolymerization kinetics or individual runs (Natta et al., 1959a).

On the basis of this preliminary and separate work, it should be possible to put forward more precise relationships by collecting the most useful kinetic information from the study of EPDM synthesis in a continuous reactor. This remains the most reliable approach even though the difficulties encountered are formidable.

D. Reactivity of Unsaturation Present in EPDM Chains

The unsaturation of termonomer not involved in the terpolymerization process may be attacked under particular conditions which are discussed below.

1. An enhanced reactivity of the second center of unsaturation of termonomer toward several agents can be an intrinsic characteristic of the molecule. This, however, improves the behavior of EPDM during the vulcanization process. This is the case, for instance, of trienes containing a system of conjugated double bonds (Arrighetti et al., 1971) and of ENB (Easterbrook et al., 1971).

2. The adoption of elevated concentration of monomers in the feed necessary for the process (see Section VII) or to produce EPDM's with high levels of unsaturations, enhances the possibility of reaction of both the centers of unsaturation of the termonomer during the polymerization step. Actually, the formation of gel was observed when such conditions were adopted (Dolinskaya, 1969; Thomalla et al., 1973).

3. In the past the assumption was made that double bonds, present both in linear and cyclic hydrocarbon structures and containing two or more substituents, could not homopolymerize with typical Ziegler-Natta catalysts. More recently (Livshits et al., 1970, 1971; Natta et al., 1961c, 1962, 1964a; Pasquon et al., 1967, p. 202) it has been shown that internal double bonds can be opened under EPDM synthesis conditions to yield copolymers of ethylene and also ethylene-propylene random terpolymers. Therefore, the fact that the less reactive unsaturation of a given

termonomer, present as an internal double bond, can react, even though at a slow rate, cannot be overlooked.

This seems to be the case of dicyclopentadiene. Homopolymerization studies, carried out with a V-based catalyst system, have shown that about 15% of the repeating units are derived from the opening of the cyclopentene double bond (Dall'Asta et al., 1969).

Preliminary IR evaluations of the homopolymer obtained from *cis*-1,4-HD with a vanadium-based catalyst, indicate that also the internal double bond of HD is reactive toward Ziegler-Natta catalysts (Shinner et al., 1972). However, apart from the fact that the cited results have been obtained under drastic conditions, the presence of three (or four) alkyl groups on the double bond should guarantee, for steric reasons, against an attack of the substituted olefinic function exerted both by Ziegler-Natta and radical catalysts (Friedlander, 1964). The existence of branching or a gel, derived from the opening of the hindered unsaturation, should be ascribed to a mechanism different from that which is responsible for the terpolymerization process.

4. There is evidence, reported mainly in the patent literature, on the existence of gelation reactions occurring in EPDM's. This is due to the presence of secondary cationic species which, in part, are originated during the stopping stage of the terpolymerization process, and in part, may be present as latent or active (see Section VB) species during the polymerization stage. The latter situation is not surprising because several components of typical Ziegler-Natta catalysts have an acidic character (Natta et al., 1959b), and sometimes, they are employed in excess with respect to the second component of the catalytic system.

The cationic nature of these side reactions is supported by some facts:

(a) The existence of an inhibiting effect exerted by Lewis bases against gelation reactions (U.S. Pat., 1970a, b; Easterbrook et al., 1971; Baldwin and Ver Strate, 1972).

(b) Solvents with a "basic" character (e.g., aromatic hydrocarbons) show effects on MW and gel similar to Lewis bases (Cunningham, 1966; Baldwin and Ver Strate, 1972).

(c) The formation of cationic species when stopping agents (alcohols, water, etc.) are mixed in defined ratios with several organometallic compounds (Imai, 1965; Ueshima, 1966; Isuchuya, 1967; Nakaniwa, 1970; Cesca 1974a) is a well confirmed fact.

Furthermore, the formation of gel is more extensive when:

(d) The character of the catalyst is more acidic (Easterbrook et al., 1971).

(e) The polymerization temperature is lowered (German et al., 1966).

(f) The nucleophilic character of the residual unsaturation is enhanced (Priola and Cesca).

It may be expected that besides the long chain branching and the gel content, the MW and MWD of EPDM chains are also influenced by the reactivity of the second double bond of termonomer.

5. In the light of our present and incomplete knowledge of the mechanism regulating EPM or EPDM synthesis, it seems unlikely that "the desired coordinated anionic polymerization proceeds side by side with Friedel-Crafts initiated polymerization" (Baldwin and Ver Strate, 1972). In fact, if Ziegler-Natta catalysts had an anionic character, this mechanism hardly could coexist with cationic reactions. Probably the anionic character of Ziegler-Natta catalysts is very small, if it exists at all (see Section V), and with this in view the question arises whether coordinated, unionized mechanism may exist simultaneously with a cationic one. At present there is no clear experimental evidence to answer this question.

Anyway, much caution is necessary in generalizing some results to support any mechanism. For instance, it is true that in EPM synthesis miscellaneous oligomers and low MW "cationic" polypropylene can be produced (Baldwin and Ver Strate, 1972), but these results depend strongly on the acidity of the catalyst used.

In fact, we have never been able to detect such oligomers when the system $\text{VAcac}_3\text{-Et}_2\text{AlCl}$ was used; moreover, EPM produced in toluene with the "acidic" system $\text{VOCl}_3\text{-Et}_3\text{Al}_2\text{Cl}_3$ showed no trace of an aromatic nucleus when examined by UV spectroscopy. UV is considered particularly sensitive in detecting low levels of aromatic species (Bhattacharyya et al., 1965).

However, the cationic products observed may be formed during the polymerization starting or stopping stages (which are not instantaneous), when the coordinated mechanism is, respectively, neither initiated nor effective. In this context, it can be useful to recall the very high rates of cationic reactions involving olefins and diolefins (Plesch et al., 1971).

The situation is completely different in the case of EPDM, as we have discussed in the foregoing paragraphs, since the use of a diene introduces further sites for side reactions.

6. The possibility that a radical attack involves the diene monomer during the terpolymerization step seems quite low. In fact, it is well known the substantial inertness of α -olefins and also of the norbornene double bond in propagating chain reactions initiated by radical species

under mild conditions. The production of relatively stable allylic radicals through abstraction of allylic hydrogen atoms (Lenz, 1967) is more common. Since the secondary unsaturation of a given termonomer is generally hindered by the substituting alkyl groups, there is little probability this double bond will propagate a chain through a radical mechanism (Firsov, 1966). A similar result was found also in the case of unsaturations constituted by conjugated dienic systems (Cesca et al., 1970a; Faucitano et al., 1974). As far as the actual efficiency as radical initiator shown by Ziegler-Natta catalysts is concerned, it has been proved (De Vries, 1961) that, from the interaction of the components the catalyst system, some radical species (mainly fragments originated from the dealkylation of labile derivatives of transition metals) can be produced (Section V C). The ability of these fragments in initiating the polymerization of appropriate monomers, sensitive to radical initiation, has been shown (Giannini and Cesca, 1962).

In this respect the situation is similar to that of inducing cationic initiation (Natta et al., 1959b). However, some perturbing effects exerted by radical species on systems containing Ziegler-Natta catalyst have been reported (Arlman, 1960) even though these perturbations have little importance because of the rapid coupling or disproportionation reactions which are subjected to the radical fragments involved.

7. Despite the good aging properties of EPDM's, due to the fact that, generally, all the double bonds are external to the ethylene-propylene backbone and to the low level of unsaturation compared to polydiolefin elastomers, the study of EPDM's as air-drying films (Singer et al., 1971) shows the occurrence of autoxidative crosslinking reactions.

In the recent past researches have been performed on the reactivity of EPDM unsaturation with oxygen in the range of low (20–60°C) and high (160°C) temperatures (Imoto and Minoura, 1970). More recently the oxygen uptake of solutions of low MW EPDM's, based on DCP, ENB, and MEHN at $T \leq 70^\circ\text{C}$ and under a daylight lamp, has been kinetically investigated (Schnecko and Walker, 1971). Also single termonomer solutions were studied: without a catalyst (cobalt dinaphthionate) autoxidation does not occur; the rate constants at 70°C are in the order MEHN > DCP > ENB. Since the oxidation reaction stops after the uptake of 20 mole % of O₂, the formation of an inhibitor is inferred. The result is surprising because in uncatalyzed diolefin autoxidation the reaction products induce autocatalytic effects (Scott, 1965).

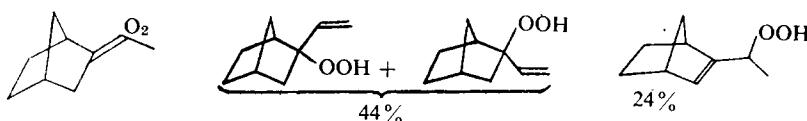
When the dienes are incorporated into polymer chains, the autoxidation rate is comparable with the value of the isolated termonomer only in the case of ENB. For MEHN-EPDM it is about twice the value and

for DCP-EPDM it is ca. tenfold. Also this result is surprising because the concentration of unsaturation and of allylic hydrogens is reduced by polymerization of termonomer. On the other hand, EPM cannot be oxidized under these conditions, whereas, ethylene-DCP copolymer shows a slower oxidation rate than DCP-EPDM. Perhaps the absence of low MW species in polymers rules out the possibility of formation of an efficient inhibitor, while the presence of tertiary hydrogen atoms in EPDM, due to propylene units, might be sites for further oxidative attack. The kinetics of oxygen uptake are similar for DCP- and MEHN-based EPDM's which have the pendant double bonds in (different) rings. ENB-EPDM shows a different behavior (higher activation energy and lower order for the rate dependence on monomer) which suggests a different autoxidation mechanism.

The small amount of knowledge of the chemical behavior of EPDM unsaturation during the curing and aging stages (see Section III A) could find a stimulating comparison in this kind of studies.

Recently, the dye-sensitized photooxidation of EPDM's (MW ca. 10^4) containing ENB or *endo*-DCP has been studied (Duynstee and Mevis, 1972). Singlet oxygen, originated by irradiating a stream of oxygen with visible light in the presence of $\alpha, \beta, \gamma, \delta$ -tetraphenylporphyrine ($6 \times 10^{-6} M$), was found to react smoothly but quantitatively with ENB-EPDM (0.28–0.93 mole of ENB/kg EPDM), whereas, DCP-EPDM did not react at all.

Two different allyl hydroperoxides are originated from the attack of the unsaturation of ethylidene-norbornane (assumed as model compound) by singlet oxygen:



in agreement with the results obtained from the photooxidation of ENB (Adams and Trecker, 1972). IR data from hydroperoxidated EPDM support the presence of tertiary hydroperoxide. An increase of "Hoekstra plasticity" in the solid rubber after photooxidation suggests that a slow decomposition of the hydroperoxides occurs (ca. a 12% decrease in 3 days at 20°C of the peroxide content). The $\text{C}=\text{C}-\overset{\text{C}}{\underset{\text{C}}{\text{C}}}-\text{OOH}$ groups are reduced by treatment with $\text{P}(\text{C}_6\text{H}_5)_3$ to allyl alcohol groups which introduce hydrogen bonds between hydroxylated EPDM chains.

It is worth noting the absolute unreactivity of propylene and DCP units present in EPDM chains towards singlet oxygen, in contrast with the metal-catalyzed autoxidation results (see above) which shows that DCP-EPDM is more reactive than ENB-EPDM. Evidently, two different mechanisms regulate dye-sensitized photooxidation and metal-catalyzed autoxidation.

E. Feeding of Monomers

To obtain EPDM's having constant composition it is important to adopt particular conditions in feeding both gaseous monomers and polyenic termonomer. The problem of olefinic monomers dissolution has already been discussed in the case of ethylene- α -olefin copolymers (Lukach and Spurlin, 1964).

A good method for guaranteeing a constant concentration of ethylene and propylene in the feed requires a violent agitation of a defined amount of solvent while a stream of gaseous monomers, having the desired composition, is bubbled in the liquid phase (Natta et al., 1957) ("semi-flow technique"). Only a small percent of the gaseous monomers dissolved are polymerized, the remaining being discharged, so that the composition of the gaseous phase (and also of the liquid phase which is in equilibrium with it) in the reactor can be assumed as constant. This has been confirmed by GC and mass spectrometry analyses (Marconi et al., 1964b).

According to other authors, the change in compositions of olefins mixture during the copolymerization reaction, due to the highest reactivity of ethylene, can be counterbalanced in a closed system by a continuous introduction of a mixture of olefins having the same composition of the copolymer formed (Lukach and Spurlin, 1964) ("closed technique").

Recently a "continuous technique" (Cozewith and Ver Strate, 1971) has been also introduced in laboratory experiments. It has been claimed as useful also in maintaining constant and low the degree of heterogeneity derived from the aging of the catalyst, i.e., the continuous changing of concentration and of type of active species (see Section II G).

The possibility of studying, kinetically, copolymerizations taking place under nonstationary conditions, due to the qualitative and quantitative change of unaged catalyst centers, has been treated by Firsov et al. (1966). The method proposed ("kinetic technique") enables the determination of the rates of entry of each monomer into the copolymer at each point of time. The rate data give the copolymer composition,

whereas, the ratios of the molar concentrations of α -olefins in the reaction zone is obtained through partial pressure measurements and knowledge of the Henry constants. From these measurements the reactivity ratios of α -olefins can be calculated without analyzing the copolymerization products.

The "kinetic technique" allows also the evaluation of the change of the reactivity ratios with time; in the case of the "unstable" catalysts, VCl_4-AlEt_2Cl and $VOCl_3-AliBu_2Cl$, a qualitative constancy of active centers was observed.

Some researches on EPDM synthesis have been carried out also in the absence of solvents. The polymer is obtained as a slurry in the solution of monomers (Seidov et al., 1966, 1969, 1970; Arutyunov, 1971; Zhuravlev, 1972; Thomalla et al., 1973). All the methods cited above can be or have been utilized to carry out copolymerization reactions under excessive (over atmospheric) pressure conditions (Marconi and Cesca, 1965; Cucinella and Mazzei, 1971a).

A continuous supply of termonomer is necessary also when the "semi-flow" and "closed" techniques are adopted and when the reactivity of the third monomer is high (for instance of the same order of propylene). In fact, in this case any significant change of concentration of polyene in the feed induces a significant modification of EPDM composition and when all the termonomer is introduced at the beginning of polymerization, EPDM with decreasing concentration of unsaturation is obtained at different times of reaction. This fact has been observed in the case of termonomers containing the norbornene ring (Cunningham, 1967; Cesca et al., 1971b) as center of reactivity in the terpolymerization reaction. This behavior agrees with the well-known enhanced reactivity of bicyclo-[2.2.1]-2-heptane double bond and it is due to the strain present in the ring (Rodd, 1953).

On the contrary, when the termonomer shows low reactivity, as in the case of double bonds of the vinyl type or belonging to cycloaliphatic rings (Cesca et al., 1968a), the composition of EPDM remains practically unchanged at different times of polymerization when the entire portion of third monomer is supplied at the start of polymerization.

Since the overall kinetics of EPDM formation depends on several experimental factors as, e.g., type of catalyst and termonomer employed, degree of interaction between active species and termonomer, use of catalyst activators or MW regulators, solvent, temperature, etc., the control of such a complex system, and hence the production of EPDM's with constant composition, seems better assured by the "continuous technique".

F. Mass Transfer Effects

The problems discussed in the previous section are very important in order to obtain a statistical and constant distribution of monomers in the chains of EPDM's. However, their solution does not assure the formation of random terpolymers because in the viscous solutions where the EPDM macromolecules are generally produced, mass transfer effects may be present. These effects come about from defined dissolution times (Lehmann and Gumboldt, 1964; Boocock and Haward, 1966) needed by gaseous monomers and from the high polymerization rate of ethylene under EPDM synthesis conditions. For instance, 2-3 min are needed to dissolve ethylene in toluene, depending on the partial pressure of the olefin and the temperature of the solvent. When $p_{C_2H_4}$ is less than 100 mmHg, the saturation time reaches 10 min (Matsuda et al., 1965). Furthermore, the dissolution rate depends also on the viscosity of the solution, i.e., on the concentration of polymer in the reaction medium. For instance, it has been reported that as the copolymerization products accumulate in *n*-heptane, the Henry constants change by a maximum of 10% under the conditions adopted (total pressure of monomers lower than 1 atm); however, their ratio remains constant (Firsov et al., 1966). The terpolymerization rate is influenced by these physical parameters because they can modify the monomer concentration (Lukach and Spurlin, 1964).

The "gel effect" invoked by Lukach and Spurlin (1964) to explain the variation in copolymer composition when soluble catalysts, supposed to give homogenous active centers, are used, is due to the limitation of the diffusivity of the monomers through the viscous mass of copolymer solution.

Practically, high stirring rates, low viscosities of the polymerization solutions, low reactions rates are adopted, and more generally, the gaseous monomers are passed through the solvent at a rate much higher than their rate of reaction. However, it is necessary to test the assumption made, i.e., that the adopted conditions avoid mass transfer effects. For example, the effect of the polymerization rate on the copolymer composition at defined feed compositions can be studied (Cesca et al., 1971b).

The existence of mass-transfer problems influences the feeding of monomers and consequently several critical properties of EPDM, e.g., the composition, MWD, and the formation of long chain branching or gel.

Recently, it has been demonstrated, through an analysis of appropriate mathematical models, that the unusual MWD's observed by many authors (Berger et al., 1969) for the Ziegler-Natta polymerization of α -ole-

fins (generally MWD lies between 4 and 40) may occur as a consequence of mass-transport limitations and of the movement of catalytic sites within the growing polymer particle (Singh and Merril, 1971; Schmeal and Street, 1972; Crabtree et al., 1973).

Even though several factors have been predicted (Schmeal and Street, 1972) in affecting the MWD of poly- α -olefins, e.g., particle geometry, nature of diffusion and of reaction, environmental history of the particle, distribution of site activities and of particle sizes, etc., the main implication of this type of analysis is that as the polymerization proceeds, the core of the growing particle progressively becomes starved of monomer, whereas, the active centers near the surface dispose easily of a great number of monomer molecules. The existence of two different physical states where the mobility of polymer chains are different and, hence, the rate constants of elementary steps are different can yield broad and also bimodal MWD, independently of the heterogeneity of the catalyst (cf. Section II B). Indeed, there is some preliminary support in the literature on this point (Berger et al., 1969; Watanabe, 1972; Tanaka, 1973). Also the influence of termonomer on the MWD of EPTM, which is narrower than the EPM MWD (Table V), might be attributed to the preferential inactivation of some active centers (cf. Section II A).

However, it should be noted that the diffusion mechanism might not be the same in the case of soluble and insoluble polymers (Chirkov, 1970). In fact, while in the case of EPM and EPDM synthesis (obtained in a homogeneous system with a "semi-flow" technique and with V-based catalyst) MW increases continuously (see, for instance, Fig. 3), in the case of polyethylene prepared under similar conditions with the system $TiCl_3$ - AlR_3 a very high MW portion is formed in the earliest moments of polymerization (Crabtree et al., 1973). It seems very likely that the formation of these huge macromolecules occurs when the active centers are not covered, i.e., not diffusion controlled by the polymer and their very high efficiency can be fully realized.

However, the problems discussed in this section and in the previous one are secondary causes of the branching formation in EPDM's as the reactivity of the pendant double bonds, the concentration of the third monomer and the acidity of the catalyst are the main causes of lack of linearity in EPDM chains (see Section II D).

G. Catalyst Decay

Since the first work on ethylene-propylene copolymerization, it was observed that vanadium-based Ziegler-Natta catalysts were more suit-

TABLE V
Properties of Ethylene-Propylene Copolymers and Terpolymers Containing IPTHI^a

Sample	Ethylene content	IPTHI content (mole %)	$[\eta]$ (dl/g)	\bar{M}_v 10^{-3}	\bar{M}_n^b 10^{-3}	\bar{M}_w^b 10^{-3}	\bar{M}_w/\bar{M}_n
Copolymer	61	0	3.02	344	124	322	3.0
Terpolymer A ^c	70	0.62	1.63	148	72	151	1.73
Terpolymer B ^d	70	1.25	1.11	86.5	49.5	88.5	2.0
Terpolymer C ^e	67	1.06	0.81	56.2	32.5	59.8	66
Terpolymer D ^f	68	0.87	2.27	132	128	214	2.0
Terpolymer E ^g	68	0.81	1.66	151	88	149	1.8

^aReprinted from Cesca et al., 1970a with the permission of Hüthing and Wepf, Basel, Switzerland.

^bFrom M distribution with gel permeation chromatography (GPC).

^cPrepared in *n*-heptane at 0°C with the catalyst VAcac₃-(C₂H₅)₂AlCl and with 14.7 \times 10⁻³ mole/liter of IPTHI.

^dAs in^b but with 29.5 \times 10⁻³ mole/liter of IPTHI.

^ePrepared in toluene as in^c.

^fPrepared at -20°C in *n*-heptane as in^c.

^gPrepared in toluene at -20°C as in^c.

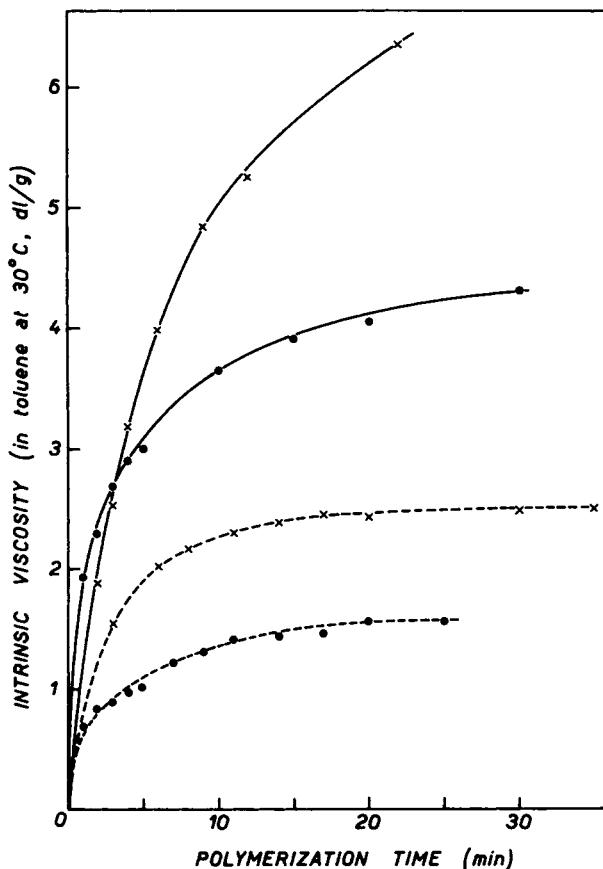


Fig. 3. Dependence of $[\eta]$ on polymerization time for EPM's (full line) and IPTHI-based EPTM's (broken line) produced in *n*-heptane with $\text{VAcac}_3\text{-Et}_2\text{AlCl}$ (\times) and $\text{VOCl}_3\text{-Et}_3\text{Al}_2\text{Cl}_6$ (\bullet) unaged catalyst systems. Experimental conditions:
--- \times --- $T = 0^\circ\text{C}$; $\text{C}_3\text{H}_6/\text{C}_2\text{H}_4 = 2.5$ in the gaseous phase; $\text{Al}/\text{V} = 6.0$, $\text{VAcac}_3 = 0.95 \times 10^{-4}$ mole/l.
--- \times --- $\text{IPTHI} = 10 \times 10^{-3}$ mole/l; $\text{VAcac}_3 = 0.87 \times 10^{-3}$ mole/l.
--- \bullet --- $T = 20^\circ\text{C}$; $\text{C}_3\text{H}_6/\text{C}_2\text{H}_4 = 2.0$; $\text{Al}/\text{V} = 10.0$; $\text{VOCl}_3 = 0.17 \times 10^{-3}$ mole/l.
--- \bullet --- $\text{IPTHI} = 7.4 \times 10^{-3}$ mole/l; $\text{VOCl}_3 = 0.62 \times 10^{-3}$ mole/l.

able to obtain random copolymers with a good catalytic activity under mild conditions. A number of catalyst systems have been derived from the combination of vanadium compounds (e.g., VCl_4 , VOCl_3 , VAcac_3 , VO(OR)_3 , VOCl(OR)_2 , $\text{VOCl}_2(\text{OR})$, etc.), organometallic aluminum derivatives (Gaylord and Mark, 1959; Magovern, 1970; Ranney, 1970),

or Al hydride (Marconi et al., 1964b, c, 1969; Marconi and Cesca, 1965) derivatives (e.g., R_3Al , R_2AlX , $R_3Al_2X_3$, $RAIX_2$, $HX_2Al.B$, $HXAlNR_2$, $(HAINR)_y$, etc., where R = alkyl group, X = halogen atom, B = Lewis base, y = number > 1), and sometimes, in union with a third component chosen among different classes of weak Lewis bases.

Table III contains the reactivity ratios of ethylene and propylene and/or their product obtained with different catalyst systems, which have been published so far. In the table we have indicated also, when it was possible, the technique of synthesis and the analytical method used.

In order to enhance the homogeneity of results having different origin and which have been subjected to different treatment, we have recalculated, when the analytical data were available in the single papers, the value and the precision of the reactivity ratios reported in the literature. The reliability of these measurements is given in Table III by twice the standard deviation deduced from a linear interpolation of the experimental data, according to the Fineman-Ross forms of the copolymerization equation.

The evaluation of the reactivity ratios can be improved through a non-linear interpolation of the copolymer-feed composition data when they have been planned opportunely according to the suggestion of Behnken (1964) and Tidwell and Mortimer (1965). We have attempted to refine the data in Table III according to this approach (Ragazzini, 1970) even though, sometimes, the experimental results were either scarce or in the less suitable range of composition.

The value of the reactivity ratios of ethylene and propylene so far collected may not have the conventional physical meaning in the light of more recent results, according to which, several V-based Ziegler-Natta catalysts are intrinsically heterogeneous (see Sections II B and V A). However, they are useful mathematical tools for relating feed composition to copolymer composition. They may be used to calculate monomer sequence distribution (Natta et al., 1960b, Davison and Taylor, 1972; Tosi and Ciampelli, 1973) when a good degree of homogeneity and composition reproducibility has been ascertained for the samples under investigation. In some cases these conditions have been satisfied, at least partly, since fair agreement has been found between the value of the product of reactivity ratios obtained through the conventional method, i.e., from the elaboration of the compositional data of the copolymer and of the feed, and through direct methods, utilizing only spectroscopic data (IR and ^{13}C NMR) obtained directly from the copolymer analysis (see Section II H 3).

Many catalyst system have been employed in the EPDM synthesis; however, aside from a few cases (Cesca et al., 1968a, b, c, d, 1971b) in which the catalyst behavior has been studied during the terpolymerization process, some specific characteristics of vanadium-based Ziegler-Natta catalysts have been evidenced mainly through ethylene-propylene copolymerization studies.

The more relevant features are summarized here.

1. The vanadium-based catalysts do not show constant activity during the polymerization time, i.e., the number of catalytic centers is, generally, decreasing with time both in the absence and in the presence of third monomer.

2. The kinetics of this decay is dependent on the particular components of the catalyst system and on the conditions of interaction adopted, e.g., temperature, concentration, solvent, modality of contact, presence of Lewis base, etc.

3. The influence of third monomer (type and concentration) is decisive to establish the diagram of catalyst decay (Cesca et al., 1968a, b, 1971b; Gladding et al., 1962).

4. The catalyst decay is related not only to the number (quantitative decay) but also to the type of active species (qualitative decay) as is evidenced by the change of the ethylene content in copolymers produced at different times under constant catalytic activity (Cesca et al., 1971b). Qualitative decay is avoided when some termonomers are employed (Cesca et al., 1968a).

5. To exclude any change in the catalyst performance, the aging of catalyst (i.e., the interaction of the catalyst components in the absence of monomers for an adequate period of time) was introduced during earlier kinetic studies (Mazzanti et al., 1957a; Natta et al., 1961d).

However, in this way, the greatest part of the potential catalytic activity is lost (Natta et al., 1961d). Only the system $VAcac_3-AlEt_2Cl$, used in *n*-heptane at 0°C (Fig. 4), shows constancy in the number of catalyst centers during ethylene-propylene copolymerization, even without any preliminary aging (Cesca et al., 1971b). This result was never accomplished in terpolymerization studies.

6. Higher catalytic activities from vanadium-based systems have been recently accomplished by adding chlorinated molecules (Duck and Cooper, 1971; Easterbrook et al., 1971; Marie and Mornet, 1971) to deactivated catalyst. The operation can be repeated several times on the initial catalyst and on the basis of a noncontinuous procedure of polymerization (Gumboldt, 1967).

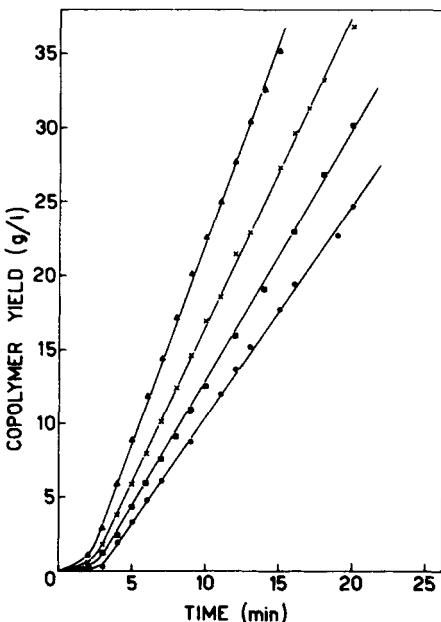


Fig. 4. Yield-time curves for EPM produced with different concentrations of unaged catalyst. Experimental: *n*-heptane = 1000 ml; T = 0°C; molar ratio in the gaseous phase C₈H₆/C₂H₄ = 2.0; flow of the monomer stream = 900 ml/hr; molar ratio of the unaged catalyst Et₂AlCl/VAcac₃ = 6.0; VAcac₃: (▲) = 0.0522 g/l; (×) = 0.0348 g/l; (■) = 0.0261 g/l; (●) = 0.0174 g/l. Reproduced by permission from Cesca et al. (1971b).

The activators action has been interpreted in terms of chlorination of V(II) inactive species to active V(III) (Natta et al., 1965b; Lehr, 1968; Lehr and Carman, 1969). However, molecules not containing halogen atoms have also been found useful as catalyst activators (Easterbrook et al., 1971).

7. Recently, in particular with EPDM synthesis studies (Cozewith and Ver Strate, 1971), a continuous feeding of the catalyst components into the polymerization medium has been adopted (Section II E). This approach realizes a steady state between the initial and final number of catalyst species, i.e., between the catalytic centers just formed and the other having entered the decay phase, by pumping constant volumes of catalyst and cocatalyst solutions and by withdrawing from the reactor solution the same volume of catalyst solution introduced.

However, the "continuous technique" does not guarantee absolutely against a limited decay (depending on the residence time in the reactor) of the catalyst and against an intrinsic heterogeneity of the active centers as a result of the catalyst components interacting. This has been evidenced for some catalyst systems from more recent studies (see Section II B).

H. Analytical Studies

As far as the analysis of EPDM's is concerned, many approaches have been proposed, starting from previous studies on straight ethylene-propylene copolymers, to obtain as much information as possible on this new class of polymers.

It is difficult to cite adequately the large amount of research carried out on EPDM's to characterize and to utilize or transform them. Recently a broad review (Baldwin and Ver Strate, 1972), dealing mainly with these arguments and reporting also a number of references, has been published.

The principal lines of research in this field may be summarized as follows (only recent references are reported):

1. Determination of composition, both of raw and fractionated polymers (Ferguson, 1971; Gardner et al., 1971; Hampton, 1972; Mitchell and Chin, 1971; Sircar and Lamond, 1972; Tosi and Ciampelli, 1973; Wandelin and Trick, 1971).
2. Studies on the structure (enchainment of monomers, monomer sequence distributions, branching, crystallinity, phase transitions, unsaturations etc.) (Bassi et al., 1970; Boyer, 1973; Carman et al., 1973; Carman and Wilkes, 1971; Cesca et al., 1971b; Crain et al., 1971; Iwami et al., 1969; Kerrutt, 1973; Mark, 1972; Michailov et al., 1971; Natta et al., 1969; Satake et al., 1971b; Schreier and Peiischer, 1972; Shyramaya et al., 1972; Takegami and Suzuki, 1971; Titova et al., 1971; Ver Strate and Wilchinsky, 1971; Zambelli, 1971; Zambelli, et al., 1971).
3. Evaluation of molecular dimensions and solution properties (Abe et al., 1969; Drott and Mendelson, 1970; Grechanovskii, 1969; Kobayashi and Ashikari, 1969; Mendelson and Drott, 1968; Ogawa et al., 1973; Smith, 1972; Uhniat et al., 1971; Wigand and Waldmann, 1968; Wild et al., 1971).
4. Statistics of binary and multicomponent systems (Corradini and Tosi, 1968; Tosi, 1968a, 1970; Tosi et al., 1969b; Ver Strate, 1970).
5. Rheological and technological properties (studies of compound-

ing, processing, vulcanization, study of the network, properties of vulcanizates, applications, modifications, chemical and physical properties, etc.) (Allara and Edelson, 1972; Baldwin, 1972; Baldwin et al., 1970; Baranwal, 1968; Baranwal and Lindsay, 1972; Bares, 1971; Capito et al., 1968; Caywood et al., 1971; Cirlin et al., 1971; Crespi et al., 1973; De Candia and Vittoria, 1973; Delyusto and Maslova, 1971; Draexler, 1970; Figini et al., 1972; Flisi et al., 1969, 1971; Frensdorff, 1968; Fujimoto and Nakade, 1969; Glaser and Eirich, 1970; Grillo, 1971; Hassan and Ray, 1971; Hazelton and Pyndak, 1971; Kaufman, 1971; Kirkham, 1971; Kodama, 1968; Kraus, 1971; Laue, 1971; Marissey, 1971; Mastromatteo et al., 1971; Meulen, 1971; Morgan, 1968; Murakami and Tamura, 1971; Pearson and Böhm, 1972; Ranney and Pagano, 1971; Saegebarth, 1968a; Satake et al., 1970, 1971a,b; Shih, 1971a,b; Stewart and Verbanc, 1971; Tokita and Scott, 1969; Westfahl, 1972; Zamboni, 1971).

Despite the large amount of work produced, (Mitchell and Chin, 1973; Wadelin and Morris, 1973) in several cases the results obtained on the subjects now listed are a matter of discussion because relatively little conclusive evidence of characterization has been collected on materials having different and complicated structures.

Very recently a comprehensive critical review, dealing mainly with the application of IR spectroscopy in determining both the composition and the sequence distribution of EPM, has been published (Tosi and Ciampelli, 1973). A detailed discussion of the fundamental premises necessary for the utilization of spectroscopic methods (and their standards) that have been employed so far in EPM study is reported. The attribution of the bands involved in structural and compositional characterization is reexamined and discussed on the basis of the structural interferences which come from the origin of the samples investigated. The comparison of the essential features of the different approaches is carried out by evaluating the molar absorptivities of several bands. Also the experimental details of spectroscopic methods and the determination of the precision of the results are reviewed. Furthermore, the authors (Tosi and Ciampelli, 1973) integrate their earlier contributions to account for some controversial points.

However, it would be out of the scope of the present work to review all the arguments cited above, whereas it is useful to consider in the following sections the topics under (1) and in part under (2) and (3). In the sections devoted to describing single EPDM's, reference will be made to some specific information referring to points (2) and (5).

1. Dosage of Olefins

In the past it was assumed that the determination of the two main components of EPDM could be carried out using the same IR bands and the same techniques as in the case of EPM. Reviews of the IR method proposed to determine the composition of ethylene- α -olefin copolymers have been already published (Drushel, 1970; Gardner et al., 1971; Hampton, 1972; Tosi and Ciampelli, 1973). However, it will be shown below that, at least when a methyl group is present on the third monomer, complications arise if the IR spectra of EPDM's are utilized to obtain their composition according to the procedure developed for EPM.

Much work has been done in the past in order to improve or refine the IR quantitative evaluation of propylene in EPM. Near-IR bands, physical blends of homopolymers, model compounds radiotracer methods, compensation procedures, pyrolysis and IR, GC or mass spectrometry analysis of pyrolyzate, calibrations with films obtained from homopolymers, NMR spectroscopy, etc., have been utilized (Brown et al., 1963; Bua and Manaresi, 1959; Bucci and Simonazzi, 1962; Ciampelli et al., 1962; Ciampelli and Valvassori, 1967; Davison and Taylor, 1972; Drushel and Iddings, 1963; Gardner et al., 1971; Garrasi, 1965; Gössl, 1960; Groton, 1964; Imhof, 1966; Ke, 1962; Kimmer et al., 1970; Lomonte and Tirpak, 1964; Michailov et al., 1971; Nencini et al., 1965; Popov and Duvanova, 1969; Porter, 1966; Szewczyk and Zielasko, 1968; Takeuchi et al., 1969a; Tosi, 1968b; Tosi et al., 1968; Tosi and Ciampelli, 1973; Tosi and Simonazzi, 1973; Tosi and Zerbi, 1973; Veerkamp and Veermans, 1961; Ver Schooten and Mostert, 1963; Wei, 1961).

Very recently (Hamptone, 1972), a detailed review, dealing with the application of IR spectroscopy to the characterization of several rubbers, among which ethylene-propylene elastomers, appeared. The main topics in the case of EPM's and EPDM's are: composition, structure, sequence distribution, and termonomer content. The use of different bands, proposed by several authors, is critically discussed in view of their analytical utilization. The perturbing effects due to the structure of polymers under examination (e.g., crystallinity, presence of unsaturation, branching, irregularities of enchainment) are taken into account.

An important conclusion of this survey is that IR methods for determining propylene content in EPM can hardly give results with a maximum total error lower than 3%. The difficulty in having satisfactory standards for this kind of measurement is stressed. The uncertainty is mainly related to the possible existence of irregularities in the chains

(cf. Section II H 3) about which, quantitatively, we know nothing a priori. The use of hydrogenated natural rubber (but the use of hydrogenated synthetic *cis*-1,4-polyisoprene or of hydrogenated poly-3-methyl alkenamers would be better) as a model for EPM's having different structural features may be doubtful due to the incompleteness of hydrogenation. Standards containing ^{14}C -tagged molecules can give a reproducibility of $\pm 0.5\%$ in radiochemical analysis when great accuracy is assured. Usually errors are within $\pm 2\text{--}3\%$ and in complicated experiments it may be difficult to obtain better than $\pm 5\text{--}10\%$ (Ayrey, 1969). Unfortunately, many publications report radiochemical analysis without giving details or any indication of the precision (Campbell and Warner, 1969).

A recent paper (Gardner et al., 1971), concerning a detailed reinvestigation of a previously reported IR method, has offered the opportunity to examine some more general aspects of the analytical problem of propylene dosage in EPM and to confirm the validity of the spectroscopic method. Carbon-14 labeled ethylene or propylene was used to prepare a series of samples of copolymers of known composition and having different (broad or narrow) compositional and sequence distributions. Improved elemental combustion analysis and counting techniques were used to determine sample composition and to compare them with IR results. Also NMR analyses were carried out on a series of radioactive samples by using the areas under the peaks due to methyl groups and to backbone protons.

The main conclusions of this work are:

1. Within the ranges systematically varied, neither compositional nor sequence distributions have been found to affect the ratios of the absorbances studied.
2. No isotopic effects exist in the polymerization reactions as both ^{14}C -tagged ethylene and propylene yielded the same results.
3. The ratio A_{1155}/A_{720} gives the best correlation with radioassay results (standard error $\pm 4.4\%$ within 95% confidence limits), whereas the band at 1378 cm^{-1} is subjected to unexplained perturbation in both polypropylenes and copolymers examined.
4. NMR and atactic polypropylene calibrations of a sufficiently large sample population give the same results as the ^{14}C analysis.

Very recently a careful investigation concerning spectroscopic researches on EPDM's containing seven different norbornenic termonomers has been published (Tosi et al., 1972). The problem of transferability of analytical methods, employed for the dosage of propylene in

ethylene-propylene copolymers to EPDM containing 5-ethylidene-2-norbornene (ENB), was examined to check the influence of a third monomer. In the case of ENB, significant absorptions are present in all spectral regions utilized for the propylene determination and an accurate evaluation of these absorptions was found practically impossible.

An empirical correction has been proposed utilizing a minimization procedure of the sum of the squares of the differences (total found-100) where "total found" is: C_2H_4 (determined radiochemically, as EPDM contains ^{14}C -labeled ethylene) + C_3H_6 (determined by near-IR spectroscopy at 5930 and 5690 cm^{-1}) - $K \times \text{ENB}$ (correction for ENB influence on C_3H_6 content through a proportionality coefficient (K) evaluated by the minimization procedure) + ENB (determined by IR spectroscopy and influenced very little by C_3H_6 content). The procedure, carried out on a set of terpolymers, yields $K = 0.5$. Hence in the case examined, the influence of ENB concentration on C_3H_6 content is not negligible when the termonomer concentration is near or higher than 4 wt %, assuming an error of IR method of $\pm 5\%$ and an average content of C_3H_6 of 40 mole %.

NMR measurements have been proposed to determine the content of α -olefin in EPM (Ferguson, 1971; Kimmer et al., 1970; Takegami and Suzuki, 1971) but current methods imply some uncertainty in the resolution of some overlapping peaks.

The introduction of instruments operating at higher magnetic field strengths (220 MHz) has not eliminated considerable overlap in the spectra, which are affected by the structural arrangements of four- and five-monomer sequences (Hampton, 1972; Parter, 1966). Hence, monomer ratio analyses are not absolute, unambiguous, or highly reproducible. At low ethylene content, only qualitative or semiquantitative estimates of tactic placements of propylene dyads and "blockiness" of ethylene sequences can be made, whereas at low propylene content, the total methyl group concentration can be evaluated.

By contrast, it has been claimed that the spectra collected at 60 MHz and 100°C show a better resolution and the results are in agreement with ^{14}C and atactic polypropylene (1378 cm^{-1} band) calibrations, provided that an adequate sample population is studied (Baldwin and Ver Strate, 1972). Even when this caution is observed and the samples are prepared with the same catalyst, the error for the correlation of EPM composition with spectral data (both NMR and IR) is higher than 3% (95% confidence limit) in a wide range of copolymer compositions.

Better results have been obtained by IR analysis of EPM pyrolyzate

(Brown et al., 1963; Takeuchi, 1969a). In fact, by using the ratios of the bands at 909/889 cm⁻¹ or 1380/1470 cm⁻¹, standard deviations of 2-3% have been reported.

A very recent investigation, carried out with IR and 220-MHz NMR spectroscopy on EPM's, prepared with different Ziegler-Natta catalysts, has shown that the same copolymer composition is given by both methods, whereas long ethylene sequences of some samples are detected only by NMR analysis (Takegami et al., 1972). Furthermore, EPM's prepared with Ti-based catalysts show high crystallinity and block character, while V-based catalysts yield random EPM containing, however, -(CH₂)₂- groups (cf. Section II H 3).

Practically no reports exist on the utilization of X-ray diffraction methods for the determination of α -olefin content in EPM and EPDM. The examination carried out in our laboratories during the last years, on a number of different samples has evidenced (Cesari and Perego) that the angular position of the maximum of the diffraction halo, due to the amorphous region of EPM and EPDM (containing low concentration of termonomer), depends only upon the C₂H₄/C₃H₆ ratio, while the width of the halo is correlated to both the composition and the type of distribution of the monomers. These conclusions have been made by a careful X-ray examination of several series of co- and terpolymers, obtained with different catalysts, in particular the VCl₄-Et₂AlCl system. Reference was made to EPM samples containing ¹⁴C-labeled ethylene and counted for their composition. The product of reactivity ratios for different catalyst systems was obtained through both classical and pyrolysis methods (Nencini et al., 1965).

X-ray spectra have been recorded with a standard Phillips diffractometer, equipped with a proportional counter and pulse discriminator. Angular 2 θ position (A) of the maximum of the amorphous halo is defined through a careful interpolation of the upper part of the diffractometer trace; the reproducibility being within 2 θ = \pm 0.05°. The half-maximum breadth (B) is defined in 2 θ degrees (CuK $\bar{\alpha}$), by keeping the height value of the trace at ca. 2 θ = 75° as a background line.

The dependence of (A) on the ethylene content is shown, for samples prepared with a VCl₄-Et₂AlCl system, in Figure 5.

The slope and the form of a diagram of this type are very slightly affected by the blockiness of copolymer.

The correlation between (A) and (B) for different samples is shown in Figure 6. It can be observed that each series of samples, produced with the same catalyst system, give rise to a curve. These curves are approximately parallel, thus an extrapolation for any r_1r_2 value, ranging

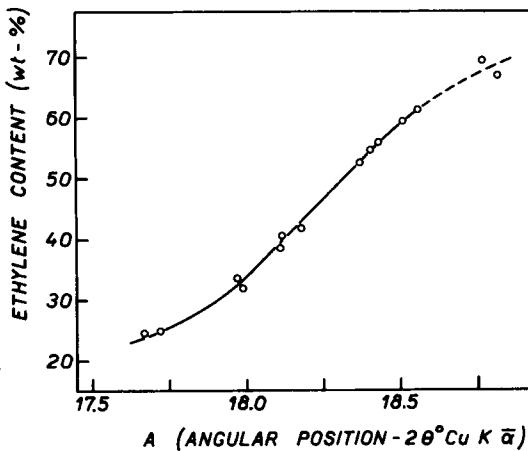


Fig. 5. Dependence of the ethylene content of EPM (catalyst system $\text{VCl}_4\text{-Et}_2\text{AlCl}$) on the angular position of the maximum of the amorphous halo.

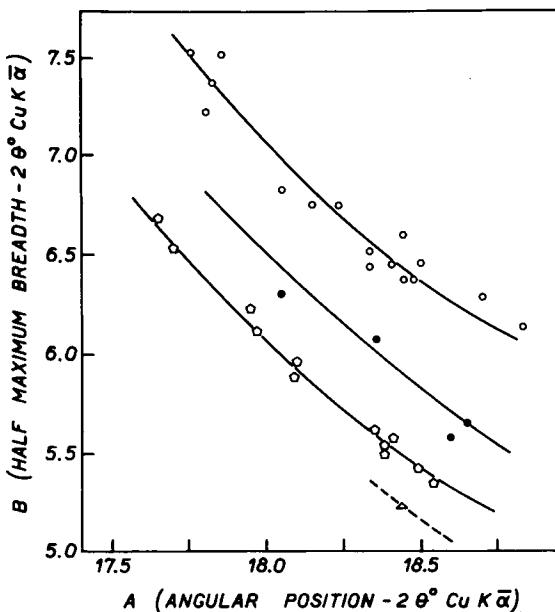


Fig. 6. Relationships between the half-maximum breadth and the angular position of the amorphous halo obtained from EPM's prepared with different catalysts; (\triangle) $r_1 r_2 = 0$ (hydrogenated *cis*-1,4-polyisoprene); (\square) $r_1 r_2 = 0.4$; (\bullet) $r_1 r_2 = 0.7$; (\circ) random EPM, i.e., $r_1 r_2 \approx 1$.

from 0 to 1, is easily accomplished. The hydrogenated *cis*-1,4-polyisoprene is kept as reference point for $r_1r_2 = 0$.

When an adequate number of well-characterized copolymers are available and experimental conditions are maintained rigorously constant, graphs similar to that previously shown can be easily obtained and time-saving routine analyses of co- and terpolymers (having a low content of termonomer) can be attained.

The most useful IR bands for propylene routine analysis of EPM (Kimmer and Schmolke, 1968) are at 1380 cm^{-1} (due to symmetrical methyl bending vibration) and 1462 cm^{-1} (due to superposition of CH_2 and asymmetrical CH_3 bending vibrations), even though there are some discrepancies between the results of different authors (Tosi and Simonazzi, 1973). The reasons for such differences are not clear, however, the bands mentioned above can be used also for obtaining the composition of EPM with a low C_3H_6 content (less than 20 wt %) with fair precision (average standard deviation between 0.9 and 5%).

Finally, laser Raman and IR spectra of EPM block copolymer (their preparation was not reported) have been recently published (Fraser et al., 1973). The main conclusions of this study are:

1. Ethylene and propylene blocks are more evident in Raman spectra (propylene segments predominate in IR patterns).
2. Homopolymers and block copolymers show the same general frequency and intensity distribution.
3. IR spectra always show absorptions near 720 cm^{-1} (doublet).
4. Raman spectra show a band at $\Delta\nu = 1417\text{ cm}^{-1}$ which is clear also in the sample containing 15% C_2H_4 .
5. IR spectra of copolymers containing 10–20% C_3H_6 do not indicate helical polypropylene fragments.
6. Raman and IR spectra of equimolar block copolymer suggest the presence of short helical sequences of isotactic polypropylene.
7. While at low ethylene concentrations there is high crystallinity due to propylene blocks and also small well-crystallized volumes due to ethylene blocks, on the contrary small amounts of propylene are unable to develop helical and crystalline characteristics. However, they alter the crystallinity of polyethylene blocks to the less normal form containing only one chain per unit cell.

2. Dosage of Termonomer

The determination of the third monomer concentration is one of the more relevant analytical problems encountered in the study of EPDM's for three principal reasons:

1. Low levels of termonomer are incorporated in EPDM chains (generally less than 10 wt %).
2. Every termonomer requires an appropriate analytical method.
3. There is a lack of knowledge about the true nature of unsaturation in polymers. As it has been pointed out previously (Tyler, 1967), there is no practical way to get absolute proof of accuracy in any method proposed because the reactivity of unsaturation can yield side reactions (branching, cyclization, isomerization) which modify (according to an undefined extent) the expected structure.

Actually, aside from the use of radioactive termonomers which have been prepared in some cases (Arrighetti et al., 1971; Cesca et al., 1968b, 1971b; Dolinskaya et al., 1969; Giuffrè and Cassani, 1963; Livshits et al., 1970; Natta et al., 1965c; Tosi et al., 1972), several chemical and physicochemical methods have been developed to determine quantitatively double bonds in EPDM's.

a. Chemical methods. Chemical methods, based on the quantitative addition of reactive species to double bonds of EPDM chains, are widespread although they are, generally, imprecise owing to the occurrence of side reactions due to the high reactivity of the reagents involved (Hank, 1965; Lee et al., 1948; Tunnicliffe et al., 1963). Furthermore, every unsaturation needs an appropriate definition of the experimental conditions to achieve an analytical procedure.

Actually, few procedures based, generally, on halogenation reactions have been published so far for some EPDM's.

In the case of terpolymers based on 1,4-hexadiene (HD) or dicyclopentadiene (DCP) it is possible to define a reproducible method by using the iodine monochloride absorption which takes into account some side reactions (Hank, 1965; Tunnicliffe et al., 1963). The iodometric results were found in good agreement with the radiometric dosages obtained from few samples of EPDM containing ^{14}C -labeled DCP. Also in the case of ENB-based EPDM a simplified version of the ICl method (60 sec of reaction time; exclusion of KIO_3 titration) gives accurate unsaturation results when carefully and consistently performed (Gardner and Ver Strate, 1973), although the values of the iodine number analysis are ca. twice the values of the radiometric method.

On the contrary, when the termonomer is, for instance, 1,5-cyclooctadiene (COD) or 1-isopropylidene 3a, 4, 7,7a-tetrahydroindene (IPTHI), no method of correction, based on the use of ICl, yields reliable values (Cesca et al., 1968b; Tunnicliffe et al., 1963). Recently it has been reported (Baldwin and Ver Strate, 1972) that the same situation was encountered in the case of vinyl-, butenyl- and isopropenyl-norbornene-based

EPDM's: they consume an excess of reagent. The anomaly of these results was confirmed by halogenation studies of model compounds (e.g., cyclooctane). Apparently one of the basic assumptions of the method does not hold: either the substitution reaction with these unsaturations is very rapid or the double bonds created by splitting out react rather rapidly with the reagents (Tyler, 1967).

These observations explain why most halogenation results of EPDM's should be considered as approximate. In fact, when the halogenating ability of the reagent is lower than, for instance, that of iodine halides, more reliable results can be obtained. This is the case of pyridinium bromide perbromide (PBPB) employed in methanolic solution, which has been used with EPDM's based on HD, MNB, ENB, COD, DCP and also tested with an olefin model (Tunnicliffe, 1970). The results obtained show a good internal consistency, but have not been referenced to an absolute method. In the case of DCP-based EPDM the reaction occurs for 50% of the value obtained with ICl (Tunnicliffe, 1970), whereas ENB shows the tendency to increase consumption of PBPB with time. However, in the case of COD satisfactory results have been obtained (referred to radiochemical data from a set of EPDM containing ^{14}C -labeled COD) with the method of Gallo et al., (1948) using I_2 and $\text{Hg}(\text{CH}_3\text{COO})_2$ in the presence of trichloroacetic acid. Better results have been obtained by ozonolysis of COD-based EPDM and titrating the active oxygen of polymer (one atom from one double bond) through oxidation of AlI_3 or of organic leucobases (Giuffrè and Cassani, 1963).

Another method for determining unsaturation in olefinic polymers employs bromination and determination of Br by combustion and titration against $\text{Hg}(\text{NO}_3)_2$, (Szewczyk et al., 1969).

More recently, the reaction of the dichlorocarbene diradical (originated from phenyl trichloromethyl mercury (Seyferth et al., 1963)) with unsaturated polymers (Levine and Haines, 1970) has been proposed for the determination of the unsaturation content via analysis of the chlorine content. In the case of ENB terpolymers the method results are in agreement with spectroscopic evaluations and with an indirect method based on the determination of the unreacted termonomer.

Also borane chemistry has been found useful for the quantitative evaluation of a variety of olefin unsaturations (Brown, 1972). In the case of EPDM there are only preliminary indications obtained (Gardner and Ver Strate, 1973) with 9-borabicyclo-[3.3.1.]nonane which contains only one $\text{B}-\text{H}$ bond and does not crosslink the polymer. However, the method is time consuming, sensitive to water and other compounds containing active hydrogen atoms. It has not yet yielded data of adequate precision.

Catalytic hydrogenation has been recently proposed (Pautrat, 1968; Sedlock, 1966) for determining unsaturation in elastomer, but the method yields asymptotic curves to completion. The time for complete hydrogenation varies from 20 min for pure low-MW olefins to 10 hr for low-MW polymers.

b. Spectroscopic methods. Analytical methods based on spectroscopic techniques are probably preferable for their speed and adequate accuracy, in particular when they are tested with an absolute method. In the case of IR methods, spectra are recorded from thick polymer films since relatively low concentrations of termonomer are involved. However, particular care is necessary in this type of measurements as thick films are susceptible to shrinkage. The quantitative IR determination of termonomer was found convenient in the case of DCP (Hank, 1965; Cooper, 1965; Szewczyk, 1969), ENB (Levine and Haines, 1970; Tosi et al., 1972), MNB (Hampton, 1972), and more recently for other five norbornenic diolefins (Tosi et al., 1972). EPDM containing DCP shows an absorption at 1611 cm^{-1} ($\epsilon = 0.74 \times 10^4\text{ mole}^{-1}\text{ cm}^2$; Tosi and Ciampelli, 1973) due to cyclopentene unsaturation. Its intensity was related to the 4310 cm^{-1} absorption (due to methylene group content and proportional to the thickness of the polymer film) and the ratios of absorbance were calibrated with iodometric results.

Table VI lists other characteristic bands of dicyclopentadiene and other dienes utilized in EPDM synthesis, which have been considered for analytical purposes.

According to Levine and Haines (1970) the 3043 cm^{-1} band is the strongest ($\epsilon = 4.67 \times 10^4\text{ mole}^{-1}\text{ cm}^2$) and perhaps the best to use for DCP, even though there are some difficulties in locating the baseline; also the ratio A_{695}/A_{1160} has been used (Giuffré and Cassani, 1963).

ENB-based EPDM has an absorption at ca. 1700 cm^{-1} ($\epsilon = 0.85 \times 10^4\text{ mole}^{-1}\text{ cm}^2$; cf. Table VII) useful for determining the termonomer content when its level is sufficiently large. The results have been checked with a chemical method (dichlorocarbene addition), NMR analysis (signals at 4.9–5.3 ppm but, unfortunately, useful only for high content of diene and low MW terpolymer), and GC evaluation of termonomer not reacted in the terpolymerization reaction. The other bands at ca. 809 cm^{-1} (the stronger) and at 3042 cm^{-1} (weak) are not considered useful for overlapping due, respectively, to the band of isolated methylene groups and to methyl hydrogen stretching band.

Furthermore, the 805 cm^{-1} unsaturation band ($\text{>}C=\text{CH}-$) has been found extremely sensitive to the catalyst and cocatalyst used to prepare the terpolymers (Gardner and Ver Strate, 1973). This observation is

TABLE VI
Characteristic Olefin IR, UV Frequencies and NMR Signals for some EPDM's and EPTM's^a

Termonomer (type)	Hydrogen stretch (cm ⁻¹)	Double bond (cm ⁻¹)	Hydrogen deformation (cm ⁻¹)	Conjugated diene system (m μ)	Chemical shift (τ , ppm)
<i>endo</i> -Dicyclopentadiene	3043	1611	740,690 ^b	—	4.55
<i>exo</i> -Dicyclopentadiene	3040	1615	784 ^c ,740,690 ^b	—	4.48
1,4-Hexadiene			965	—	4.7
5-Methylene-2-norbornene	3069	1662	872	—	5.25 and 5.5
5-Ethylidene-2-norbornene	3040	1688	809	—	4.8 and 4.9
Methyltetrahydroindene	—	—	795 ⁱ	—	—
1,5-Cyclooctadiene	—	—	—	—	4.55
IPTH ^d	—	—	672	255	8.37
IPDCP ^d	3055-3035	1656	—	253	8.28
DPT ^e	—	—	—	243	—
MCNM ^f	3050(sh)	1615	—	254	—
DMPNB ^g	3080	1620	885	284	4.5-5.4 and 8.31
NTMCM ^h	—	1640	—	246	3.8-5.0

^aCesca et al., 1970a, 1971b, 1973a, Hampton, 1972; Sewell and Skedmore, 1968.

^bFor *exo*-DCP-based EPDM $D_{690}/D_{740} > 1$, whereas for *endo*-DCP-based EPDM the same ratio is < 1 .

^cNo assigned band.

^dCf. Section III B 4, p. 135.

^eCf. Section III B 5, p. 144.

^fCf. Section III B 5, compound (XXXX, a), p. 146.

^gCf. Section III B 6, compounds (XXXIII-XXXIV), p. 154.

^hCf. Section III B 6, compounds (XXXV-XXXVII), p. 154.

ⁱFor a commercial sample not independently verified.

further evidence of the sensitivity of ethyldene unsaturation present in EPDM to side reactions, originated, very likely, by cationic mechanisms (cf. Section II D) and which are responsible of branching or gel in terpolymers (Section II J). Despite the interference of the 805 cm^{-1} band with the rocking vibration absorption due to two methylene groups, a good relationship has been obtained between the IR and the radio-tracer data collected from EPDM samples prepared with catalyst systems having an enhanced tendency to the alternate distribution of olefinic monomers. However the method is sensitive to compositional and sequence distribution changes, while a number of scans is necessary to reduce the errors involved in the evaluation of the coefficients of the absorptions adopted (at 805 and 1155 cm^{-1}).

EPDM containing *trans*-1,4-HD shows an unique suitable band at 965 cm^{-1} but it is disturbed by the methyl rocking region (935 – 971 cm^{-1}), whose shape depends on sequence distribution. However the sharpness of 965 cm^{-1} band permits (Tosi and Ciampelli, 1973) a fair evaluation of the diene ($\varepsilon = 18 \times 10^4\text{ mole}^{-1}\text{ cm}^2$).

No problem exists in the case of MNB-based EPDM because the sharp band at 873 cm^{-1} is relatively free from interference ($\varepsilon = 19.6 \times 10^4\text{ mole}^{-1}\text{ cm}^2$). Another band occurs at ca. 1660 cm^{-1} but it shows a lower value of ε with respect to ε_{873} .

The other five EPDM's containing norbornenic termonomers cited above (Tosi et al., 1972) are: 5-vinyl-2-norbornene (VNB), 5-isopropenyl-2-norbornene (IPNB), 5-(3'-butenyl)-2-norbornene (3-BNB), 5-(*cis*-2'-butenyl)-2-norbornene (*cis*-2-BNB), and 5-methyl-allyl-2-norbornene (MANB). For all the termonomers investigated, two bands have been utilized: either the band around 1670 cm^{-1} , due to $\text{C}=\text{C}$ stretching vibration, or the band due to out-of-plane deformation of the hydrogens of the double bond and ranging between 910 and 715 cm^{-1} , depending on the type of unsaturation. The absorptivities of the IR bands typical of the termonomers, deduced from NMR calibration obtained on samples with high termonomer content, are reported in Table VII.

Tosi et al. (1972) have investigated particularly EPDM containing ENB. The principal conclusions of their work are:

1. The $\nu(\text{C}=\text{C})$ band useful for quantitative evaluation of ENB is at 1688 cm^{-1} (instead of 1700 cm^{-1} , according to Levine and Haines, 1970).
2. ENB is a mixture of two steric isomers, differing in the position of the methyl group with respect to the bicyclo-[2.2.1]-2-heptene structure, separable by preparative GC, equally reactive in terpolymerization, and having very different molar absorptivities (Table VII).

TABLE VII
Wavelength λ , Molar Absorptivity ϵ , and Coefficient K for IR Bands of Norbornenic Dienes in EPDM's^a

Monomer ^e	Kind of double bond	C=C stretching band			$=\text{C}-\text{H}$ out-of-plane deformation band		
		λ (cm ⁻¹)	$\epsilon \times 10^{-4}$ (mole ⁻¹ cm ²)	K^b (cm ⁻¹)	λ (cm ⁻¹)	$\epsilon \times 10^{-4}$ (mole ⁻¹ cm ²)	K^b
MNB	vinylidene	1611	4.9 4.5 ^c	0.215	872	19.6	0.054
VNB	vinyl	1639	4.8 3.5 ^c	0.250	907	22.6	0.053
ENB	trisubstituted	1686	0.85 0.54 ^{c,d}	1.415			
IPNB	vinylidene	1645	5.8 4.0 ^e	0.231	883	24.4	0.055
3-BNB	vinyl	1642	4.9 4.65 ^c	0.330	908	18.3	0.081
cis-2-BNB	cis	1653	1.2 1.02 ^c	1.22			
MANB	vinylidene	1650	4.3 4.3 ^c	0.347	887	22.4	0.066

^aReprinted from Tosi et al., 1972 with permission.

^b $K = \text{coefficient by which the ratios of absorbance}/(\text{thickness cm}) \text{ found in individual spectra of terpolymers should be multiplied to obtain the wt \% of termonomer.}$

^cMolar absorptivity found in the monomer.

^dThe monomer is actually a mixture of two steric isomers having $\epsilon = 0.28$, and $0.65 \times 10^4 \text{ mole}^{-1} \text{ cm}^2$.

^eCf. Table II; MANB = 5-methylallyl-2-norbornene.

3. The difference of absorptivity between the two isomers of ENB does not explain the higher absorptivity of ENB when it is present in EPDM (respectively, 0.28–0.66 and 0.85×10^4 mole $^{-1}$ cm 2). The release of the strain of the norbornenic ring, due to the opening of the double bond, was found to be the reason for the difference in absorptivity.

4. In order to check the reliability of ENB determination via IR spectroscopy, three different approaches were adopted: (a) preparation of C₂H₄-ENB copolymer with ¹⁴C-labeled ethylene; (b) preparation of C₂H₄-C₃H₆-ENB terpolymer with ¹⁴C-labeled ENB; (c) material balance determination by GC. All the tests results were in good agreement with IR determinations, hence the hypothesis of reaction of ENB through the formation of nortricyclene structure (completely saturated) was definitely ruled out (Levine and Haines 1970; Tosi et al., 1972).

5. The molar absorptivity of a double bond present in a given termonomer is generally different from that of the same unsaturation present in EPDM or in a suitable model compound (e.g., the selectively hydrogenated termonomer). Such a conclusion holds, for the most part, for the dienes investigated so far (Table VII).

In the case of 1,5-cyclooctadiene-EPDM the out-of-plane deformation and the double bond stretching vibration are present at 665 and 1650 cm $^{-1}$ (Tosi and Ciampelli, 1973), but their molar absorptivities are rather low (respectively, 0.3 and 0.7×10^4 mole $^{-1}$ cm 2). A strong overlap between the CH₂-rocking band of C₃H₆ (815 cm $^{-1}$) and the unsaturation absorption (796 cm $^{-1}$, $\epsilon = 1.74$ mole $^{-1}$ cm 2) occurs in the case of EPDM based on methyltetrahydroindene (MTHI). A calibration line with samples containing ¹⁴C-labeled MTHI was obtained only by drawing the base line from 785 to 810 cm $^{-1}$.

Semiquantitative evaluations have been proposed for other EPDM's containing different termonomers, for instance, 4-vinylcyclohexene (Caywood, 1971), fulvene and acetylene derivatives (Sonnenfeld et al., 1969).

The presence of a residual system of conjugated double bonds in some EPTM's (see Table VI and Sections III B 4, 5, 6) makes possible the use of UV spectroscopy in determining the content of this kind of unsaturation. Generally, the high values of the molar extinction coefficients of conjugated double bonds allows a higher sensitivity from the UV method than IR method. In the case of 1-isopropylidene-dicyclopentadiene (IPDCP), methylcyclopentadienyl-5-norborn-2-enyl-methane (MCNM) and dehydro-iso-dicyclopentadiene (DPT) (see Sections III B 4, 5), the UV data were calibrated with the absorbance of model compounds of

these termonomers, i.e., having a selectively hydrogenated norbornenic double bond. Furthermore, ^{14}C - or ^3H -labeled trienes have been employed in the synthesis of EPTM's which have been counted for their radioactivity and also studied by UV spectroscopy. Generally the radiochemical values were found in satisfactory agreement with UV data. However at high concentration of third monomer, the former data had higher values than the latter ones.

NMR spectroscopy (Table VI) has been utilized as an absolute method in finding the termonomer content of EPDM's (Tosi et al., 1972). Unfortunately only high contents (ca. ≥ 15 wt %) of termonomer can be determined with significant precision. Thus, the utility of the method, for normal operating conditions is of little value in the range of more usual compositions of EPDM's. The time-averaging technique has been recently introduced, (Altenau et al., 1970; Sewell and Skidmore, 1968) in order to enhance the termonomer signal which is of low intensity due to its low concentration. Thus the separation of olefinic proton signals of termonomer from the ethylene and propylene signals is possible. On the basis of 100–200 scans for the olefinic protons of termonomer, 10 scans for the signals of α -olefins, and the presence of trichloroethylene and *p*-dioxane to increase the accuracy of the measurements, the reproducibility of the method, verified in the case of EPDM's based on HD, DCP, and ENB, was found ± 10 to 15% (Sewell and Skidmore, 1968).

c. Pyrolysis and other physico-chemical methods. The combination of EPDM pyrolysis with the GC analysis of resulting products, offers another method for evaluating the termonomer content of EPDM's. Actually the method was tested only in the case of DCP-based terpolymer (Hank, 1965). The method can be realized as direct pyrolysis in the carrier gas stream or pyrolysis products can be collected before the GC analysis. Better results can be obtained associating density or refractive index measurements to pyrolysis experiments.

In the case of ENB-based EPDM the refractive index method, carried out at 90°C on polymer films and compared with radiometric data obtained from 19 samples containing different levels of ^{14}C -EMB, gives a precision of $\pm 0.32\%$ (Gardner and Ver Strate, 1973) at 95% confidence level (single determination). Probably favorable results may be collected also from density data (Stemmer, 1966). However in the case of ENB-based EPDM, the comparison of different methods (iodine number analysis, borane chemistry, IR, NMR) with the refractive index method

has indicated that the latter procedure combines adequate precision with speed of operation and is the most reliable among the methods investigated (Gardner and Ver Strate, 1973).

A photometric method has been developed during the examination of pyrolyzate derived from DCP-based terpolymers, although the presence of a yellow color has been observed also in the case of 1,5-cyclooctadiene-based EPDM. A linear correlation was found between the absorption at 436 m μ and the DCP content of EPDM subjected to pyrolysis (Hank, 1965). No reproducibility data have been given.

3. Structure, Microstructure, and Conformation

The investigations related to the structure of ethylene-propylene copolymers started with the study of copolymerization kinetics (Natta et al., 1957). There was noticeable improvement in research when the calculation of the monomer sequence distribution, initiated on statistical basis, found, through IR measurements, a preliminary confirmation of the methylene sequences length (Natta et al., 1960b). Since that time many papers have been published on the statistics of multicomponent polymeric systems (Tosi et al., 1969b; Ver Strate, 1970) and about IR and NMR investigations carried out with the aim of elucidating the structure and the monomer sequence distribution of EPM. (Ciampelli and Valvassori, 1967; Popov and Duvanova, 1969; Tosi et al., 1969b; Van Schooten and Mostert, 1963; Veerkamp and Veermans, 1961; Zambelli, 1971; Zambelli et al., 1971, 1972).

In the case of EPM the intimate arrangement of monomeric units (microstructure) depends on: (a) the relative spatial disposition of adjacent head-to-tail propylene units; (b) the sequence distribution of the monomeric units along the chain; (c) the presence of different repeating units.

The problems involved under (a) were initially related in particular to EPM and propylene homopolymers, both containing block sequences of propylene units (stereoblock copolymers). Successively, the problem of transmitting stereoregularity through ethylene units present in EPM chains was tackled theoretically and tested spectroscopically (Kissin et al., 1967), in particular, very recently, with ^{13}C -NMR studies (see below). Thus one can speak of stereospecific copolymerization (Crain et al., 1971).

The insertion of propylene units into EPM chains through two different steric configurations (denoted as *d*- and *l*-units) can be treated

statistically on the basis of nine chain propagation reactions which are related to six copolymerization constants. Four of these are particularly significant,

$$r_2^d = \frac{K_{DE}}{K_{DD}}, \quad r_3^d = \frac{K_{DL}}{K_{DD}} = \frac{K_{syndeo}}{K_{iso}}$$

and the corresponding r_2^l , r_3^l , since the theoretical degree of isotacticity depends only on them and on the copolymer composition.

Some equations have been derived for the main parameters of the copolymers obtained, i.e., the copolymer composition, the ratio of *d*- and *l*-propylene units in the copolymer and the statistical equations for the block distribution of three types of units (ethylene, *d*- and *l*-propylene). An experimental confirmation of the theoretical degree of isotacticity has been attempted on EPM's having known composition and produced with different catalysts. The reactivity ratios reported in the literature were also used. Single values of r_2^d and r_3^d (Table VIII), were obtained from IR measurements at 973 and 1380 cm⁻¹ (Kissin et al., 1967). In all cases the actual distribution of isotactic propylene blocks in copolymers of different composition would agree fairly well with the calculated one for statistical models of Bernoulli three-component chains.

TABLE VIII
Values^a of Constants r_3^d and r_2^d

Catalytic system	r_2^d	r_3^d
$\alpha\text{-TiCl}_3\text{-Al(C}_2\text{H}_5)_3$	9.45	0.040
$\text{VCl}_3\text{-Al(C}_2\text{H}_5)_3$	7.16	0.075
$\text{VOCl}_3\text{-Al(i-C}_4\text{H}_9)_3$	17.6	0.227
$\text{VCl}_4\text{-Al(C}_2\text{H}_5)_2\text{Cl}$	15.1	0.286
Vanadium acetylacetone-Al(C ₂ H ₅) ₂ Cl	38.5	0.540

^aFrom Kissin et al., 1967.

Unfortunately, little information was given on the preparation (synthesis and fractionation) of the samples tested, thus the significance of the results obtained is limited. However, the trend of values reported for r_2^d and r_3^d in Table VIII agrees with other information derived from homopolymerization studies on propylene.

More recently, the introduction of powerful analytical methods (essentially high resolution ¹H-NMR- and ¹³C-NMR spectroscopy) has offered the possibility of obtaining useful information also on the microstructure of random EPM by studying the configurations of a

restricted number of monomeric units (triads, tetrads, pentads, etc.).

While the study of sequence distribution has made considerable use of methods derived from statistical mathematics whose results, however, have been related to spectroscopic (IR, ^{13}C -NMR) studies of EPM (not always prepared under controlled and selected conditions), the presence of different possible α -olefin base units in EPM was observed firstly by IR spectroscopy. The existence of head-to-head propylene units (propylene inversion) was detected (Van Shooten et al., 1961). Furthermore, in the presence of cationic initiators (Tosi et al., 1965) or with $\text{VCl}_4 \cdot \text{FeAcac}_2 \cdot \text{AlEt}_3$ as catalyst, propylene was found to react through 1,3-addition (Yuguchi and Iwamoto, 1964).

As far as the structure of EPM's is concerned, in the IR region there is the possibility of distinguishing crystalline ethylene blocks (730 cm^{-1}) in a copolymer from crystallinity due to ethylene homopolymer (Lomonte and Tirpak, 1964; Bly, 1966), because the band at 721 cm^{-1} has a greater sensitivity to the ordering of the chains. However for this kind of problem, polymer fractionation data, associated with differential thermal analysis, furnish a valuable contribution to IR spectroscopy in distinguishing between random, stereoblock, and random block polymers (Maurer, 1965).

Isolated head-to-tail propylene units are evidenced by the band at 1155 cm^{-1} which has been subjected to extensive analysis (Natta et al., 1965) and now it is accepted that this absorption is present in all regular head-to-tail propylene polymers regardless of tacticity. However, the bands at 1155 and 972 cm^{-1} are absent in polypropylene prepared with cationic initiators.

Tail-to-tail propylene units are recognizable by the absorption at 1133 cm^{-1} resulting from a vibration of two methyls on adjacent methine groups (Van Schooten and Mostert, 1963; Ciampelli and Tosi, 1968; Tosi and Zerbi, 1973), whereas, side ethyl groups show a band at 775 cm^{-1} . Head-to-head propylene units can be detected by the band at 752 cm^{-1} due to the rocking vibration of the group $-\text{CH}_2-\text{CH}_2-$ bound at both sides to $-\text{CHCH}_3-$ groups (Ciampelli and Tosi, 1968; Tosi and Zerbi, 1973).

The experimental conditions adopted in polymerization (type of catalyst, nature of solvent, temperature, etc.) regulate the distribution of monomers in EPM. When the reactivity ratios are known, the sequence length of monomeric units can be calculated (Natta et al., 1960b). Actually, a variety of reactivity ratios has been reported for supposedly similar catalysts (cf. Table III) but, unfortunately, for a long time the reactivity ratios product has not been independently verified. Only very recently it has been possible to make such a calculation starting from IR

(Tosi et al., 1968; Goldenberg and Pilipovskii, 1973) and ^{13}C -NMR (Carman and Wilkes, 1971) data alone. However, as it has been previously said (cf. Section II B), the calculation of monomer sequence distribution from reactivity ratios obtained with catalysts formed by multiple species, is of limited meaning. The problems involved in the heterogeneity of EPM and their influence on the structural characterization will be discussed in Section II J.

The experimental check of theoretically calculated monomer sequence distribution has been attempted by detailed and accurate IR analyses starting from the examination of a number of low-MW hydrocarbons, tail-to-tail polypropylene, hydrogenated natural rubber, hydrogenated poly-3-methyl alkenamers, all being models of the structures involved in EPM. The extensive overlapping of the bands, the necessity of some subjective judgement in the compensation technique and in the establishment of a proper baseline, make a quantitative analysis difficult (cf. Figure 7). However through comparative evaluations, the bands at 812, 750, 733, and 721 cm^{-1} have been attributed, respectively, to isolated methylene groups and sequences of 2,3, or more methylene groups. Other authors (Cooper et al., 1965; De Kock and Veermans, 1966) use the bands at 752, 733, and 721 cm^{-1} for methylene sequences of 2,3, or > 4 . The application of computer resolution technique of digitized spectra (Drushel et al., 1968) has indicated the bands at 750, 732, and 721 cm^{-1} as typical for the aforesaid sequences.

In the range between $724\text{--}728\text{ cm}^{-1}$, and more probably at 728 cm^{-1} (Van Shooten et al., 1961) an absorption due to a sequence of four methylenes should be present. Some interference exist at the 721 cm^{-1} band. The bands at 972 and 937 cm^{-1} have been adopted to determine, respectively, the content of propylene as head-to-tail sequence or as isolated unit, although this absorption does not take into account propylene units linked to both propylene and ethylene units (terminal units).

According to Tosi and Ciampelli, (1973), who have recently reexamined the attribution of the IR bands and the influence of the environment on them, IR evidences do not support the existence of a $(\text{CH}_2)_4$ sequence. Furthermore, ^{13}C -NMR investigations indicate that the number of four methylene sequence is the lowest among the others (Wilkes et al., 1973).

Anyway, it is worth noting that the use of near-IR bands (at 5682 and 5917 cm^{-1} , i.e., 1.69 and $1.76\text{ }\mu$) in determining the propylene content of EPM (Bucci and Simonazzi, 1962) is preferable over other methods using bending vibrations (e.g., 1380 and 1462 cm^{-1} bands), since the former

are influenced in a lower degree than the latter by the monomer sequence distribution.

The characterization of the enchainment of EPM can be made, in the first approximation, through IR spectroscopy, since isolated units or sequences of C_2H_4 and C_3H_6 can be detected, respectively, at 733 and 722 cm^{-1} (ethylene) and at 935 and 973 cm^{-1} (propylene).

The presence of a third monomer introduces in EPDM spectra new bands or signals which, in many cases, might interfere with the bands due to propylene and methylene sequences. No direct study has been carried out up to now, but from preliminary observations in the IR region it should be possible to evaluate methylene groups of 2,3, and 4 units or, however, to correct the bands more involved in the interference of other perturbing absorptions (Hampton, 1972).

In the case of catalyst system $\text{VOCl}_3\text{-AlEt}_3$ the agreement between the number of propylene sequences calculated (for a random EPM) and found was considered satisfactory, but for the system $\text{VOCl}_3\text{-Et}_2\text{AlCl}$ an excess of $-(\text{CH}_2)_2-$ was found and attributed to propylene inversion. Furthermore, the data suggested that propylene inversion was favored by the presence of ethylene units. (Tosi et al., 1969a)

By using the absorptivities at 937 and 972 cm^{-1} , a distribution index, Φ , defined as the ratio of isolated propylene units to propylene units in sequences, was calculated and found in good agreement with distribution data calculated from the product of reactivity ratios. Since the bands utilized are insensitive to the presence of terminal units, the value of the distribution index has been recently questioned (Baldwin and Ver Strate, 1972); furthermore, the evaluation of sequence distribution from it would not always possible. (See, however, Tosi and Ciampelli, 1973). The use of the distribution index, Φ , has enabled the calculation of the copolymerization reactivity ratios from only IR spectra data of the copolymers. This was the first attempt in calculating the EPM reactivity ratios product independently of kinetic measurements and in conjunction with an appropriate expression of their product, a new parameter, characteristic of any copolymer, was defined (Tosi et al., 1969b; Corradini and Tosi, 1968). According to the information theory from which it has been derived, the new quantity has been named "informational entropy" and defines mathematically the number of ways in which the sequences in a copolymer can be arranged, i.e., gives a measure of the copolymer randomness.

Also the quantitative study of pyrolyzate obtained from a given EPM has offered the possibility of calculating the reactivity ratios of the

copolymer under investigation (Michailov et al., 1968, 1971). The method involves several assumptions and at present the validity of the approach has not been confirmed by other experiments.

Perhaps the most promising and recent method for studying the microstructure of polymers is offered by ^{13}C -NMR spectroscopy because the normal range of ^{13}C chemical shifts is very large (200 ppm) compared to protons (10 ppm). The possibility of detecting and quantifying long range chemical shift effects on carbon atoms in different configurational and conformational environments, has enabled the calculation (Carman and Wilkes, 1971) of detailed methylene sequence distribution of 1,2,3,4, and 5 or more units in ethylene-propylene copolymers. One sample was produced at -10°C in *n*-hexane with the system $\text{VAcac}_3\text{-Et}_2\text{AlCl}$. The presence of groups of 2 and 4 methylenes indicates the existence of inverted propylene units, since a regular head-to-tail enchainment would yield only odd numbered methylene sequences. The agreement of the product of reactivity ratios value with the literature value is not completely satisfactory, but it should be noted that some spread exists also in the literature data (cf. Table III) and the presence of some heterogeneity might be inherent in the sample investigated.

More recently, the ^{13}C -NMR spectra of eleven branched alkanes, ranging from C_7 to C_{25} have been studied (Carman et al., 1973) for revising previous empirical coefficients (Grant and Paul, 1964) and corrective terms necessary to predict ^{13}C chemical shift of alkanes. The compounds studied, i.e., 2,4-dimethylpentane, 2,4,6-trimethylheptane, 2,5-dimethylhexane, 2,5,8-trimethylnonane, 2,5,8,11-tetramethyldodecane, 2,6-dimethylheptane, 2,6,10,14-tetramethylpentadecane, 2,7-dimethyloctane, 2,8-dimethylnonane, 2,8,14,20-tetramethyleneicosane, and 2,9-dimethyldecane are model compounds of regular, repeating methylene sequences (up to $(\text{CH}_2)_6$) inserted between tertiary carbon atoms. The sequences are similar to those encountered in ethylene-propylene-based multicomponent polymer system. The resulting revised parameters, being more accurate than previous ones, enhance the diagnostic possibilities of ^{13}C -NMR in predicting the microstructure of hydrocarbon polymers.

The determination of dyad and triad fractions has been calculated (Tanaka and Hatada, 1973) for commercial samples of EPM and EPDM based on *endo*-DCP by referring to ^{13}C -NMR spectra obtained from squalane and hydrogenated natural rubber, in addition to polyethylene and atactic polypropylene. The deviation from the calculated values of signals was at most 12% for each of the signals. The results obtained are summarized in Table IX where good agreement between the calculated and determined values of the fractions f_{EP} and f_{PEP} supports the validity

TABLE IX
Distribution of the Monomeric Units in EPM, *endo*-DCP-Based EPDM and Hydrogenated Natural Rubber (HNR)^a

Sequence	HNR	EPDM ^b			EPM ^c		
		1	2	3	1	2	3
Dyad fraction							
f_{PP}^0 ^e	—	0.062	0.042	0.086	0.161	0.188	0.128
f_{PP}	—	0	0	0.026	0.059	0.053	0.019
f_{EP}	1.020	0.421	0.446	0.456	0.562	0.580	0.560
f_{EE}	—	0.537	0.552	0.484	0.338	0.328	0.377
$\Sigma(f_{PP}^0 + f_{PP} + f_{EE} + f_{EE})$		1.020	1.040	1.052	1.120	1.149	1.084
Triad fraction f_{EEP}	0.483	0.094	0.076	0.107	0.098	0.075	0.111
Sequence length							
$\langle E \rangle$	0.91	3.34	3.23	2.97	1.71	1.47	2.08
$\langle P \rangle$	1.03	1.41	1.39	1.42	1.85	1.98	1.49

^aReprinted with permission from Tanaka and Hatada, 1973.

^bComposition (by ¹³C-NMR); E:(1) = 0.704; (2) = 0.691; (3) = 0.677; P:(1) = 0.296; (2) = 0.309; (3) = 0.323; DCP (by ¹H-NMR); (1) = 0.014; (2) = 0.006; (3) = 0.011 mole %.

^cComposition (by ¹³C-NMR); E: (1) = 0.481; (2) = 0.426; (3) = 0.582; P: (1) = 0.519; (2) = 0.574; (3) = 0.418.

^dPP = head-to-head dyad sequence, i.e., -C(CH₃)—CH₂—CH₂—C(CH₃)—. The absence of tail-to-tail sequence was evident in the spectra of the polymers investigated.

of the method and the accuracy of the measurements (cf. also the value of the sum of the dyad fractions in Table IX which is near to unity). In Table IX the high content of the head-to-head propylene sequences is noticeable, in particular in EPM, while the "normal" propylene enchainment (i.e., head-to-tail) is always lower both in EPM and EPDM.

A feature of EPDM is the higher value of the ethylene average sequence length and of the f_{EE} dyad fraction.

Unfortunately, we do not know the history of the samples investigated, hence is impossible, by comparing the data of Table IX, to draw any mechanistic conclusion, attributable to the presence of termonomer or to the experimental conditions adopted in synthesizing the samples studied.

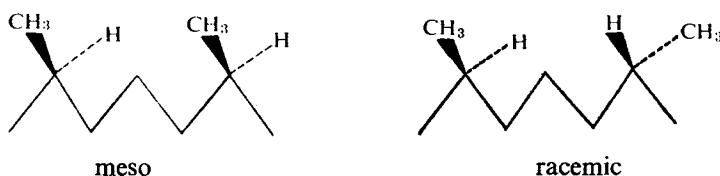
The reassessments of the ^{13}C chemical shifts for tertiary carbon atoms present in moieties similar to the sequences encountered in EPM (Carman et al., 1973) and the adoption of the Fourier transform in recording $^{13}\text{C-NMR}$ spectra, has enabled Wilkes et al. (1973) to refine the evaluation of the olefins contents in EPM and EPDM. Furthermore, by neglecting the low content of termonomer in EPDM, which is usually less than 3 mole %, the product of the reactivity ratio of ethylene and propylene has been calculated. In fact, the statistics of copolymerization gives a simple relation (Carman and Wilkes, 1971) between the reactivity ratios product, the copolymer composition, and the relative percentages of (PPP + PPE)/EPE, i.e., the propylene centered triads, including those with inverted propylene units. For three different catalyst systems based on VAcac_3 the same value of $r_1r_2 = 1.0$ was found with a precision better than ± 0.2 (cf. also Table III). The result is practically independent of the presence of termonomer. However, the above cited relation is based on the validity of the classical copolymerization equation, which implies the existence of only one type of active species (cf. Section II B).

The calculation of the monomer sequence distribution succeeded rather well in the case of propylene. The percentage of EPE sequences was found to be between 46–51 for three samples of EPDM based on ENB (produced in the presence of chain transfer agents) and containing 28–32 mole % of C_3H_6 ; the corresponding value of PPE + PPP sequences was 54–49 %. Of course the percent of EPE sequence decreases markedly when C_3H_6 content increases; in fact, EPM samples having 26–34–62 mole % of C_3H_6 show, respectively, 57.3–47.0–13.4 % of EPE.

Even though good internal consistency was found between the propylene sequences distribution calculated from methyl and methine resonance (provided that methyl assignments were refined), no accurate values for the ethylene sequence distribution were obtained. This was

due to the presence of inverted propylene units which add (or subtract, in the case of head-to-head units) methylene groups to those ethylene units.

IR spectra of EPM show, in general, an absorption at ca. 750 cm^{-1} which is characteristic of a sequence of two methylene groups between two tertiary carbon atoms. This is evidence of the propylene inversion, as stated above; on the other hand, the absence of significant absorption at ca. 1130 cm^{-1} means that head-to-head enchainment of propylene is irrelevant, at least for amounts of C_2H_4 higher than 15 mole %. A more recent study (Zambelli et al., 1969) has shown that the head-to-head addition of propylene is favored by the absence of steric problems, since after an inverted propylene unit, the insertion of an ethylene molecule is four times more probable than the insertion of a normal propylene unit. In another recent paper (Crain et al., 1971) the microtacticity of EPM's containing 10–20 % of ethylene and prepared with isospecific ($\text{TiCl}_3\text{-AlEt}_2\text{I}$ at 15°C), syndiospecific ($\text{VCl}_4\text{-Et}_2\text{AlCl}$ -anisole at -78°C), and aspecific catalyst ($\text{VCl}_4\text{-Et}_3\text{Al}$), has been studied by $^{13}\text{C-NMR}$. The spectra obtained were fairly well resolved (in particular for the isotactic sample), thus the comparison of experimental and calculated (Zambelli et al., 1967) chemical shifts was possible (Table X). The ethylene portions of the spectra of atactic and syndiotactic samples are generally similar. Further investigations (Zambelli et al., 1971), carried out on EPM prepared from $1\text{-}^{13}\text{C}$ 60 % enriched ethylene, have confirmed that the transmission of isotactic regularity takes place also through an ethylene unit. Therefore copolymerization with ethylene does not change the fundamental stereospecific behavior of the catalysts. On the contrary, in the case of syndiospecific or aspecific catalyst, a mixture of meso and racemic configurations have been observed to occur with comparable frequency:



Probably the most exciting results obtained from microstructural investigations have been reported very recently by Zmabelli et al. (1972). An accurate IR analysis of EPM, prepared with syndiospecific catalyst and containing labeled ethylene (both ^{14}C and tetradeuterated monomers were used), has been performed with the aim of elucidating the mechanism of propylene inversion. From a quantitative evaluation of $-(\text{CH}_2)_n-$

TABLE X
Chemical Shifts of Ethylene-Propylene Copolymers^a

Carbon	Calculated ^b	Experimental ^b		
		I ^c	S ^c	A ^c
<i>a</i>	148.9	147.5	{ 147.2	{ 147.5
<i>b</i>	149.2	147.8	{ (145.6-148.0)	{ (145.1-148.8)
<i>c</i>	149.5			
<i>d</i>	155.8	{ 155.6	{ 154.7	{ 154.6
<i>e</i>	156.1	{ 156.0	{ 155.9	{ 155.9
<i>f</i>	156.4		{ 167.9	{ 157.8
			{ 158.7	{ 158.7
<i>g</i>	161.5	160.3	{ 160.2	160.2
<i>h</i>	162.7	163.3		
<i>i</i>	164.0	162.9	162.7	162.8
<i>j</i>	165.8	166.0		
<i>k</i>	166.5	165.2	165.5	165.5
<i>l</i>	168.3	168.9	168.7	168.7
<i>m</i>	172.9	{ 171.6	{ 172.7	{ 173.1
<i>n</i>	173.2	{ 172.0	{ 173.3	{ 172.8
<i>o</i>	173.5	{ 172.5		{ 173.5
		{ 173.5		

^aReprinted from Crain et al., 1971, with the permission of the American Chemical Society, Washington, D.C.

^bAll chemical shifts are in parts per million upfield from CS₂ (calculated assuming δ_{CS_2} for benzene equal to 65.0 ppm and for chloroform equal to 115.3 ppm).

^cI = isotactic, S = syndiotactic, A = atactic EPM.

(where *n* = 2, 3, and ≥ 5) and -CH(CH₃)-CH(CH₃)- groups, carried out on a series of copolymers with a broad range of compositions, and also on a sample of syndiotactic polypropylene prepared under the same

conditions, four main results have been obtained: (a) both the propylene homopolymer and the copolymers contain $-(CH_2)_2-$ and $-CH(CH_3)-CH(CH_3)-$ groups; (b) the highest level of $-(CH_2)_2-$ groups in copolymers is about fivefold the content in the corresponding polypropylene; (c) at low ethylene concentration, almost all ethylene units give rise to $-(CH_2)_2-$ groups and this means that they lie between two inverted propylene units, whereas $-(CH_2)_3-$ sequences appear in noticeable amounts only at higher ethylene content; (d) the content of $-CH(CH_3)-CH(CH_3)-$ groups is not greatly decreased by introducing ethylene, until $-(CH_2)_3-$ sequences become detectable. Three important conclusions have been drawn from the interpretation of the results collected:

1. The propylene insertion on vanadium-based syndiospecific catalysts would take place preferentially on a vanadium-secondary carbon bond (tail-to-head insertion), in agreement with previous preliminary results (Takegami and Suzuki, 1969; Suzuki and Takegami, 1970).
2. Steric effects exerted by the last-entered unit of the growing chain are responsible for changing the insertion of propylene from the secondary (normal) to the primary one (i.e., occurring as a vanadium-primary carbon bond).
3. The polarity of the catalytic metal-carbon bond has little or no effect on the monomer orientation and its influence on insertion is, in any case, lower than that of steric factors.

It is evident that the general validity of these conclusions should be confirmed by further investigations, since they are an important new contribution to the definition of the mechanism of Ziegler-Natta catalysis. Indeed, very recently, the possibility of both primary and secondary insertion of propylene on vanadium-based active sites has been observed during the copolymerization of propylene with isoprene (Furukawa, 1973b) (cf. also Section VI A and Table XXX). We will refer to these results during the discussion of the mechanistic aspects of EPDM synthesis (cf. Section V).

In another paper (Mark, 1972) the configurational statistics of EPM is tackled calculating theoretically (Abe et al., 1966; Flory et al., 1969; Flory, 1969) the characteristic ratio (abbreviated as c.r.) $\langle r \rangle_o^2/nl^2$, where $\langle r \rangle_o^2$ is the unperturbed dimension of the chains, n is the number of skeletal bonds, each of length l . The calculation yields the values of temperature coefficient of $\langle r \rangle_o^2$ which, in two cases, agree fairly well with previous experimental values (Barrie and Standen, 1967) of $d\ln\langle r \rangle_o^2/dT$, obtained from force-temperature dependence studies on elongated, non-crystalline networks prepared from these copolymers (Flisi et al., 1969). In a third case the agreement with the results arising from the study of

an incompletely hydrogenated sample of *cis*-1,4-polyisoprene is poor (Opschoor and Prins, 1967).

However, the most interesting conclusion of the work can be summarized as follows.

1. The dependence of c.r. on p_2 (the probability that a given unit is of type 2, i.e., propylene) is a function of the stereochemical composition p_r (replication probability, i.e., probability of isotactic arrangement) and also of the reactivity ratio product (r_1r_2).

2. The introduction of propylene induces in any case (i.e., when $p_r = 0.95-0.50-0.05$ which corresponds, respectively, to high isotactic, atactic, or syndiotactic propylene sequences) a reduction of the value of c.r., because propylene units cause departures from the extended all-trans conformations, which is the more stable for ethylene sequences. The same behavior is observed when ethylene units disrupt the extended 3_1 helical sequence, but only for $p_r = 0.95$ or 0.05 . In fact when $p_r = 0.50$ (atacticity), addition of ethylene units has little effect on c.r. (see Fig. 8), since the propylene sequences being essentially random in stereochemical structure are not present in any regular extended conformation. This situation accounts for the absence of a sharp dependence of c.r. on r_1r_2 at constant p_2 (see in Fig. 8). On the contrary, for large values of p_r the c.r. might serve as a means for determining values of r_1r_2 .

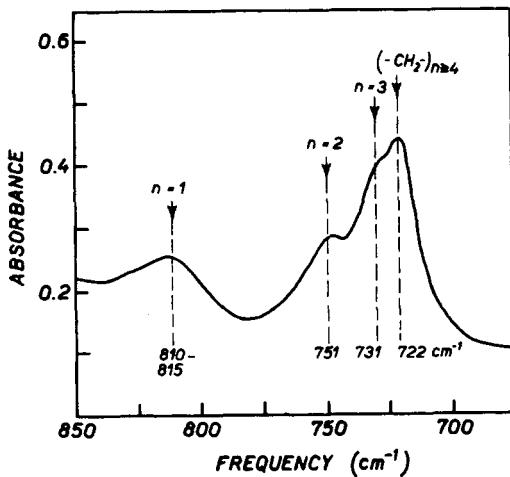


Fig. 7. IR spectrum of EPM (54.3 wt % of C_2H_4) in the methylene rocking region. Reproduced from Drushel et al., 1968 with the permission of the American Chemical Society, Washington, D.C.

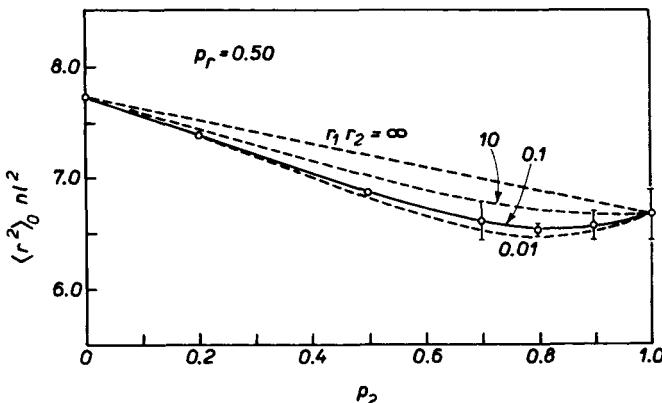


Fig. 8. Dependence of the characteristic ratio at 25°C of EPM having atactic (i.e., $p_r = 0.5$) propylene sequences. Reproduced from Mark, 1972 with the permission of the American Chemical Society, Washington, D.C.

3. The values of $d\ln \langle r \rangle_0^2 / dT$ are invariably negative in the range of $0.9-1.5 \times 10^{-3}$; they are due largely to transitions from *trans* to *gauche* states. However, the coefficient temperature of $\langle r \rangle_0^2$ is not excessively dependent on the quantities reported under 1 and on this basis the comparison with some heterogeneous experimental data has been possible.

4. The values of c.r. increase when $r_1 r_2$ increases, i.e., when the average sequence lengths increase.

Two recent papers deal mainly with statistical and mathematical aspects of terpolymer sequence distributions (Tosi, 1970; Ver Strate, 1970). The works have a prevailingly theoretical value and experimental tests are not presented. The different difficulties existing between copolymers and terpolymers in calculating relationships concerning sequence distribution are noticeable. For instance, the reactivity ratios cannot be determined from the equations giving the terpolymer composition (Price, 1962) and the knowledge of the feed composition is essential to describe the sequence distribution in terpolymers. However, some relationships between polymerization parameters (reactivity ratios or their product) and the number of sequences or other indexes (fractions of sequences; bond fractions or average number of monomeric units) characterizing the distribution of monomeric units, are derived. A different degree of reactivity in a given comonomer, compared with the reactivity of other monomers, can induce different levels of alternance in the resulting polymer. Distribution functions, deduced from the Flory theory of copoly-

mer crystallinity (Flory, 1955) have been presented to calculate the expected degree of crystallinity for particular cases of copolymers and terpolymers.

Crystalline characteristics of EPDM's have been investigated by a freezing technique (Shih and Cliff, 1973), wherein the onset temperature crystallization, T_f , is a characteristic of the ethylene content of polymer according to the relationship:

$$1/T_f = K_1 \ln(C_2H_4) + K_2$$

which is similar to the Flory's classical equation deduced from the random copolymer theory.

The size and the position of the melting regions of several multicomponent polymer systems (not only EPDM's, but also EPM's, EVA's and polyethylenes) based on relatively high ethylene contents (i.e., ranging between 63 and 84 mole %) was found dependent not only on their composition but also on the thermal history of the polymer.

4. Some Comments on Analytical Problems of EPDM's

There are some sources of uncertainty in the literature which seem due to some assumptions influencing the evaluation of the composition of EPDM's at level both of olefin or of polyene dosage and of structural characterization.

However, the following remarks can be pointed out.

1. The study of polymeric multicomponent systems always meets with the problems of chemical and physical homogeneity (e.g., composition, MW, monomer sequence length etc.) of the samples under investigation. The best way to attempt the preparation of samples with distribution of properties as narrow as possible is the fractionation (cf. Section II J) of the whole polymer, even when it has been prepared under controlled conditions (cf. Section II E).

2. In the absence of a preliminary, effective (and possible) fractionation, each spectroscopic method used should be referred to the particular experimental conditions adopted (e.g., catalyst system, temperature, solvent, kinetic control, absence of mass transfer effects, etc.) to synthesize the EPDM under investigation. In fact, the distribution of the monomeric units and of the composition may influence the spectroscopic behavior of the polymer, even though recent results (Gardner et al., 1971), obtained on straight ethylene-propylene copolymers, seem to reduce the importance of this problem (see Section II H 1).

3. The observations reported under 1 assume particular incidence when the preparation of samples for structural investigations is needed, e.g., monomer sequence distribution analysis, derivation of reactivity ratios independently of kinetic measurements; investigation on the structure of the repeating units; tacticity of α -olefin present in the chain, etc. In this context particularly important are the polymerization conditions and the equipment adopted: the best technique seems to be the continuous one (cf. Section II E) or the adoption of very low conversion, obtainable at low polymerization temperatures (e.g., -78°C). However, little information is available on the degree of heterogeneity of the catalytic centers originated at low temperatures.

4. The spectroscopic evaluation of every terpolymer (or copolymer) should be calibrated, for many monomer compositions, with an absolute analytical method, e.g., by using ^{14}C - or ^3H -labeled monomers, or NMR spectroscopy. As a consequence, since IR and NMR methods fail to give reliable results when the molecule under investigation is present at low concentrations (ca. less than 3 wt %) and owing to possible complications stressed under points 1, 3, and 5, only the composition data obtained by terpolymerization (or copolymerization) experiments employing radioactive monomers, or referring to them through calibration curves, should be considered reliable (cf., however, Section II H 1).

5. The validity of a spectroscopic calibration curve relative to two-component system when a third component is also present, has to be ascertained for any three component system in order to check the existence of direct or indirect influence on the bands used for determining the other two components. However, it should be anticipated that the spectroscopic study of a three component system implies enormous difficulties if the effect on each constituent is taken into account. The adoption of empirical approaches becomes sometime necessary under such conditions.

6. UV spectroscopy offers interesting possibilities when it can be utilized because, generally, the specific values of the molar extinction coefficients of the cromophor groups are in the UV region one or two powers of ten higher than in the IR region.

7. Although today we have only preliminary accounts on the application of ^{13}C -NMR spectroscopy to the problems involved in ethylene-propylene-based elastomers, the exceptional diagnostic value offered by this relatively new method of analysis suggests that several structural problems of EPM, connected with the mechanism of action of catalyst system, will find valuable answers not yet available from other sources.

Also the more complicated situation of EPDM should find in ^{13}C -NMR new possibilities for knowledge. For instance, the use of enriched ^{13}C termonomers should give us other informations on the microstructure of the same termonomer and on the modification induced in the ethylene-propylene enchainment with respect to the situation of EPM.

8. Despite the complications encountered in determining the composition of EPDM's, the comparison of results descending from radiochemical and spectroscopic or other physico-chemical methods, based on functional groups of termonomers, may give information about the reactivity of the secondary center of unsaturation of termonomers (cf. Section II H 2 b).

The combination of two or more methods, among which one should be absolute and the other(s) should give analytical information through the physico-chemical properties of the residual unsaturation of the third monomer, seems the best way to solve the inherent uncertainty of knowing a priori the type and the extent of the residual unsaturation present in EPDM's.

9. The problem of a thorough characterization of EPDM structure is the real task of these studies because the methods of synthesis available for preparing EPDM do not guarantee the formation of chains with a defined structure as is the case of several polymers initiated by anionic catalysts.

I. MW and MWD

The regulation of MW in α -olefin polymers synthesis can be accomplished with several agents, among which the action of molecular hydrogen (Natta et al., 1958; Brit. Pat., 1955b; Belg. Pat., 1956) or zinc diethyl (Natta and Pasquon, 1959) have been extensively investigated. Both the molecules are active chain transfer agents and their mechanisms have been evidenced in the study of α -olefins homopolymerization (cf. also Bercaw and Brintzinger, 1969). Many chain transfer agents (metal hydrides; alkyl halides; metal halides, etc.) or catalyst modifiers (Lewis bases; compounds containing active hydrogen atoms; carbonyl compounds, etc.) have been described in the patent literature (Magovern, 1970; Ranney, 1970) as MW regulators (Pozamantir, 1962; Weber and Kiepert, 1964). However, the use of H_2 offers some advantages with respect to other agents, in particular its high efficiency and reduced interference with catalyst centers are worth noting.

Recently Seidov et al. (1973) have investigated the influence of H_2

on the EPM synthesis, carried out in the presence of an excess of liquefied propylene and with the system $VAcac_3-iBut_2AlCl$. The decrease in MW was found dependent on the square root of the H_2 partial pressure, whereas H_2 changes the catalyst species into more active ones. The latter result disagrees with the evidence collected by us (and by other authors: cf. Karol et al., 1972; Natta et al., 1959a; Schindler 1964, 1966) during the homo- and copolymerization of α -olefins, carried out in homogeneous and heterogeneous systems. There are, however, other authors (Hoffman et al., 1964; Mason and Schaffauser, 1971) who have found results similar to Seidov's. Unfortunately, there is, at present, insufficient evidence to explain the contrasting data of the literature and to attribute, with certainty, to H_2 an activation effect on the catalytic species.

A modified version of the copolymerization equation has been derived for EPM produced in the presence of H_2 (Seidov et al., 1973); as a consequence the reactivity ratios of C_2H_4 and C_3H_6 are modified by the presence of the chain transfer agent (cf. Table III). In agreement with our results (see below), the reactivity of ethylene increases in the presence of H_2 , whereas that of propylene decreases slightly.

In the case of EPDM's MW can be controlled as in poly- α -olefins synthesis (Cesca et al., 1974a; Duck and Cooper, 1971; Easterbrook et al., 1971), even though side reactions (e.g., hydrogenation) involving the more reactive unsaturation of termonomer may occur.

In fact, in the case of EPTM based on DPT (dicyclopentatriene, cf. Section III B 5) the presence of $ZnEt_2$ apparently reduces only MW, whereas H_2 modifies markedly UV and IR spectra of terpolymer. When the concentration of H_2 is elevated, the UV dosage of DPT becomes impossible, while the content of ethylene increases (Cesca et al., 1974a). The latter result can be observed also in EPM prepared under the same conditions (Fig. 9), the increase being ca. 10%, i.e., beyond the error limits of the analytical methods involved (IR and NMR).

Therefore, it is evident that H_2 is able to react with the diene system of DPT under the terpolymerization condition adopted; furthermore, it reduces (as $ZnEt_2$ does) the number of catalyst sites and also their type, as is suggested by the change of C_2H_4 content in both EPM and EPTM. Very likely, the hydrogenolytic action of H_2 on the carbon-metal bond of active centers, which originates metal-hydride bonds (Natta et al., 1959a), changes the active sites in some relevant aspects, probably through a modification of their coordinative ability which may reduce the tendency of propylene to enter ethylene-propylene enchainment. Previous findings, obtained during α -olefins homopolymerization (Cesca

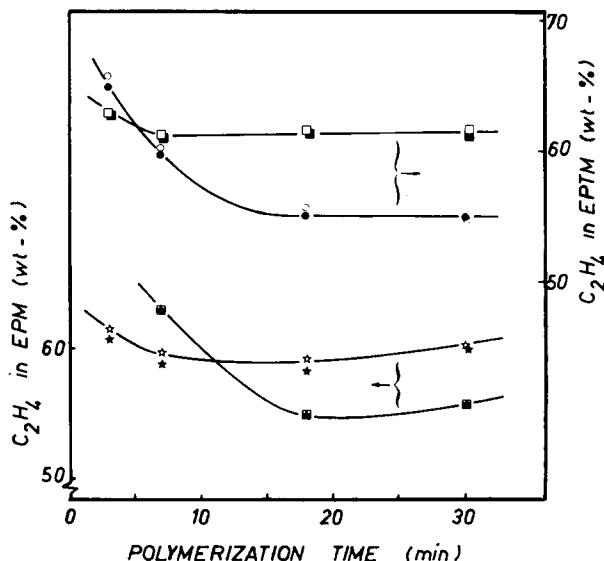


Fig. 9. Influence of H_2 on the C_2H_4 content of EPM and EPTM based on DPT (cf. Section III B 5). Conditions: catalyst = $\text{Vacac}_3\text{-Et}_2\text{AlCl}$ ($\text{Al:V} = 8.0$); solvent = toluene (1 liter); $T = 0^\circ\text{C}$; $\text{C}_3\text{He}/\text{C}_2\text{H}_4 = 2.0$ in the gaseous phase; $\text{H}_2 = 3.3$ mole % in the monomer stream; (■), (☆), (★) = EPM; (●, ○) and (□, ■) = EPTM; (★, ●, ■) = NMR data; (□, ○, ☆, ★) = IR data; (□, ☆) = H_2 . Reprinted from Cesca et al., 1974a with the permission of Hüthing and Wepf, Basel, Switzerland.

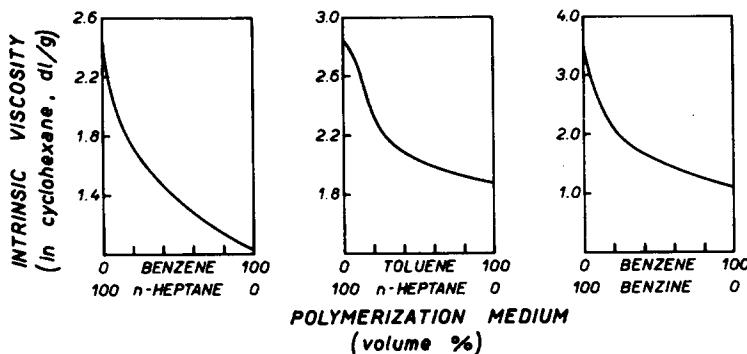


Fig. 10. Relationship between $[\eta]$ of EPDM containing endo-DCP (5.4 wt %) and the composition of the polymerization solvent mixture. Reproduced from German et al., 1966 with the permission of Verlag für Radio-Foto-Kinotechnik GMBH, Berlin.

et al., 1969a, b, c, d) and copolymerization studies (Marconi, et al., 1969), carried out with coordinate catalysts based on Al hydride derivatives, indicate that the resulting systems are less stereospecific and propylene less reactive than what had been observed with the corresponding systems based on alkyl Al derivatives.

Another recognized MW regulator of EPDM's is the solvent. In fact, in aliphatic hydrocarbons, MW's are generally higher than in aromatic ones and the use of solvent mixtures (Fig. 10) confirms this solvent effect (German et al., 1966; Baranwal and Jacobs, 1969). Similar results have been obtained also in the case of EPM (Fig. 11).

The polymerization time is another parameter influencing MW both of EPM's and EPDM's. Depending on the experimental conditions (in

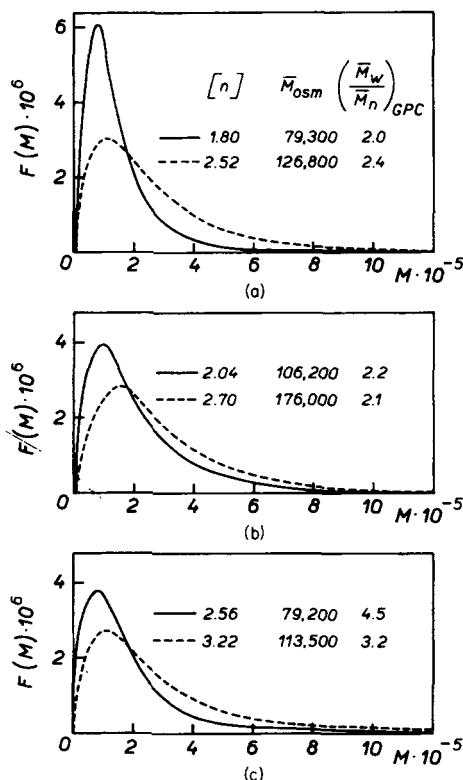


Fig. 11. Differential MWD of EPM's prepared in *n*-heptane (full lines) and in toluene (broken lines) at 0°C with different catalyst systems; a—VAcac₃-Et₂AlCl; b—VCl₄-Et₂AlCl; c—VOCl₃-Et₂AlCl.

particular type of solvent and temperature; see, however, Section IV), MW has been found increasing for very different periods of time (Fig. 3).

Obviously a discussion on MW control in an ethylene-propylene-based elastomer implies the knowledge of some solution properties of these polymers, which intrinsic viscosity data are related to. The lack of adequate information in this field has been recently emphasized (Baldwin and Ver Strate, 1972), even though some relationships between $[\eta]$ and MW have been obtained in the past. In attempting to fill this void, Baldwin and Ver Strate (1972) collected some private information from different workers concerning $[\eta]$ -MW relationships for some EPM's. However other results have been published (Cesca et al., 1970a), thus, in order to give other information on solution properties of EPM, we have tried to complete the summary of data so far reported (Table XI). Unfortunately these correlations have been given, in general, as final results, therefore the discussion of them can be made only on comparative basis.

In our laboratories (De Chirico) it has been found that a typical EPM, prepared on a laboratory scale with the catalyst $\text{VAcac}_3\text{-Et}_2\text{AlCl}$, containing 72 mole % of C_2H_4 and having $[\eta] = 1.56 \text{ dl/g}$ in toluene at 30°C (M_w/M_n being ca. 2), can be dissolved in several solvents. At 30°C the following order of solvents was found as good: cyclohexane $\geq n\text{-heptane} >$ chloroform \geq chlorobenzene $>$ tetraline (at 135°C) $>$ iso-octane \approx toluene \gg benzene. From viscosimetric measurements obtained from iso-octane, toluene and benzene in the range $15\text{--}40^\circ\text{C}$, the chain dimensions were found, respectively, constant, slightly, and sharply decreasing with the decrease of temperature. In fact, the sample under investigation separates from the benzene solution near room temperature. Some physico-chemical parameters obtained from the aforesaid fractionated EPM are reported in Table XII. The relationship found (De Chirico) between $[\eta]$ and \bar{M}_w is:

$$[\eta]_{\text{toluene}}^{30} = 3.1 \times 10^{-4} \text{ }_w\bar{M}$$

The refractive index increment dn/dc can be calculated for EPM with an interpolation method based on Huglin's results (1965), obtained for polyethylene and polypropylene in α -chloronaphthalene at elevated temperature ($125\text{--}140^\circ\text{C}$) and at $\lambda = 536 \text{ m}\mu$. More directly the following gvalues of $dn/dc = 0.116, 0.058$, and -0.047 have been found in iso-octane, cyclohexane, and toluene at 25°C and with $\lambda = 436 \text{ m}\mu$ for the EPM sample aforesaid. Moreover, the extrapolation of dn/dc

TABLE XI
Intrinsic Viscosity—Molecular Weight Relationships Obtained for Some EPM's and EPDM's

Polymer	Type	C_2H_4 (mole %)	Method	Conditions			α	Ref.
				solvent (type)	temperature (°C)	$K \times 10^{4,a}$		
EPM	60	\bar{M}_w ; dibromobenzene, 23°C; fractions	tetralin	135	3.36	0.70	Baldwin and Ver Strate, 1972	
EPM	70	\bar{M}_w ; α -chloronaphthalene, 135°C; fractions	decalin	135	4.07	0.74	Baldwin and Ver Strate, 1972	
EPM	70-75	\bar{M}_w ; isoctane, 25°C; fractions	toluene	30	3.1	0.72	De Chirico, unpubl. results	
EPM	ca. 60	linear interpolation of single homopolymers results.	tetralin	135	3.15	0.74	Moraglio, 1959	
EPM	60-70	linear interpolation of single homopolymers results.	decalin	135	3.8	0.74	Baldwin and Ver Strate, 1972	
EPM	ca. 60	linear interpolation of single homopolymers results.	all good solvents	—	3.9	0.73	Van Krevelen and Hoffwyer, 1966; Baldwin and Ver Strate, 1972	
EPM	50	\bar{M}_n ; alternating EPM ^c ; fractions having \bar{M}_w/\bar{M}_n 1.1-1.2	tetralin	135	2.93	0.74	Crespi et al., 1973	
EPM	75	\bar{M}_n ; alternating EPM ^d ; fractions having \bar{M}_w/\bar{M}_n = 1.1-1.2	tetralin	135	2.40	0.74	Crespi et al., 1973	
EPDM ^b	70	\bar{M}_n ; fractions	tetrachloro- ethylene	30	1.38	0.81	Shih, 1970	
EPDM	—	\bar{M}_n ; fractions	cyclohexane	40	3.31	0.75	Abe et al., 1969	
EPDM	—	\bar{M}_n ; fractions	—	—	0.22	0.99	Uhnat et al., 1971	
EPDM	—	unknown	tetralin	135	3.5	0.73	Imoto et al., 1968	

^a $[\eta] = KM\alpha$ ^bContaining 1,4-hexadiene.^cHaving as a repeating unit $(-\text{CH}_2\text{CH}_2-\text{CH}(\text{CH}_3)\text{CH}_2-)_n$.^dHaving as a repeating unit $[(-\text{CH}_2\text{CH}_2)_3-\text{CH}(\text{CH}_3)\text{CH}_2-)_n$.

TABLE XII
Characterization of a Typical EPM through Fractionation and Evaluation of Some Solution Properties

Fraction	C ₂ H ₄ (mole %)	[η] _{30°C} (dl/g)	[η] _{30°C} toluene (dl/g)	[η] _{30°C} isooctane (dl/g)	[η] _{135°C} tetrahydro (dl/g)	\bar{M}_w $\times 10^{-3}$ ^b	$\bar{M}_{sp}[\eta]$ $\times 10^{-3}$, ^c	S_o (Svedberg) ^d
1	72	4.23	4.40	—	—	545	—	7.40
2	—	2.49	2.48	2.72	—	233.2	—	5.20
3	73	2.28	2.26	2.64	236	—	—	—
4	73	2.09	2.15	2.44	200	—	—	4.95
5	74	1.76	1.83	1.96	169	—	—	4.21
6	74	1.43	1.50	1.68	127	—	—	3.85
7	73	0.98	0.98	1.10	70	—	—	—
8	70	0.78	0.83	—	49	—	—	2.55
9	—	0.37	0.42	—	—	19.6	1.70	—

^aObtained by precipitation fractionation (addition of anhydrous ethanol to an isooctane solution of EPM, at 25°C).

^bDetermined by light scattering (Brice Phoenix mod. 1000 Photogoniometer) with isooctane solvent at 25°, $\lambda = 436 \text{ m}\mu$ and using the dissymmetry method. Isooctane is suitable for measurement of the specific increment of the refractive index (see text).

^cCalculated from sedimentation coefficients and [η] values, both obtained in isooctane, according to the Mandelkern-Flory relationship.

^dSedimentation coefficient determinations were carried out with a Spinco E ultracentrifuge (42,040 rpm); the results were obtained by extrapolating the experimental data to normal pressure and infinite dilution.

toward the refractive index values of the solvents used, allows one to obtain the value of the refractive index (1.48) for the copolymer containing 72 mole % of C₂H₄.

Through ultracentrifugation and density measurements in isoctane at 25°C it has been possible to obtain the parameter (1- $\nu\rho$) = 0.23, which enables the correlation between intrinsic viscosity and sedimentation coefficient data.

Osmometric studies, having the aim to find the theta temperature for another sample of EPM containing 71 mol % of C₂H₄ and showing $[\eta]_{\text{toluene}}^{30} = 2.10 \text{ dl/g}$ ($M_{\text{osm}} = 1.22 \times 10^5$), have given (De Chirico) the results reported in Table XIII for the values of second virial coefficient at different temperatures. By interpolation, a theta temperature results of 26°C. Kalfus (1964) found for EPM's ranging between 54–75 mole % of C₃H₆, the theta temperature of 20°C, using the mixture *n*-heptane-acetone (3.4:1) as solvent.

Zimm plots of EPDM containing ENB have been obtained from light-scattering data (Morimoto and Okamoto, 1972). The diagrams are unusually distorted and the value of the second virial coefficient is extremely low (i.e., $1.8 \times 10^{-4} \text{ cm}^3 \cdot \text{mole/g}^2$) when the content of termonomer or the MW is high.

TABLE XIII

Dependence of the Value of the Second Virial Coefficient (A₂) on Temperature for a Benzene Solution of a Typical EPM

Temperature (°C)	A ₂ × 10 ⁴ (ml × mole/g ²)	[η] (dl/g)
38	3.75	1.70
33	2.52	1.55
30	2.04	1.48
28	0.90	1.41
25	-0.50	1.27

Another interesting observation has been reported recently (Baldwin and Ver Strate 1972) in the field of EPM solution properties, i.e., the agglomeration phenomenon which occurs in solution at near room temperature even when the samples are amorphous. The explanation of this effect, which tends to reform with time after the removal of insoluble fractions and which might be related to the presence of gel in the case of EPDM, but EPM should contain only huge macromolecules (up to MW > 10⁷) and no gel (cf. Section II J), has been proposed

(Rietveld and Scholte, 1973) on the basis of some careful solubility and light-scattering measurements. The existence of amounts of insoluble material has been attributed to aggregation phenomena between sequences of ethylene units, whose length increases with increasing MW of single fractions (Morimoto and Okamoto, 1972). This was suggested also by some rheological and mechanical dynamic investigations (Crespi et al., 1973; cf. also Section III A). However, in the case of Zimm plot anomalies a relevant contribution seems to originate from abundant amounts of highly branched or gelled material and more generally, from compositional heterogeneity. In fact, in the case of other terpolymers, i.e., based on acrylonitrile, styrene, and methyl methacrylate, the compositional heterogeneity was found to spread the apparent MW (obtained in different solvents from light scattering measurements) and to distort the Zimm plots remarkably, while the second virial coefficient shows apparently a smaller dependence on solvent and difference of composition (Kambe et al., 1973).

On the other hand, there is a moderate agreement (within 10%) between MW_v , determined at high and low temperatures (respectively, 135° and 30°C), provided that cyclohexane or tetrachloroethylene is used at low temperatures (Baldwin and Ver Strate, 1972). Evidently, the level of our knowledge in this field is quite unsatisfactory since the "old" method of Moraglio (1959) for interpolating EPM intrinsic viscosity between polyethylene and polypropylene data is considered a good approximation (Baldwin and Ver Strate, 1972) for all EPM, crystalline or not. In fact, it has been shown very recently (Crespi et al., 1973), by relating viscosimetric and osmotic measurements carried out on EPM fractions having high sequential homogeneity and narrow MWD (i.e., $M_w/M_n = 1.1-1.2$), that there is no agreement between experimental results and the theoretical predictions (Moraglio, 1959). Actually, the linear relationship between $\log [\eta]$ and $\log M_n$ obtained for an EPM fraction containing 50 mole % of C_2H_4 cannot be interpolated by drawing the line falling exactly half-way between the two parallel lines for polyethylene and polypropylene (Fig. 12). The anomalous behavior of EPM solution is confirmed also by examining the position of the diagram $\log [\eta]$ vs. $\log M_n$ referring to an EPM fraction containing 75 mole % of ethylene. (See Fig. 12).

The discrepancies cited above, both in the case of Zimm plot distortion and of $\log [\eta]$ - $\log M_n$ relationships, seem due either to the dependence on composition of the polymer-solvent interaction parameter or, more generally, to interaction (e.g., aggregation) phenomena involving relatively short sequences of ethylene units (cf. also Section III A).

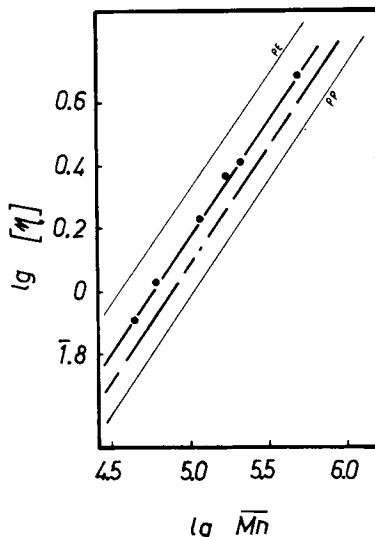


Fig. 12. Relationship between intrinsic viscosity and MW for regular EPM's, i.e., having $(-\text{CH}_2-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}_2-)_n$ or $[(-\text{CH}_2-\text{CH}_2)_3-\text{CH}(\text{CH}_3)-\text{CH}_2-]_n$ as repeating units, and related homopolymers. Measurements in tetralin at 135°C. Reproduced from Crespi et al., 1973 with permission of the Editrice di Chimica S.p.A., Milan.

Contradictory results have been found for MWD of EPDM's. In fact, when the polymerization solvent is gradually changed from benzene to *n*-heptane, the gradual transformation of MWD curves from mono-modal to bimodal distribution (Fig. 13) has been reported for DCP-based EPDM (German et al., 1966). The occurrence of a bimodal MWD was observed also when the polymerization temperature was lowered from +10°C to -30°C, with $\text{VOCl}_3\text{-Et}_2\text{AlCl}$ as catalyst.

The behavior of some EPDM's samples, subjected to milling for different times and under different temperatures, has been investigated by GPC (Baranwal and Jacobs, 1969); nonrandom chain degradations were observed with a narrowing of MWD.

The use of GPC technique for studying samples of EPM and *endo*-DCP-based EPDM, both produced on a laboratory scale, has ascertained a more complicated situation than that which has arisen from previous investigations (German et al., 1966). We have investigated three groups of catalyst systems based, respectively, on VOCl_3 , VAcac_3 , and VCl_4 . Different alkylaluminium halides, namely Et_2AlCl , $\text{Et}_3\text{Al}_2\text{Cl}_3$, and EtAlCl_2 have been associated with the vanadium compounds above

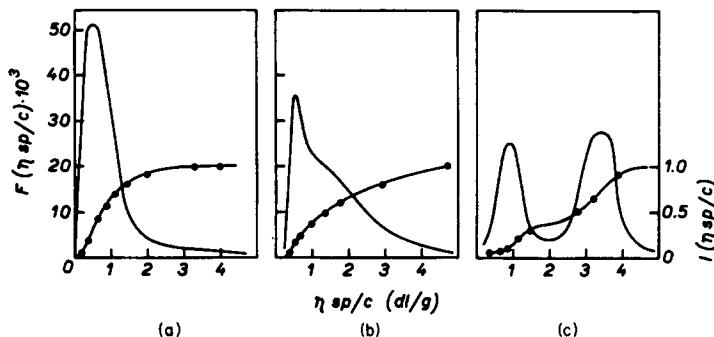


Fig. 13. Change of MWD as a function of the composition of the polymerization medium; a—100% benzene, $[\eta] = 1.05$ dl/g; b—benzene 25% and *n*-heptane 75 vol %, $[\eta] = 2.04$ dl/g; c—100% *n*-heptane, $[\eta] = 2.83$ dl/g. Reproduced from German et al., 1966 with permission of Verlag für Radio-Foto-Kinotechnik GMBH, Berlin.

specified and both EPM and EPDM have been prepared under the same experimental conditions. Furthermore, two solvents *n*-heptane and toluene and different polymerization temperatures have been adopted.

No general rules can be derived from the results obtained; every catalyst system shows a specific behavior which, in turn, depends on the specific conditions of polymerization adopted. As it will be seen below, the experimental conditions have a great importance in determining MWD's of polymer obtained with this kind of catalysts.

We can summarize the most interesting evidences as follows (see also Fig. 14).

1. Catalysts systems based on VOCl_3 always furnish EPM's or EPDM's with monomodal MWD when they are prepared *in situ* and in *n*-heptane. In toluene they always show a bimodal MWD. These results are not modified in their essential feature, i.e., mono- or bimodality, by termonomer concentration, polymerization temperature, type of ethyl aluminium halide, molar ratio Al/V.

2. EPM's and EPDM's produced with $\text{VAcac}_3\text{-Et}_2\text{AlCl}$ in *n*-heptane always have a monomodal MWD; but when *endo*-DCP-based EPDM is produced in toluene, its MWD is bimodal. Also EPM obtained with the system $\text{VAc}_3\text{-Et}_3\text{Al}_2\text{Cl}_3$ shows a bimodal MWD. However, the type of termonomer is decisive in determining monomodal MWD; for instance, this is the case of EPTM's based on IPTHI or the triene MCNM (cf., respectively, Section II B 4, 5). The molar ratio Al/V does not significantly modify the MWD.

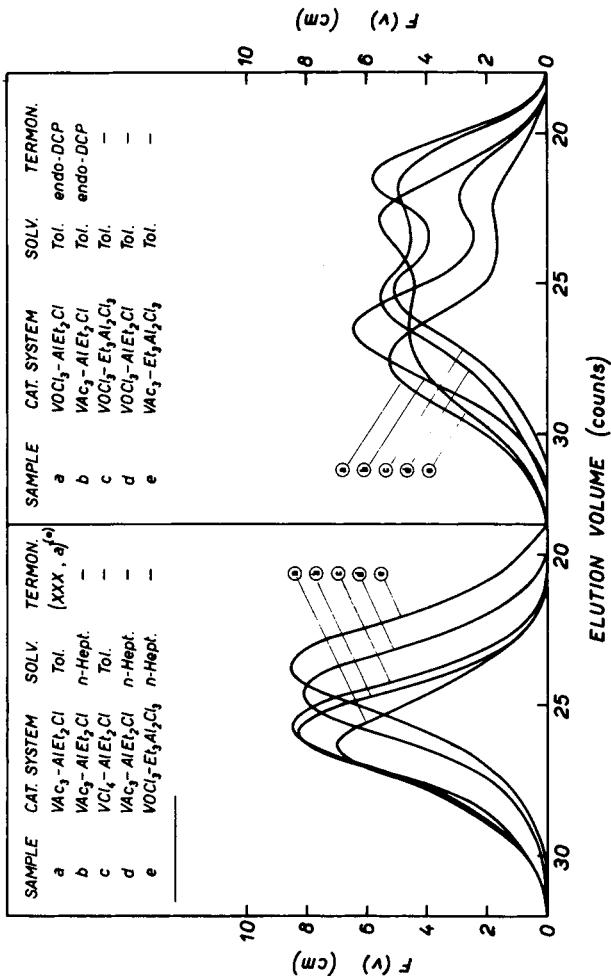


Fig. 14. Differential MWD of some EPM's and EPDM's prepared with various catalyst systems.

The examination of the MWD obtained from samples produced at different polymerization times is very interesting. Only the shift of the position of the maximum distribution toward higher MW is observed in EPM samples; the shape of MWD remains strictly the same. This occurs when the copolymer is produced in toluene, whereas in *n*-heptane higher MW fractions are produced between the third and tenth minute (Fig. 15), but not beyond this time. These results confirm previous kinetic conclusions regarding the relative long lifetimes of the growing chains and seem to rule out the formation of relevant amounts of huge macromolecules (Baldwin and Ver Strate, 1972), at least in the case of EPM's produced under the conditions we have adopted.

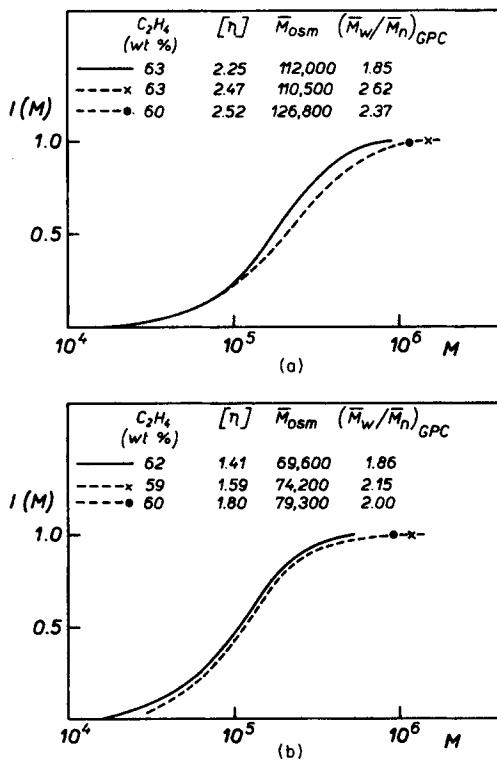


Fig. 15. Integral MWD of EPM's produced with the same unaged catalyst system ($VAcac_3-Et_2AlCl$) in (a) *n*-heptane and (b) toluene at different polymerization times (—) = 3 min; (---x---) = 10 min; (---●---) = 20 min.

Variations in the breadth of the peaks (modification of polydispersity) or in their relative positions (variation of the different averages of MW) can be observed in dependence of the factors regulating the process of polymerization. For instance, when IPTHI (cf. Section III B 4) is used as termonomer, a reduction of both M_w/M_n and of M_v have been observed in comparison to corresponding EPM (Table V), but also the polymerization temperature and the termonomer concentration change MWD's, whereas they are independent of the type of solvent. The presence of *endo*-DCP lowers the intensity of the first peak observed in our EPM GP chromatograms (corresponding to higher MW) of bimodal MWD's. Therefore, such MWD's seem to be not the direct consequence of the formation of branched polymer chains due to the reactivity of the secondary DCP unsaturation.

3. The catalyst system $\text{VCl}_4\text{-Et}_2\text{AlCl}$ has been found to yield, in any case, EPM's with monomodal MWD. Also the system $\text{VCl}_4\text{-Et}_3\text{Al}_2\text{Cl}_3$ furnishes the same result when *n*-heptane is used. The bimodality occurs in toluene. The same behavior is observed in the presence of *endo*-DCP.

The results now referred to are only apparently contradictory with the previous ones (German et al., 1966). Aside from any preliminary comparison of the separation ability offered by different techniques (e.g., GPC and other fractionation methods), is likely to assume that also in polymerization promoted by Ziegler-Natta catalysts, when different propagating species are present and they are unable to interconvert one into the other during the growth of the chains, the resulting polymer should possess either broad MWD or, in most favorable cases, polymodal MWD. Therefore the study of MWD can furnish very useful and fast information about the propagating species involved in the synthesis of the polymer studied (Cozewith and Ver Strate, 1971; Masuda and Higashimura, 1971).

Indeed, after the first results on bimodal MWD of some EPDM's, the changing of the catalyst lifetime was invoked; it was found that the average lifetime of the growing chains (taking into account transfer and termination reactions) increases fourfold when the temperature is lowered from 10°C to -30°C (German et al., 1966).

On the basis of recent results (Cozewith and Ver Strate, 1971) and old suggestions (Baker and Tait, 1967; Belov et al., 1966, 1967; Carrick, 1967; Carrick et al., 1960; Meshkova et al., 1969; Muharashi, 1960; Overberger and Ang, 1960; Phillips and Carrick, 1962; Wesslau, 1958; Wilman and Rubim, 1966), it seems likely to attribute the complex behavior of MW and MWD, both of EPM's and EPDM's, to the chemical (some-

times also physical) heterogeneity of the catalytic species (cf. Section II B). This, in turn, depends on a number of important variables (e.g., nature of the catalyst components and of the medium of reaction; co-ordinating ability of termonomer; decay rate of catalyst; modality of interaction, etc.) influencing the lifetimes of the growing chains, since different type of active species can be generated.

Relationships between MW or MWD and kinetic parameters of polymerization could be theoretically derived (Jackson et al., 1973; Peebles, 1971) when kinetic schemes and experimental values of the kinetic constants involved were obtained. This is particularly true in the case of homogeneous free-radical or of some ionic polymerizations, when the mechanism of polymerization is well understood; then the MWD can be derived either from the polymerization kinetics or from simple probability arguments. The limited value of GPC results (when the way to transform the arbitrary GPC distributions into true MWD's is known) rests on the fact that MWD is the final result of elementary steps which are kinetically controlled and already take place statistically in the early polymerization stage. Unfortunately, the lack of kinetic data is the case of EPDM's (see Section II C), hence satisfactory explanations of the experimental evidences on MW and MWD can hardly be given on the basis of results so far obtained. Only in the case of polyethylene, prepared with soluble Ti-based catalysts and in the presence of solvents containing reactive chlorine atoms, has the combination of kinetic measurements and MWD data ascertained two types of active centers partly defined. They are different in growth and termination constants and their relative amount can be regulated by the content of the halogenated solvent, by the polymerization time, and by the presence of another olefin (propylene) (Belov et al., 1970).

J. Branching and EPDM Heterogeneity

The theoretical study of branching in polymers dates back a long time and many difficulties have been encountered in describing on a quantitative basis the phenomenology of macromolecules (Grechanovskii, 1969; Zimm and Stockmayer, 1949; Tsvetkov, 1951). Two main approaches have been proposed to tackle the problem: the older way compares the hydrodynamic behavior of linear and branched species by studying the solution properties of polymers (Grechanovskii, 1969); the second way is more recent and is related to the study of rheological properties, in particular to bulk properties (Baldwin and Ver Strate, 1972; Tokita and Scott, 1969; Mendelson et al., 1970; Vinogradov and Ivanova, 1967).

Recently the combination of solution viscosity measurements with GPC data, taking into account the effect of various branching models and degrees of branching upon GPC calibration curves, has been proposed to evaluate the branching frequency of polyethylene (Mendelson and Dratt, 1968; Drott and Mendelson, 1970).

Sometimes, indirect evidence, having generally a qualitative character, can be obtained from chemical studies (cf. Section II D), spectroscopic (cf. Section II H 2 b) and other physico-chemical measurements (Gardner and Ver Strate, 1973).

In the case of EPM and EPDM there is relatively little information which has a prevailingly preliminary character (Baldwin and Ver Strate, 1972; Easterbrook et al., 1971; Tokita and Scott, 1969). This situation arises from the existence of experimental and, sometimes theoretical difficulties which are summarized below; moreover, limited work has been performed in this field.

1. The first obstacle met in fractionation experiments which, in the range of elevated MW, is not very efficient (Koenningveld and Staverman, 1968 a, b, c). Furthermore, in many cases, the evaluation of the fraction breadth is difficult.
2. There are some discrepancies between the $[\eta]$ -MW relationships obtained by different authors (Baldwin and Ver Strate, 1972).
3. Polymodal MWD's can be present in ethylene-propylene-based elastomers, probably as a consequence of the intrinsic heterogeneity of several catalyst systems (cf. Section II B). MW dispersion indexes (\bar{M}_v/\bar{M}_n) ranging between 1.5 and more than 10 have been observed for EPM's prepared with several catalysts (Cozewith and Ver Strate, 1971).
4. The situation described under 1-3 suggests the association of some absolute measurements to nonabsolute methods (e.g., GPC or $[\eta]$ measurements).
5. The bulk rheological properties suffer from some uncertainties on a theoretical level. The approach should take into account both MW and the molecular geometry of the polymer under investigation (Baldwin and Ver Strate, 1972). At present, theoretical treatments predict reduced bulk viscosities when branching is present at a given \bar{M}_w , but, actually, experimental results are either enhanced or diminished. Furthermore, also the relationship of bulk viscosity-MW is uncertain. In the case of EPM, "expected" relationships, based on the studies of Berry and Fox (1968), have been obtained (Baldwin and Ver Strate, 1972); the result is always linear in the absence of branching. At elevated \bar{M}_w branched polymers have higher viscosities than linear ones, whereas the opposite occurs for $\bar{M}_w < 10^5$.

These results indicate that many efforts are in progress in order to gain more precise information on branching, despite the difficulties now emphasized.

In the case of EPDM's there is common agreement on the existence of branching (Abe et al., 1969; Easterbrook et al., 1971; Tokita and Scott, 1969), and very recently some interesting evidence has been collected both through fractionation and intrinsic viscosity measurements (some results are reported in Table XIV) and through rheological experiments (maximum relaxation times; Tokita and Scott, 1969). In the case of EPM the evidence is more ambiguous and less numerous. Indeed it seems unlikely that ethylene-propylene copolymers, prepared with vanadium-based catalysts of Ziegler-Natta type, are more branched than, for instance, linear polyethylene, obtained under similar mild conditions as EPM (Drott and Mendelson, 1970). In fact it is difficult to explain how branching would be generated, since the terminal double bond of macromolecules, produced via catalyst-hydride bond formation (Natta and Pasquon, 1959) and invoked as the point of attack for branching through a copolymerization mechanism (Baldwin and Ver Strate, 1972), would have very low reactivity if one bears in mind the trend of reactivity ratios shown by the first three low linear α -olefins (Pasquon et al., 1967, p. 177). Furthermore, the concentration of double bond at the end of chains is, generally, quite low in linear polyethylene or EPM (Livshits, 1970; Raff and Doak, 1964), in particular when H_2 is used as MW regulator (Natta et al., 1959a).

These considerations have been confirmed by evaluation of the ratio $g = [\eta]_b/[\eta]_l$ (where $[\eta]_l$ is calculated by analysis of MWD curve obtained via GPC) carried out on a number of EPM's prepared under different conditions (Table XV). The results are compared with the measurement of the same index g verified on samples of polyethylene containing different degree of branching. Our conclusion is confirmed by the rheological studies of Tokita and Scott (1969). They consider EPM's as normal linear hydrocarbon polymers, at least relatively to EPDMs', and as far as hydrodynamic volume measurements are concerned, Table XV gives an apparent indication of the absence of branching in EPDM's, when catalyst systems having low acidic character are used. Probably the conviction of some authors (Baldwin and Ver Strate, 1972) on the existence of branching in EPM's rests on the overestimation of some facts that are not explained very well (e.g., agglomeration phenomena; existence of relatively low slope in some relationship $[\eta]-\bar{M}_v$ or of $\bar{M}_v \simeq \bar{M}_n$; absence of linearity in the relationship $\log [\eta]$ vs. \bar{M}_w) which may have

TABLE XIV
Evaluation of Branching in EPDM's Prepared with Different Catalysts by Measurement of Solution Properties^a

Fractions (cumulative range %)	MNB-EPDM ^b <i>g'</i> ^e	CEM ^f <i>g'</i> ^e	ENB-EPDM ^b <i>g'</i> ^e	CEM ^f <i>g'</i> ^e	MNB-EPDM ^c <i>g'</i> ^e	CEM ^f <i>g'</i> ^e	MNB-EPDM ^d <i>g'</i> ^e	CEM ^f <i>g'</i> ^e
20-30	0.82	4.1	0.88	3.3	no branching	no branching	no branching	no branching
30-40	0.82	4.1	0.92	2.8	no branching	no branching	no branching	no branching
40-50	0.60	8.8	0.85	3.8	no branching	no branching	no branching	no branching
50-60	0.77	4.9	0.82	4.1	no branching	no branching	no branching	no branching
60-70	0.67	6.2	0.82	4.1	no branching	no branching	no branching	no branching
70-80	0.73	5.5	0.95	2.6	—	—	0.84	1
80-90	0.60	8.8	0.85	3.7	1	—	—	—
90-100	0.36	20	—	—	—	—	—	—

^aReprinted from Baldwin and Ver Straete, 1972 with the permission of the Division of Rubber Chemistry Inc., A.C.S., Akron, Ohio.

^bEPDM prepared with catalyst VCl₄-Et₂AlCl in *n*-heptane at 30°C.

^cCatalyst: V(Acac)₃-Et₂AlCl in *n*-heptane at 30°C.

^dCatalyst: VO(Acac)₂-Et₂AlCl in benzene.

^e*g'* = [*η_b*/*η₁*] evaluated at constant \bar{M}_w ; subscripts *b* and 1 refer, respectively, to branched and linear macromolecules.

^fCEM = chain ends per molecule.

occasional character. However, there is a general concordance on the existence of very high MW fractions in EPM; the ratio \bar{M}_w/\bar{M}_n , determined on many samples of whole copolymers produced with the "semi-flow technique" (cf. Section II E), was found in the range 2.0–7.5 (Table XV). Both results are generally explained as a consequence of the intrinsic heterogeneity of the catalyst centers (Cozewith and Ver Strate, 1971), even though the theory establishes (Grechanovskii, 1969) that an increase of the degree of branching leads to the appearance of high MW tails (both for Stockmayer's (1944) and Beasley's (1953) distributions), whereas the maximum of the MWD is shifted into the low-MW region (Stockmayer's distribution).

The absence of linearity in the diagram $\log [\eta]$ vs. $\log M_w$, i.e., the decrease of the slope with increasing MW, observed for different samples of EPDM and also of EPM, has been attributed (Morimoto and Okamoto, 1972) to not well-identified molecular aggregations between ethylene sequences, whose length tends to increase in the high-MW region (see below and Table XVI).

Since the existence of branching in EPM is quite unlikely (see above) and as EPM and EPDM show the same behavior in the diagram $\log [\eta]$ vs. $\log M_w$, the effect of branching on the hydrodynamic behavior of EPDM should be small in comparison with the ethylene sequence distribution effect.

Other possible explanations of the anomalous behavior shown by EPM and EPDM solutions as, for instance, the existence of particular types of ordered aggregates or of disordered entanglements cannot be ruled out a priori. They are known to play a noticeable role in the case of polyelectrolytes (Miller, 1966) or of polar macromolecules solutions (Matsuo, 1959). However, very recently some evidence has been reported (Rietveld and Scholte, 1973) on the necessity of employing long dissolution times and high temperatures (up to 140°C) in order to obtain true EPM or EPDM solutions, reproducible M_w measurements¹ and to avoid anomalous high MW.

On the other hand, the well-known effect of broad MWD on the distortion of the Zimm plots (cf. Section II I) and on the value of the second virial coefficient (Benoit, 1948) should be ruled out when the samples investigated have been fractionated as is claimed in the case of the aforecited paper (Morimoto and Okamoto, 1972) and provided that the compositional homogeneity of the samples has been ascertained (Kambe et al., 1973).

The case of EPDM's is different. The introduction of the diene has

TABLE XV
Evaluation of Branching in EPM Through GPC Measurements

Sample	$[\eta]_{\text{exp}}$	$\bar{M}_{\text{osm}} \times 10^{-3}$	$[\eta]_{\text{calc}}$	$\bar{M}_n \times 10^{-3}$	$[\bar{M}_w / \bar{M}_n]_{\text{GPC}}$	$g' = [\eta]_b / [\eta]_1$ ^a
1	1.51	68.5	1.40	64.5	2.0	1.08
2	2.17	116.5	2.25	109	2.3	0.97
3	2.56	79.2	2.58	72.5	4.5	0.99
4	2.70	176	2.70	151	2.1	1.00
5	2.04	106	2.02	96	2.2	1.01
6	3.22	113.5	2.90	110	3.2	1.11
7	3.55	122	3.80	101	5.3	0.94
8	3.53	—	3.41	—	7.4	1.03
9	3.37	—	3.30	—	4.5	1.02
10	1.95	—	1.75	—	2.1	1.11
11	3.74	230	3.74	215	2.3	1.00
12	4.80	345	4.70	319	2.1	1.02
HDPE/BMWD ^b	2.15	13.8	2.10	14	11	1.02
LDPE/A _b	1.11	21.9	1.83	20.2	6	0.60
LDPE/A _b	1.13	20.9	2.00	20.5	7	0.56

^aThe average value of g' , determined on many samples of EPDM, prepared under different conditions and with various catalysts, is 1.01 ± 0.02 .

^bSamples and results of branched and linear polyethylene kindly supplied by Prof. H. Benoit, Strasbourg, France.

TABLE XVI
CH₂ Content in Various Sequences of EPDM^a Fractions^b

Fraction no.	[η] (dl/g)	<i>T_g</i> (°C)	C ₆ H ₆ (mole %)	Sequences ^c				
				g ₁	g ₂	g ₃	g ₄	g ₅
1	4.00	-55.1	21.9	8.8	0	0	4.1	87.1
2	3.73	-54.0	21.3	9.8	0	0	3.3	85.9
3	3.64	-52.7	22.4	10.5	0	0	17.2	72.3
4	2.58	-55.5	29.5	17.8	1.5	0	10.2	67.1
5	2.53	-54.9	33.7	23.8	2.5	7.2	2.9	63.7
6	2.49	-53.8	34.0	24.5	3.3	2.0	9.4	60.9
7	2.09	-54.5	32.1	21.3	0.9	0.6	15.5	61.6
8	1.82	-56.0	34.8	23.5	3.9	2.4	9.1	61.1
9	1.48	-56.4	35.2	24.9	4.5	2.4	7.2	60.0
10	1.39	-53.8	35.8	24.6	5.6	2.9	13.7	53.2
11	1.09	-56.5	37.4	24.8	3.3	8.9	7.5	55.5
12	0.78	-54.5	42.2	27.1	6.8	6.9	18.3	40.8

^aBased on ENR.

^bReprinted by permission from Morimoto and Okamoto, 1972.

^cRefers to g_n = grams CH₂/100 g, corresponding to the (CH₂)_n sequences, with n = 1, 2, 3, 4 and more than 5.

been recognized as the cause of branching due to the presence of two centers of reactivity in termonomer (cf. Section II D); furthermore, its ability of modifying the catalyst activity (cf. Section II A) may contribute to modify the MWD.

By comparing the results obtained with various techniques in determining the unsaturation level of ENB-based EPDM, it has been concluded that commercial terpolymers samples are highly branched and semigelated materials (Gardner and Ver Strate, 1973). Light scattering and filtration experiments confirmed such a conclusion (Baldwin and Ver Strate, 1972). It has been calculated by referring to the ICl-¹⁴C calibration curve (cf. II H 2 a) that in the case of ENB-EPDM, the gel point is past at ca. 0.2 wt % of ENB.

Very recently an analysis of the insoluble portions (in organic solvents) of some EPDM's based on *endo*-DCP and ENB, has been carried out (Morimoto and Okamoto, 1973) through solubility test, differential scanning calorimetry, X-ray diffraction, IR spectrometry, and electron microscopy. By reference to α -olefins block copolymers, it has been evidenced that, actually, two types of gels exist in the insoluble portions. Namely, a microcrystalline gel, due to the strong intra- or inter-molecular association of methylene sequences, and a crosslinking gel based on the reactivity of the pendant unsaturation of EPDM. Therefore, the randomizing function exerted by the termonomer on the distribution of the monomers in EPDM chains is scarcely relevant as the concentration of diene in the polymer is rather low. Hence, physical crosslinking is nearly the same in EPM and EPDM having the same composition and origin, while the chemical crosslinking is peculiar to the unsaturated elastomer.

But there are other factors indirectly responsible for the heterogeneity of EPDM's (e.g., decay of catalyst, influence of adventitious impurities, statistical fluctuations, mass transfer problems, etc.) sometimes out of the common possibility of control. In practice, almost all the aspects of Section II of this review deal with problems which refer, directly or indirectly, to study and control possible heterogeneity of EPDM's.

Actually, different kind of heterogeneity can be distinguished in EPDM's, i.e., relative to: (a) terpolymer composition; (b) type of propylene repeating unit; (c) type of diene repeating unit; (d) monomer sequence distributions; (e) tacticity of propylene units; (f) branching; (g) MW (related to different extents of chain-breaking reactions); (h) multiplicity of MWD.

As far as the causes of heterogeneity are concerned, it may be schema-

tized, on the basis of results reported in Section II, that the type of catalyst seems to regulate more directly point (h) and to influence, in different degree, all the other points for which there is a marked influence by the monomers (both propylene and termonomer). But also the experimental conditions (e.g., ratio catalyst/cocatalyst, type of solvent, temperature, concentration of termonomer, type of reactor, etc.) play a noticeable role. In general, MW, compositional and sequential heterogeneity of EPM's and EPDM's has been considered for long time to be closely related and, therefore, almost impossible to evaluate the different degree of heterogeneity from solubility data. Only very recently some successful attempts have been performed (see below and Cozewith and Ver Strate, 1971; Morimoto and Okamoto, 1972; Ogawa et al., 1973).

From the experimental point of view the heterogeneity of a given polymer is studied through fractionation methods which furnish information on MWD and also on monomer sequence length distributions in the case of copolymers. A general rule is to work with polymers having narrow MW and compositional distribution when structural information has to be related to mechanistic problems or to physical properties; hence, fractionation experiments are an important part of the characterization work of a multicomponent polymeric system. Of course, the microstructural analysis and the determination of the monomer sequence distribution attain the best results when the work is carried out on narrow fractions.

Depending on the type of information needed and on the type of polymer under investigation, different methods of fractionation can be used; the more common are: gel permeation chromatography (GPC), precipitation fractionation, elution fractionation, ultracentrifuge and thin-layer chromatography (TLC). Each method has specific limits and different degree of reliability; these aspects have been recently reviewed (Smith, 1972). Relatively few studies have been published in the case of EPM's and EPDM's. GPC investigations, which have the great advantage of rapidity of execution but also the difficulty of generating the true MWD from GPC curve, have been limited so far to MWD measurements for some simple polyolefins (Drott and Mendelson, 1970).

However, on the basis of these initial approaches a more general theoretical treatment of MWD of polydisperse polymers, considered as chains having randomly distributed tri- and tetrafunctional branch points, has been put forward (Shultz, 1970).

Preparative scale fractionation by GPC has been recently introduced; very few results have so far been communicated. Despite these difficulties, a computer program has been proposed for relating GPC data to

different MW averages (Pickett et al., 1966; Cazes and Dobbins, 1970).

Fractionation methods by solubility are more useful in the case of copolymers, since single fractions can be collected and examined also for their composition. Precipitation fractionation has been used to investigate MWD of EPM (Barbè and Zanetti, 1965) and also to obtain the compositional and MW distributions of some commercial samples of EPDM's containing different termonomers (Figs. 16-19). It is known (Rosenthal and White, 1952; Kudryatseva and Litmanovich, 1967) that fractionation by precipitation is complicated in the case of copolymer by overlapping of both MW and composition effects. Therefore, the separation of narrow fractions is difficult. A cross-fractionation procedure,

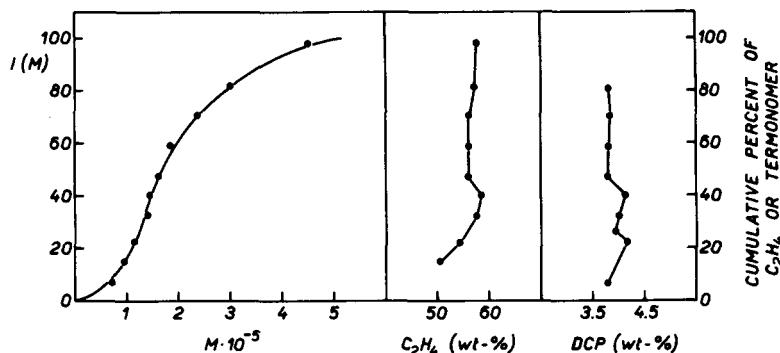


Fig. 16. Fractionation data obtained for a commercial sample of EPDM containing DCP, by using the precipitation technique.

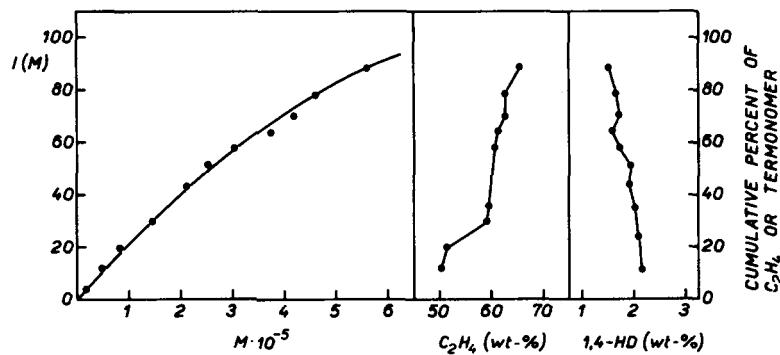


Fig. 17. Fractionation data for a commercial sample of EPDM based on 1,4-HD (precipitation method).

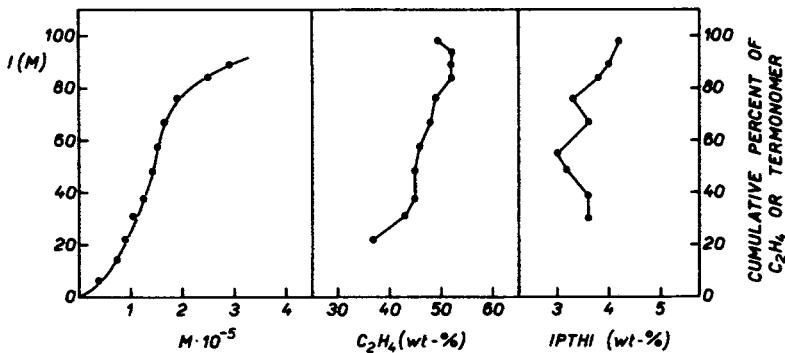


Fig. 18. Fractionation data (precipitation method) for a sample of EPTM based on IPTHI prepared on laboratory scale.

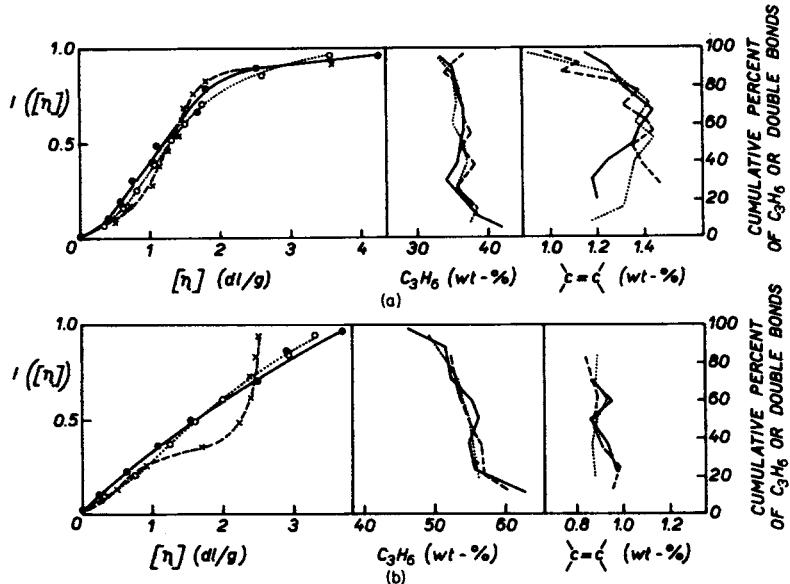


Fig. 19. Fractionation data obtained with different techniques (PF, SGE, TGE, cf. the text) from two EPDM's; (○) = PF; (×) = SGE; (●) = TGE. Properties of the starting EPDM's; (a) $[\eta] = 1.49$ dl/g, $C_3H_6 = 37$ wt %, double bond 1.28 wt %. (b) $[\eta] = 1.73$ dl/g, $C_3H_6 = 56$ wt %, double bond 0.91 wt %. Reproduced from Barlic and Zanetti, 1965 with the permission of the Editrice di Chimica, S.p.A., Milan.

based on the use of a second different solvent-precipitant system with the fractions previously obtained, has been suggested to distinguish the simultaneous effects (Litmanovich and Shtern, 1967).

Elution fractionation, carried out in column and frequently associated with a temperature gradient along the column, besides other specific improvements to obtain better results, has been claimed as, probably, the best method for preparative fractionation (Smith, 1972). Various efficiencies have been observed by different authors, depending on the type and properties of starting polymer. However, in the case of several EPDM's a fractionation was attempted using a diatomaceous earth column and a mixture of ethylbenzene and MeOH:BuOH (2:8) or ethylene glycol monoethyl ether as eluents at 55–75°C, but neither the solvent/nonsolvent combination nor the temperature affected the fractionation (Wigand and Waldmann, 1968).

On the contrary, a column fractionation procedure was considered (Ogawa et al., 1973) efficient in order to obtain a MW and a compositional fractionation for some EPM samples. The systems xylene-butyl Cellosolve and tetraline-ethyl carbitol were used, respectively. The monomer sequence length fractionation was achieved by solvent extraction (in a Soxhlet extractor) by using ethyl ether, *n*-hexane, cyclohexane, and *n*-heptane successively. Very broad distribution for the three factors investigated have been found, the samples of EPM studied having been prepared with the catalyst systems $\text{VOCl}_3\text{-Et}_2\text{AlCl}$ and $\text{TiCl}_3\text{-Et}_2\text{AlCl}$.

Interesting results have been recently reported (Morimoto and Okamoto, 1973) on the molecular fractionation of EPM and ENB-EPDM samples by the usual precipitation method (toluene as good solvent and isopropanol as poor solvent). The efficiency of fractionation has been proved by the values of the polydispersity index which for each fraction varied no more than 1.5 ± 0.2 . Furthermore, a linear plot of $\log ([\eta] \times M_w)$ vs. $\log \langle S^2 \rangle$ with a slope of $3/2$ ($\langle S^2 \rangle$ is the square radius of gyration) was obtained according to the Flory-Fox equation (Flory, 1953) for the points of both EPM and EPDM.

An enhanced compositional heterogeneity was shown for all the samples of ENB-EPDM studied (and produced with a soluble vanadium salt-alkyl aluminium halide catalyst in a continuous-flow stirred reactor) by plotting the propylene content vs. $[\eta]$. The composition spread observed was higher than $\pm 10\%$ about the mean. The result was confirmed by DSC measurements on single fractions; the values of T_g gradually rise with an increase of $[\eta]$ and ethylene content (see Table XVI).

Finally, the methylene sequence distribution in each fraction was

evaluated by spectroscopic measurements in the near IR region (Bucci and Simonazzi, 1964). The results are reported in Table XVI, and show that the percentage of $(-\text{CH}_2-)_5$ sequences increase with increasing $[\eta]$ while the content of $(-\text{CH}_2-)_1$ groups, derived from the head-to-tail enchainment of two propylene units, has an opposite trend. The results have to be considered reliable even if the IR method used was derived from EPM studies. In fact, the content of ENB is constant in the single fractions; moreover, the compensation for the presence of the diene would increase the values of $(-\text{CH}_2-)_5$ reported in Table XVI.

The data of Table XVI, agree with previous results (Cozewith and Ver Strate, 1971) according to which the ethylene content of EPM, obtained under conditions very similar to those used by Morimoto and Okamoto (1973), show a gradual increase with increasing MW. The implication of this inherent heterogeneity of the $\text{C}_2\text{H}_4\text{-C}_3\text{H}_6$ enchainment on some anomalous solution properties of EPM and EPDM has been discussed in the first part of this section. However, the primary cause of this experimental observation remains still obscure for the lack of other experimental data. For instance, it should be very interesting to know the dependence of the ethylene sequence length distribution as function of the polymerization time.

The comparison of three methods of fractionation, namely precipitation (PF), elution with solvent gradient (SGE), or with temperature gradient (TGE), have been evaluated for EPM's and EPDM's (Barbè and Zanetti, 1965). The TGE technique allows the separation of very high MW fractions which, generally are not obtained through PF (Fig. 19). Despite the elevated temperatures involved, TGE yields $\sum[\eta]_i w_i$ very close to $[\eta]$ of the starting EPDM.

More recently the fractionation of EPM's through column elution, using ethanol-heptane as eluent, has been successfully performed. A compositional spread of $\pm 3\%$ was attributed to adventitious effects (statistical fluctuations, imperfect mixing, start up, etc.); therefore, in these cases, it was inferred that the copolymers studied were derived from catalysts formed by an unique species. Other catalysts yielded EPM's with compositional spread higher than $\pm 10\%$, according to a systematic tendency, while the fractions having higher ethylene content had higher MW. Moreover, frequently MWD's were polymodal and M_w/M_n was higher than 10 (Cozewith and Ver Strate, 1971).

Also kinetic studies have been utilized to evidence the heterogeneity of the catalyst systems employed in EPM synthesis (Karasev and Minsker, 1971). In fact, in the case of $\text{VOCl}_3\text{-Et}_2\text{AlCl}$ and VOCl_3 -

EtAlCl₂ systems, a graphical analysis of the kinetic curves has shown that catalyst sites originate two types of growing chains and they decay according to a monomolecular law.

The importance of these data, combined with MWD results, is related to the possibility of drawing indications on the minimal number of active species generated by the catalyst (cf. Table IV).

As matter of fact the literature and the foregoing results indicate that classical approaches to fractionation can detect EPDM heterogeneity only of type (a), (g) and (h), whereas, in the other cases spectroscopic and rheological (for branching) investigations furnish more pertinent information.

Certainly much remains to be studied about the heterogeneity in EPDM's since all the foregoing topics have begun to be tackled rigorously in the recent past; up to now almost only qualitative approaches have been realized. The next steps will be concerned with the transfer on quantitative basis of the stimulating observations so far collected and with the connection of EPDM structural data to the polymerization conditions.

III. CLASSES OF TERMONOMERS USED IN THE SYNTHESIS OF ETHYLENE-PROPYLENE TERPOLYMERS

A number of possible termonomers have been proposed for the synthesis of EPDM's, mainly in numerous patents and also in some reviews and papers devoted to α -olefins elastomers (Magovern, 1970; Ranney, 1970; Crespi et al., 1964; Natta et al., 1969; Valvassori and Cameli, 1969; Pasquon et al., 1967; Phung et al., 1967)

In an attempt to classify most of the compounds suggested, the list in Table XVII was made adopting the ASTM nomenclature (American Society for Testing and Materials, 1970) to distinguish between terpolymers containing a diene (EPDM) or a triene (EPTM).

Several classes of compounds reported in Table XVII have only been claimed in patents. For instance, in the case of EPDM's, no papers have so far been published about terpolymers employing compounds belonging to classes 1.1 and 1.2, whereas in the case of EPTM much work has been made on terpolymers obtained with termonomers of class 2.3. However, the existing literature on the subject will be examined in detail in the next Sections.

TABLE XVII

Classification of Unsaturated Ethylene-Propylene-based Terpolymer According to the Type of Termonomer Involved

1.	<i>EPDM</i>
1.1	Allene derivatives
1.2	Conjugated dienes
1.3	Nonconjugated dienes
1.3.1	Linear nonconjugated dienes
1.3.2	Monocyclic diolefins
1.3.3	Alkenylcycloalkenes
1.3.4	Bicyclic diolefins
1.3.5	Dialkenylcycloalkanes
1.3.6	Alkenyl- or alkylidene norbornenes
1.3.7	Polycyclic diolefins
1.3.8	Alkylnorbornadienes
1.4	Acetylenic hydrocarbons
1.5	Cyclic monoolefins with a strained ring
2.	<i>EPTM</i>
2.1	Nonconjugated trienes
2.1.1	Linear nonconjugated trienes
2.1.2	Trialkenylcycloalkanes
2.2	Conjugated trienes
2.2.1	Cumulene derivatives
2.2.2	Fulvene derivatives
2.2.3	Alkenylacetylenes
2.3	Partly conjugated trienes
2.3.1	Conjugated alkylidene derivatives of polycyclic diolefins
2.3.2	Conjugated cyclodienic norbornenes
2.3.3	Linear or cyclic alkadienyl norbornenes

A. EPDM: Structure and Properties

The class of dienes which has been more largely investigated is the broad group of nonconjugated dienes, which, for the sake of clarity, will be further subdivided into some subclasses (Table XVII). They contain at least one double bond of enhanced reactivity (e.g., vinyl or norbornene double bond) which allows the diene to react with catalyst as an α -olefin.

As far as the type of second double bond present in a given termonomer is concerned, its position markedly influences the rate of vulcanization or its percentage of utilization in the curing process. For instance, an internal double bond has been found to vulcanize more rapidly than a vinyl or vinylidene double bond (Baldwin et al., 1970; Natta et al.,

1963b; Sartori et al., 1965); if the double bond is part of a seven- or eight-membered ring, EPDM is fast curing, whereas it is slow curing when the unsaturation is part of a five-or six-membered ring (Natta et al., 1963b).

Other data concerning the influence of the termonomer structure on the curing rate of the resultant EPDM have recently been communicated (Kodama, 1968; Ver Strate et al., 1973) and are reported in Tables XVIII and XIX. According to Table XVIII, the highest network chain density is offered by EPDM's based on PNB, CNB, and ENB (in the first 50 minutes of curing and by taking into account the content of diene). Dienes which have no allylic hydrogens fail to cure (MVNB), whereas the behavior of VNB and MANB EPDM's seems to not depend only on the number of allylic hydrogens.

The situation is similar in Table XIX for EPDM's based on IPDNB and ENB, while the stereochemical situation of the unsaturated group present in IPNB markedly influences the behavior of the EPDM, as happens in the case of *endo* and *exo*-DCP (cf. Table XX and also Section III A).

However, aside from these preliminary results, the rationalization of the complex behavior shown by EPDM unsaturation during vulcanization means to enter into the chemistry of accelerators, activators, sulfur, competing kinetics of crosslinking and reversion, etc. The reactivity of curing sites plays an important role in the complicated system constituting the vulcanization stage, but it is difficult to understand unambiguously the chemical behavior of unsaturation or the influence of structural modifications of its immediate environment.

In a recent paper (Baldwin, 1970) the attempt has been made, to clarify the complexity above depicted, of studying comparatively the behavior of nine EPDM's, containing different norbornene dienes and crosslinked with various levels of peroxides. The unsaturations were of alkylidene, vinylic, or alkenylic type and had a different degree of substitution with methyl groups. It has been shown that the general rules which preside over radical polymerization can predict qualitatively the behavior of various double bonds during the peroxide cure. For instance, terminal methyl groups, in an α position to unsaturation, are involved in cross-linking processes (24% in the case of ENB). Actually, the number of allylic hydrogens, their type and structure, are important features of the unsaturated system.

In another paper (Fujimoto and Wataya, 1969) the comparison of EPDM's based on MNB, DCP, and HD and vulcanized with peroxides,

TABLE XVIII
Influence of the Diene Structure on Vulcanization of Some EPDM's^a

Diene	Name	$\bar{M}_n \times 10^{-3}$	Ethylene (mole %)	Unsaturation (mole %)	Sulfur-accelerator cure ^b : ν_c (mole/cm ³)	50 min	100 min	200 min
	5-methylene-2-norbornene (MNB)	84	48	0.8	0.19	0.50	0.50	0.64
	5-vinyl-2-norbornene (VNB)	55	52	0.5	—	—	—	0.39
	5-ethylidene-2-norbornene (ENB)	70	44	1.2	0.43	0.57	0.57	0.63
	5-propenyl-2-norbornene (PNB)	70	46	0.9	0.46	0.62	0.62	0.72
	5-isopropenyl-2-norbornene (IPNB)	56	46	1.4	—	0.35	0.35	0.47
	5-methyl-5-vinyl-2-norbornene (MVNB)	61	47	0.9	0.9	insufficient curing	insufficient curing	insufficient curing
	5-crotyl-2-norbornene (CNB)	65	44	0.9	0.35	0.49	0.49	0.58
	5-methallyl-2-norbornene (MANB)	71	47	0.6	—	0.30	0.30	0.39
	5-(2'-buten-2'-y)-2-norbornene (2-BNB)	72	46	1.7	0.47	0.65	0.65	0.71

^aFrom Ver Strate et al., 1973.^bPolymer = 100, ZnO = 5, stearic acid = 1, TMTDS = 1, MBT = 1, S = 0.5, di-(*t*-butyl)-*p*-cresol = 0.2; temperature 176°C.

TABLE XIX
Influence of the Diene Structure on the Vulcanization Rate of Some EPDM's^a

Diene	Name	Intrinsic viscosity (dl/g)	Propylene (mole %)	Iodine number	Cure rate ^b (kg/cm/min)
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$	1,4-hexadiene (1,4-HD)	2.13	38.6	15.5	18.5
	5-methylene-2-norbornene (MNB)	2.37	39.5	7.2	13.5
	5-ethylidene-2-norbornene (ENB)	2.28	34.3	14.8	28.3
	5-isopropylidene-2-norbornene (IPDNB)	1.61	36.0	18.4	29.8
	<i>endo</i> -5-isopropenyl-2-norbornene (<i>endo</i> -IPNB)	1.40	35.4	17.1	6.9
	<i>exo</i> -5-isopropenyl-2-norbornene (<i>exo</i> -IPNB)	1.40	31.8	10.3	16.1
	<i>endo</i> -dicyclopentadiene (<i>endo</i> -DCP)	1.55	27.5	10.7	10.6

^aAfter Kodama, 1968.

^bObtained under comparable conditions at 160°C.

indicates that the rate of unsaturation disappearance was, respectively, in the order 4:2:1.

In the case of EPDM sulfur vulcanization, carried out in the presence of recipes which recall the studies performed on low-unsaturated elastomers, the fundamental evidence is that double bonds which carry no hydrogen atoms in α position are unvulcanizable (Baldwin and Ver Strate, 1972; Baldwin, 1970). However, unsaturation is also involved, in part, during accelerated vulcanization. The rate of unsaturation loss on curing was found (Fujimoto and Wataya, 1969) in the order MNB > HD > DCP, in the ratio of 5:2:1; generally the bridgehead allylic positions are considered inactive.

In order to ascertain the behavior of cyclic unsaturations, model compounds derived from cyclohexene have been treated with sulfur, accelerators, and activators. Generally alkenyl sulfides (allyl attack) are better than 1,2-dialkyl sulfides (addition to double bond) and only without accelerators or activators is the ratio of products obtained reversed. However in these cases monoalkyl sulfides and monocyclohexyl mercaptan are also present (Moore, 1965; Wolfe, 1968).

Other studies on model compounds conclude that the crosslink shortening reaction also depends on the position of double bond. For instance, MNB-EPDM shortens crosslinking faster than ENB (Baldwin and Ver Strate, 1972).

The reversion process seems related to the presence of one hydrogen atom on both the α positions of double bond; however, high temperatures of vulcanization give relevant reversion, independent of the type of unsaturation (Stemmer, 1965). The transformation of polysulfide linkages into di- and monosulfide bridges were found to be in the order ENB > HD, MNB > DCP (Fujimoto and Nakade, 1969).

Certainly it has been proved that di- and polysulfide links can be destroyed by thiolate anions. Furthermore, polysulfides are thermally cleaved, but at the same time, they tend to recombine. The character of the reactions involved in vulcanization processes is, therefore, not unique since radical and ionic mechanisms seem to coexist. At present we know very little about: (a) the type of reacting species involved; (b) their exact fate; (c) the mechanism of their transformation. The recent literature indicates that many efforts are in progress to elucidate the complexity of phenomena involved in the vulcanization processes.

As far as the relationship between the structural properties of EPDM and their physical characteristics or rheological behavior is concerned, an enormous amount of work has been performed. The reader can be

referred to a recent and excellent review (Baldwin and Ver Strate, 1972) dealing mainly with these topics; it is sufficient to report here some successive interesting results.

From a general standpoint it should be noted that EPDM's are elastomeric materials within a wide range of compositions (Natta et al., 1963b). Their behavior is influenced by several molecular and physical parameters among which the more important are: (a) The relative content of ethylene and propylene and the composition distribution; (b) The type, the content, and the distribution of termonomer; (c) The microstructure and the sequence length distribution of monomers; (d) The value of MW, which must be within certain critical values, and the width of MWD; (e) The type of chain, i.e., linear or branched; (f) The existence of inter- and intramolecular interactions; (g) The presence and the amount of crystallinity; (h) The value of the glass transition temperature. The properties (f, g, h) depend more directly on points (a) and (b).

Very recently a noticeable effort has been made (Crespi, 1973) in order to correlate some of the parameters mentioned above with some properties as: crystalline structure and heterophasic transitions; isophasic transitions; solution properties; rheological properties; mechanical and dynamic properties.

Four main groups of EPM and EPDM have been studied, differing for their microstructure, i.e., (1) EPM's having a regular alternance of one propylene and n ethylene units, where $n = 1, 3, 4, 5$; EPM's and EPDM's having (2) high, (3) medium and (4) low sequential homogeneity as deduced from IR measurements (Tosi et al., 1968; Tosi and Catinella, 1970) and expressed conventionally by the product of the reactivity ratios $r_{C_2H_4} \times r_{C_3H_6}$.

The main results of this study can be summarized as follows.

1. X-ray and calorimetric studies show that in C_2H_4 -rich EPM, propylene units enter polyethylene chains isomorphically by expanding the basal plane of the polyethylene unit cell. Such an influence depends not only on composition, but also on the distribution of the monomeric units. The influence of the microstructure is also evident in the diagram of the melting temperature vs. the molar composition. EPM's having a C_3H_6 content lower than 30 mole % are amorphous under normal conditions and may crystallize only under stretching or at low temperature, while the 1/1 alternated copolymer shows an atactic conformation and is completely amorphous.

2. Below glass transition and above the melting temperature, the enthalpic spectra of different EPM's appear almost coincidental with poly-

α -olefins spectra, while near T_g different, high enthalpic contributions, due to melting, rearrangement and different molecular motions, are evident for copolymers having different composition and microstructure. On the contrary, T_g (DSC) appears hardly dependent on these two molecular parameters.

3. Relaxation spectra of EPM having high sequential homogeneity show a constant relaxation period ($\tau_0-\tau_e$) independent of the C_3H_6 content (within 26–43 mole %), while a clearer differentiation is evident in the terminal region of the spectrum, where the decrease of the modulus should be attributed to the flow of entanglements and to the deformation of molecular aggregates. In fact, samples with reduced sequential homogeneity show some broadening of the rubbery plateau of the diagram and much higher value of τ_m as a consequence of the increase of friction forces due to association of ethylene sequences. Similar effects are also evident in the mechanical dynamic spectra (next point).

4. The response to mechanical and dynamic stress is mainly dependent upon the average composition. Equimolecular EPM is hardly influenced by the microstructure as evidenced by tensile properties and by the dependence of the dynamic properties on temperature. On the contrary, the stress-strain curves of uncured EPM having a molar ratio C_2H_4/C_3H_6 of ca. 3/1 show the existence of green strength at room temperature and of different crystallization temperature (from –16 to +34°C) when passing from the alternate model to samples with low sequential homogeneity. The increase of the value of T_c with increasing the stretching ratio is a typical behavior of elastomers crystallizing under stretching. The dependence of T_c on the sequential homogeneity is a consequence of the modification of the lattice dimensions of crystallites depending, in turn, on the propylene content of the homosequential segments entering the crystallite.

The permanence of intermolecular interactions, due to low sequential homogeneity, is evident also in cured EPDM's through the measurement of their dynamic properties.

EPM's with high ethylene content ($C_2H_4/C_3H_6 = 5$) show a true crystallinity of polyethylene type; both X-ray and calorimetric measurements evidence that such crystallinity is lower for samples with high sequential homogeneity when a defined composition is considered.

5. The highest sulfur cure rate has been observed for EPDM's containing ENB and PNB, the remaining examined EPDM's being based on *trans*- and *cis*-1,4-HD, DCP, MNB, and MTHI, and the unsaturation level ranging between 0.2 and 0.9 mole/kg. The vulcanization efficiency has been found excellent for MNB-based EPDM.

The properties of some raw EPDM's (based on 1,4-HD and ENB) and gum vulcanizates with respect to thermal transitions, stress relaxation, and swelling behavior have recently been evaluated (Kirkham, 1973). Besides the ethylene content, the microstructure of the sample investigated was found to influence the above cited properties. In fact, while no evidence of crystallinity was detected by X-ray diffraction or IR spectroscopy, EPDM of nominally similar ethylene contents can show disparate behavior as a consequence of different compositional heterogeneity. At high ethylene contents structural features (viz. $-\text{CH}_2-$ sequences and, perhaps, other regular sequences may undergo alignment (Sanchez and Eby, 1973) within the amorphous matrix) are originated which yield associated regions (Morimoto and Okamoto, 1973) (microcrystallites) that determine the observed effects.

However, the low melting points measured are the evidence of relatively short ethylene sequences, even though the presence of low concentration of microcrystallites produces polymers having thermoplastic behavior.

Actually, when the ethylene content is high, i.e., 65 wt % and independently of any microstructural characterization, the methylene sequences are relatively long (blocks) and originate some crystallinity which is shown by Raman spectroscopy. In fact, the ratio $R = (I_{1065} - I_{1080})/I_{1080}$ is particularly sensitive and assumes values = 0.2 in the region where röntgenographic measurements are unable to detect traces of crystallinity, i.e., below 65 wt % C_2H_4 (Kerrutt, 1973).

As expected, EPDM's with an elevated content of C_2H_4 approach a thermoplastic behavior as they contain crystalline regions which originate physical crosslinks. Therefore, the tensile properties of the vulcanizates of these materials are enhanced with respect to the same properties of EPDM's containing 35–65 wt % C_2H_4 .

The influence of the type of unsaturation, i.e., the termonomer structure on some properties of the corresponding EPDM (especially effects of thermal aging on crosslink density, crosslink type, tensile properties, stress-relaxation of gum and vulcanizates, etc.) have been studied in another recent paper (Baranwal and Lindsay 1972). Five EPDM's, containing equimolar unsaturation and based on ENB, BD, DCP, MTHI and 1,4-HD were investigated. Curing rate results have confirmed previous data (Fujimoto and Nakade, 1969) reported in the sections devoted to single EPDM in this review. Crosslink density and crosslink type analyses indicate that butadiene units are block distributed (3–15 monomer units) in BD-based EPDM, while all other EPDM's studied have the same crosslink densities.

Both gum and filled vulcanizates of HD-EPDM have the highest content of monosulfidic crosslinks (ca. 50%); however, this higher initial content does not give any particular advantage during the aging of HD-EPDM with respect to other EPDM's. ENB- and HD-based EPDM's show at 175°C the same energy-to-break (E_b), while MTHI-EPDM has the highest value of E_b .

At higher temperature (ca. 290°C) all the vulcanizates have crosslinks of monosulfidic type; however, the crosslink densities and E_b values are very low, probably as a consequence of oxidative degradation. The temperature of decomposition of vulcanizates (TGA) is nearly the same both in air and under nitrogen, i.e., in the range 390–500°C.

A quantitative treatment of the complicated process of crosslinks formation in EPDM's has been put forward on the basis of four main assumptions (Ghetti et al., 1969). Namely:

1. An initial crosslinking reaction between sulfur and unsaturation yields polysulfidic intermolecular crosslinks.
2. The formation of active species takes place by breaking of the crosslinks formed under 1.
3. An inactivation reaction involves the active species reported under 2 and the consequent destruction of a crosslink.
4. The formation of more stable intermolecular crosslinks (very likely of monosulfidic type) occurs as a consequence of reaction 2.

The scheme adopted is certainly a simplified representation of the reality since it does not take into account neither the breaking of bonds involving primary chains nor cyclization reactions. However, it is able to describe the overall vulcanization process by means of two rate constants, i.e., K_i and K_f , the former refers to the inactivation reactions and the latter to the reactions yielding the polymer network. (cf. Table XX).

An experimental check of the final equations, deduced from the elaboration of the kinetic expressions deduced from the above reported assumptions, has been carried out through the evaluation of some mechanical properties, since there are noticeable difficulties in determining the unsaturation content of vulcanizates during the curing period. As it can be seen in Figure 20, very good concordance has been found between the experimental and calculated data for the crosslinking kinetics of some EPDM's and EPTM's.

It is also worth noting that, by evaluating the rate constant of the overall crosslinking process (K_f) at different temperatures for some EPDM's and one EPTM based on IPTHI, the same activation energy (Fig. 21) of 22 kcal/mole has been calculated. The mechanistic impli-

TABLE XX
Kinetic Parameters of the Crosslinking Process of Some EPTM's^a

Sample	Termonomer type ^b	Termonomer concentration (mole/kg)	t_i ^c	K_f ^d	$K_t \cdot 10^3$ ^e	$a/K_e \times 10^2$ ^f
1	methyl-IPTHI	0.457	1 min 30 sec	0.30	0.25	0.14
2	IPTHI	0.484	2 min 30 sec	0.14	0.12	0.08
7	(XXXII-XXXIV)	0.292	3 min 50 sec	0.16	0.13	0.09
8	(XXXV-XXXVII)	0.194	3 min 40 sec	0.08	—	—
9	(XXX, a)	0.320	2 min	0.36	0.30	0.03
Curing recipe: polymer 100; HAF 50; naphthene oil 5; zinc oxide 5; MBT 0.5; TMD 1; sulfur 2. Curing temperature: 145°C.						

^aCf. Ghetti et al., 1969.

^bCf. pp. 135, 146 and 154.

^c t_i = Induction time.

^d K_f = Crosslinking reaction rate constant.

^e K_t = Scission reaction connected constant.

^f a/K_e = Constant connected to the equilibrium time between crosslinking and scission reactions.

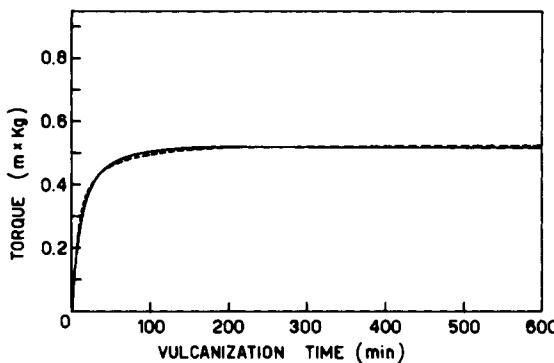


Fig. 20. Vulcanization rate evaluation for EPTM based on triene (XXX, a). Comparison between experimental curve (full line) and theoretical curve (broken line).

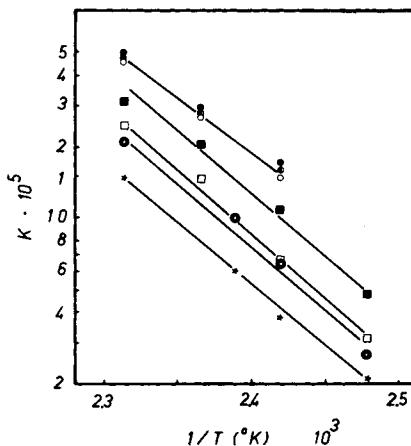


Fig. 21. Arrhenius plots of the rate constant for the crosslink formation in some EPDM's and one EPTM. (○) = IPHTHI (0.242 mole/kg); (●) = IPHTHI (0.392 mole/kg); (■) = IPHTHI (0.453 mole/kg); (□) = 1,4-HD (0.470 mole/kg); (□) = ENB (0.630 mole/kg); (★) = *endo*-DCP (0.450 mole/kg) (☆) = MNB (0.470 mole/kg).

cations of this result are not evident since the value obtained refers to the overall process of network formation which is the final result of several individual steps, consecutive and concurrent. However, the approach is interesting and probably it may be improved to obtain more analytical information.

As a conclusive remark, it can be noted that microstructural properties play a noticeable role in influencing several physical properties of EPM's and EPDM's when the ethylene content is high or medium, whereas when the propylene content is high, the influence of the microstructure is secondary. This is observed, probably, because we have very preliminary information on the microstructural homogeneity of propylene units (Zambelli et al., 1972). Ethylene sequences formed by three units are already able to influence markedly the physical behavior of these elastomers through crystallization (under stretching) or aggregation (physical crosslinks) phenomena due to association of ethylene sequences. It is worth noting that similar explanations have been invoked (Morimoto and Okamoto, 1972) to account for anomalous behaviors observed in EPM and EPDM solution properties (cf. Section II I) and this fact indicates the importance attributed by several authors to the influence (not yet fully elucidated) shown by the monomers distribution on different properties of ethylene-propylene-based rubbers.

However, it is quite interesting that by choosing appropriate catalyst systems, a complete range of elastomers having a continuous series of microstructural properties can be obtained. The next sections are just devoted to the chemical aspects of EPDM synthesis and to the action mechanism of the catalysts involved.

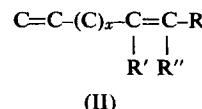
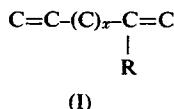
1. Allene Derivatives and Conjugated Dienes

There has been little interest in EPDM's derived from the classes of termonomers 1.1 and 1.2 of Table XVII. Conjugated dienes have been considered and, generally, are highly efficient poisons toward catalytic species. As a consequence, low quantities of unsaturation are introduced in the resulting polymer which is accompanied by the formation of EPM and other heterogeneous products due to the tendency of repressing the polymerization of the α -olefin used. These results are not surprising because of high coordinating ability of conjugated diolefins to catalytic centers. Similar results are also encountered whenever highly reactive termonomers (e.g., class 1.4, of Table XVII) are employed. As matter of fact, EPDM containing butadiene (BD; Ital. Pat. 1968, 1969) carries the diene as 1,4-*trans* units; the length of the blocks is 3–15 units. As a consequence, the comparative study of five EPDM's based on DCP, MTHI, 1,4-HD, ENB and BD has shown (Baranwal and Lindsay, 1972) that BD-EPDM possesses the lowest cure rate, the lowest total chemical crosslink density (both filled and gum stocks), the lowest abrasion resistance and the highest heat build-up, permanent set and number of sulfur atoms per polysulfide crosslink.

Allene derivatives have to be considered as highly poisonous termonomers also, as an allenic system in more susceptible than an acetylenic system to nucleophilic attack. To be considered, also, is the possibility of existence of allene-acetylene rearrangements.

2. Linear Nonconjugated Dienes

This class of termonomers contains a vinylic double bond as primary unsaturation (reactive towards catalyst centers) and a secondary unsaturation (for the curing process) as terminal (vinylidenic) (I) or internal double bond (II):



where $\text{R} = -\text{CH}_3$ or a higher alkyl group; R' and $\text{R}'' = \text{H}$ or an alkyl group; $x \geq 1$.

The simplest and most studied representative of this class is 1,4-hexadiene (HD) which can be obtained directly from ethylene and butadiene in the presence of catalyst prepared from transition metal compounds of VIII group and organometallic aluminum derivatives (Alderson et al., 1965; Cramer, 1967; Iwamoto et al., 1967). HD can be obtained in the *cis* (Hata, 1964; Iwamoto and Yuguchi, 1968; Henrici-Olivè and Olivè, 1972) or *trans* (Su and Callette, 1971; U.S. Pat. 1968, 1969c, 1971a) form, although the first experiments were, probably, carried out with a mixture of two isomers. On heating 1,4-HD isomerizes to 2,4-hexadiene, while by passing 1,4-HD over catalysts at 200°C the relative amounts of *cis* to *trans* isomers can be regulated (U.S. Pat. 1969d). High *trans*-to-*cis* 1,4-HD proportions were obtained using Ni compounds + R_2AlCl + triphenyl phosphine (Su and Callette, 1971). However, now it is known that *trans*-1,4-HD is more favorably incorporated into EPDM chains than *cis*-1,4-HD (see Table II) and the *cis* isomer is isomerized to the *trans* configuration at the polymerization stage and not before (Skinner et al., 1972).

No evidence has been collected for isomerization of *cis*-1,4-HD in the presence of single catalyst components (VOCl_3 or $\text{Et}_3\text{Al}_2\text{Cl}_3$) or for a post-polymerization isomerization.

On the other hand, *cis*-1,4-HD has been found (Skinner et al., 1972) to homopolymerize rapidly at 0°C in the presence of the system VOCl_3 - $\text{Et}_3\text{Al}_2\text{Cl}_3$ (1:5). The brittle, soluble polymer obtained showed the pres-

ence of both a *trans* double bond (970 cm^{-1}) and vinyl groups (910 and 955 cm^{-1}). This confirms that both unsaturations of HD are reactive with Ziegler-Natta catalyst in the absence of ethylene and propylene.

Analogous results have been obtained in the case of 1,5-heptadiene, the superior homolog of HD, in the presence of Ti-based Ziegler Natta catalyst (Romanov, 1963).

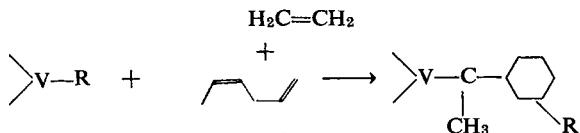
Other investigated termonomers of this class are: 5,7-dimethyl-1,6-octadiene and 3,7-dimethyl-1,6-octadiene (Wilbur and Marvel, 1964), 1,9-octadecadiene, and 11-methyl-1,10-dodecadiene (Christman and Keim, 1968). The reactivities of these compounds, with respect to propylene, are reported in Table II, whereas 6-methyl-1,5-heptadiene and 11-ethyl-1,11-tridecadiene have been described with HD in the first paper devoted to the EPDM synthesis (Gladding et al., 1962).

Dienes with two vinylic double bonds, such as 1,5-hexadiene, can also be used, but the identical reactivity of the double bonds yields an insoluble portion of crosslinked material. Furthermore, there is the tendency to incorporate this type of symmetric diene as cyclized structure (Marvel and Stille, 1958; Butler and Brooks 1963), and this means a loss of unsaturation, although it has been reported that cyclization reactions can be partly avoided by using suitable catalysts and appropriate experimental conditions (Valvassori et al., 1962).

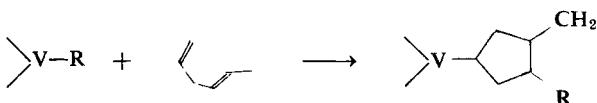
The tendency of the internal or vinylidinic secondary double bond of linear dienes to react during the EPDM synthesis has been evidenced by using severe conditions, e.g., absence of solvent (Seidov et al., 1970) and ^{14}C -labelled termonomers (Livshits et al., 1970). In the first case the formation of gel was proportional to the HD concentration, while the comparison of radiochemical and chemical dosage of unsaturation showed the formation of large amounts (60–90%) of saturated cyclic units as function of the acidic character of the catalyst and of the position of the methyl substituent in the termonomer molecule. All the dienes investigated, namely, 1,5-hexadiene (1,5-HD), 2-methyl-1,5-hexadiene, 1,5-heptadiene, 2,5-dimethyl-1,5-hexadiene, yield a dramatic fall in the catalytic efficiency and sharp reduction of MW (except 1,5-HD) in comparison with EPM produced under comparable conditions.

Also *cis*-1,4-HD yields EPDM containing 65% of the incorporated termonomer as saturated rings (Livshits et al., 1971) in the presence of the acidic catalyst $\text{VOCl}_3\text{-Et}_2\text{Al}_2\text{Cl}_3$. Catalyst systems based on VCl_4 or VAc_3 and R_2AlCl give EPDM with a higher amount of HD as unsaturated side chains (ca. 47%). A recent review (Baldwin and Ver Strate, 1972) reports the data of patent literature according to which HD reacts about 25% with the internal double bond to yield saturated cycles de-

rived from the simultaneous reaction of HD and ethylene:



The resulting structure and, in particular, the concerted mechanism involved seem unlikely. In the absence of more precise data the experimental observation of saturated repeating units derived from HD might be explained by intramolecular cyclization reaction of type:



which have been found for the higher homologs of HD (Marvel and Stille, 1958; Butler and Brooks, 1963), or through the formation of more complicated cyclic structures, as has been observed in the case of divinyl ether (Guaita et al., 1969) which simulates the monomeric unit of 1,4-dienes.

The comparison between the behavior of HD and of aliphatic dienes with widely separated double bonds (Gladding et al., 1962) indicates that when the double bonds move closer to one another there is a strong tendency to diminish the overall terpolymerization rate and the reactivity of α -olefin. This effect is particularly enhanced in the case of HD but it is common, in different degree, to all the termonomers investigated.

Recently, the behavior of HD in terpolymerization has been investigated by using the system $\text{VOCl}_3-\text{Et}_3\text{Al}_2\text{Cl}_3$ at 20°C (Duck and Cooper, 1971); the incorporation of the diene has been found to be 25% at low HD levels and a strong dependence of the polymer yields on the termonomer concentration has been confirmed. However, in the presence of catalyst activators (e.g., esters of trichloroacetic acid) the reciprocal of MW, polymer yields, and termonomer utilization are favorably increased. The properties of EPDM based on HD, during and after vulcanization, are interesting; however, the cure rate, the air aging at 125°C and the covulcanization behavior with highly unsaturated elastomers, compare less favorably with more recent EPDM's containing norbornene derivatives (see Section III A 7).

Much work has been carried out on HD-based EPDM (Saegebarth, 1968a), in particular on more recent types of terpolymer (Morgan,

1968), in order to evaluate and compare many technological properties of different EPDM's. The effects of varying the polymers composition on the cut growth characteristics (Stewart and Verbanc, 1971); stress-relaxation behavior studies (Shih, 1971b); investigations concerning both the rate of crosslinking and the structure of crosslinks (Berger et al., 1969; Fujimoto and Nakade, 1969; Saegebarth, 1968b); the influence of the unsaturation type of EPDM on its bonding to textiles (e.g., rayon and nylon) and metals (Meulen, 1971), are examples of specific topics particularly investigated. An extensive study of the sulfur vulcanization chemistry and mechanism of HD-EPDM (Saegebarth, 1968a) has evidenced that ca. 50% of the double bonds are saturated and about one crosslink is generated from each two double bonds initially present.

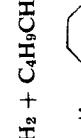
According to other studies (Satake et al., 1970), HD-EPDM is excellent as a tread polymer and shows well-balanced properties such as abrasion resistance, flex-crack resistance, and processability. From laboratory experiments HD- and ENB-based EPDM have evidenced similar behavior in hardness, modulus, elongation, resilience, heat build-up, and skid resistance when MWD and composition were comparable (Satake et al., 1971a).

EPDM based on 5,7-dimethyl-1,6-octadiene was synthesized both in the presence of V- and Ti-based Ziegler-Natta catalysts and found to contain IR absorption characteristic of a trisubstituted olefin bond (Wilbur and Marvel, 1964). Also bromine titration showed the presence of significant amount of unsaturation, but, despite this evidence, the elastomeric behavior after vulcanization was very poor. By contrast 3,7-dimethyl-1,6-octadiene was found unable to homopolymerize in the presence of Ziegler-Natta catalysts. Metathesis reaction (Calderon et al., 1968) has recently offered (Lal et al., 1972) the opportunity to prepare, starting from cyclooctene and 1-hexene, a mixture of unsaturated hydrocarbons among which di-, tri- and tetraolefins are prevalent, the double bonds being in different positions (cf. Table XXI). The reaction mixture has been used to prepare, in the presence of $\text{VOCl}_3\text{-Et}_3\text{Al}_2\text{Cl}_3$ system, an EPDM about which, only its vulcanizability has been reported.

3. Monocyclic Diolefins

Cis-cis-1,5-cyclooctadiene (COD) and its 5-methyl derivative are the termonomers of this class most investigated (Natta et al., 1965a). They can be prepared in high yields from butadiene and, respectively, from isoprene-butadiene mixture by means of catalytic processes employing Ni-carbonyl derivatives or Ziegler type systems, e.g., Ni-acetylacetone

TABLE XXI
Scheme of Metathesis Reaction^a between Cyclooctene and 1-Hexene (Catalyst, $WCl_6 \cdot EtOH/EtAlCl_2$; Reaction Time, $\frac{1}{2}$ hr).

			Yield (%)
	$+ \begin{array}{c} CH_2 \\ \\ CH - C_4H_9 \end{array}$	\rightleftharpoons	$CH_2=CH(CH_2)_6CH=CHC_4H_9$
			58
$CH_2=CHC_4H_9$	$+ \begin{array}{c} CH_2 \\ \\ CH_2=CHC_4H_9 \end{array}$	\rightleftharpoons	$CH_2=[CH(CH_2)_6CH]_n=CHC_4H_9$
			$n = 2,3$
$CH_2=CH_2$	$+ \begin{array}{c} CH_2 \\ \\ CH_2=CHC_4H_9 \end{array}$	\rightleftharpoons	$CH_2=CH_2 + C_4H_9CH=CHC_4H_9$
			24
$C_4H_9CH=$	$[CH(CH_2)_6CH=]_nCHC_4H_9$	\rightleftharpoons	$C_4H_9CH=[CH(CH_2)_6CH=]_nCHC_4H_9$
			$n = 1,2,3$
	$+ CH_2=CH_2$	\rightleftharpoons	$CH_2=CH(CH_2)_6CH=CH_2$
			12
$CH_2=[CH(CH_2)_6CH=]_nCH_2$			$n = 2,3,4$

^aAfter Lal et al., 1972.

and alkyl aluminum derivatives in the presence of electron donor molecules (Reed, 1954; U.S. Pat., 1960, 1961b; Wilke, 1963).

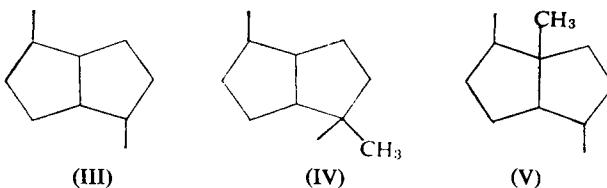
The possibility of employing termonomers as COD followed the discovery of Natta et al. (1961c, 1962b) according which Ziegler-Natta catalyst can open internal double bonds and insert such units in copolymers with ethylene.

However, a sharp difference in reactivity exists between ethylene or α -olefins and cyclic olefins, hence a relatively high concentration of the latter is needed to obtain a terpolymer with practical levels of unsaturation.

The insertion of COD in EPDM chains was tested and quantitatively determined by means of IR spectroscopy and referred to terpolymers containing ^{14}C -labeled COD (Natta et al., 1965c). The most typical Ziegler-Natta catalysts have been found suitable for producing true terpolymers having interesting properties in the vulcanization process (Natta et al., 1963). Some parameters regulating the terpolymerization reaction have been examined: temperature; Al/V molar ratio of the catalyst; catalyst concentration; α -olefins molar ratio; diene concentration; MW regulation. The results obtained are quite regular, i.e., corresponding to expectations derived from previous studies on EPM. Furthermore, they agree with other results obtained in analogous investigations carried out with different termonomers. These results are unified and summarized in Section IV because of their substantial similarity.

It is worth noting that, by using COD- ^{14}C -1,3,5,7 (the catalyst being $\text{VCl}_4\text{-AlEt}_2\text{Cl}$) and comparing iodometric and radiometric titers of unsaturation, the second double bond of COD has been found to participate in secondary reactions (Dolinskaya, 1969). In fact the radiochemical dosage of COD gives results which are always higher than chemical method; the difference increases with the reaction time and the COD concentration. Furthermore, MW also shows the same dependence, and under more severe conditions, amounts of gel are observed. However, since gelled samples have been found completely soluble in toluene, it seems that the secondary processes continue without the appearance of crosslinked material and only up to the stage of branching.

During the terpolymerization reaction, the presence of a methyl group in position 5 of COD is expected to reduce the reactivity of the substituted double bond. Anyway, this has not been the case in homopolymerization experiments because both COD and 5-methyl-COD (Belikova et al., 1961; Valvassori, 1963b) have been found to give repeating units of type (III), (IV), or (V):



which are not present in corresponding EPDM's.

4. Alkenyl Cycloalkenes

Despite the large number of potential termonomers ascribable to this class, only two papers have been reported on the corresponding EPDM's. The main reason of such a situation is due to the low reactivity of termonomers containing alkenyl or cycloalkenyl unsaturation with respect to norborne one (cf. Section III A 7).

The first paper (Caywood, 1971) deals with 4-vinyl-1-cyclohexene (VCE), the dimer of butadiene obtainable via Diels-Alder reaction from the conjugated diolefin on standing or slightly warming. In the presence of isospecific catalysts VCE yields, with low rate, a crystalline, isotactic polymer (Marconi et al., 1964a), whereas amorphous products, ranging from viscous liquids to solid polymers of undefined structure, have been produced with cationic catalysts (Brit. Pat., 1945; U.S. Pat., 1950, 1951). VCE has been terpolymerized with the system $\text{VOCl}_3 \cdot \text{Et}_3\text{AlEt}_2\text{AlCl}$ and $\text{C}_6\text{H}_5\text{CCl}_3$ as activator. The unsaturation content was determined by bromine titration and ascertained by IR spectroscopy, while the random distribution of monomers was shown by fractionation and analysis of single fractions.

In comparison with HD, VCE has been found hardly reactive during the terpolymerization reaction; both diolefins contain a vinyl double bond reactive toward Ziegler-Natta catalyst, but the relative reactivity of HD to VCE is 7:1. On the other hand, VCE is effective in chain breaking processes and in order to obtain sufficiently high MW and unsaturation concentration, the temperature of polymerization must be lowered.

A peculiar behavior of cyclohexenyl unsaturation has been found during the study of the vulcanization process with sulfur, since about only one effective crosslink for four double bonds has been shown by VCE-based EPDM compared with one for 1.5–2.0 double bonds in a similar HD-based terpolymer. On the contrary, the peroxide cure takes place quite well.

The unusual behavior of cyclohexenyl unsaturation seems confirmed by the behavior of EPDM obtained starting from dipentene (DL-limonene) or from optical active D-limonene (Magin et al., 1965). In both cases a methyl cyclohexenyl group should be present in the chains but, actually, this presence was tested only by iodometric titration. Despite the fact that good levels of unsaturation were present (ca. 0.3 mole/kg), the vulcanization tests gave highly undercured vulcanizates.

An adequate explanation of these results is not possible on the basis of the small amount of data available, although it has been pointed out that unsaturations present in seven- or eight-membered rings give fast curing EPDM's. On the contrary, unsaturation derived from five- or six-membered rings should give terpolymers which vulcanize slowly; the difference might be due to different ring tensions (Sartori et al., 1965). However, the chemistry of vulcanization processes is quite complicated and, at present, little is known about its features and the role played by the type of unsaturation (cf. Section III A); thus in the view of little and incomplete data, any comment would be mere speculation.

5. *Bicyclic Diolefins*

The more frequently cited termonomers of this class are bicyclo-[4.3.0]-3,7-nonadiene (i.e., 4,5,8,9-tetrahydroindene, THI) derivatives, which can be easily prepared through Diels-Alder reactions (Plate and Belikova, 1960) starting from butadiene (or its superior homologs) and cyclopentadiene, which should react as dienophile in order to obtain the THI structure (Sauer, 1967). Actually a mixture of possible adducts is formed, but by choosing optimal experimental conditions (mainly temperature), it is possible to obtain more favorable yields of THI derivatives (Titona et al., 1971; Plate and Belikova, 1961).

Unfortunately, little information was published on the synthesis of THI-based EPDM. It has been reported (Pasquon et al., 1967; Capito et al., 1968) that the tendency of THI and its methyl derivatives to incorporate into EPDM chains is of the same order of propylene and quite near to open-chain diene reactivity (Table II). Presumably THI, and more certainly 6- or 7-methyl THI and 6,7-dimethyl THI, enter the resulting EPDM chains via the cyclopentene double bond opening. It is known that cyclopentene is more reactive than cyclohexene toward vanadium-based Ziegler-Natta catalysts.

According to Seidov et al. (1971) the MW regulation of EPDM based on THI or methyl THI is possible, but when $ZnEt_2$ is used as chain

transfer agent, the terpolymer is practically unreactive with sulfur. The result is quite surprising and not accounted for by the current views on the α -olefins terpolymerization mechanism. On the contrary, we have observed (Cesca et al., 1974a) spectroscopic (IR, NMR, UV) modification in EPM and EPTM (cf. Section II I and Fig. 9) when H₂ was used as MW regulator (and not with ZnEt₂). The results have been attributed to a hydrogenating activity exerted toward both active centers (which transform from Cat-R into Cat-H bonds) and termonomer unsaturation.

The presence of methyl groups on the indene ring markedly influences the vulcanization rate (Crespi et al., 1966; Valvassori and Cameli, 1969). In agreement with the availability of allylic hydrogen atoms (cf. Section III A) on the resulting EPDM's, the following order of reactivity results in the vulcanization process: 6,7-dimethyl THI > 6- or 7-methyl THI > THI. Another termonomer of this class is bicyclo-[3.2.0]-2,6-heptadiene (BCH) which has been said (Valvassori and Cameli, 1969) to give slow-curing EPDM. Probably the diolefin enters the polymer chains most frequently via cyclobutene unsaturation opening which can be considered more reactive than the cyclopentene double bond. However, it cannot be overlooked that BCH reacts, at least in part, through the cyclobutene ring cleavage, as it has been shown in the case of 1,2-divinyl cyclobutane (see the next section).

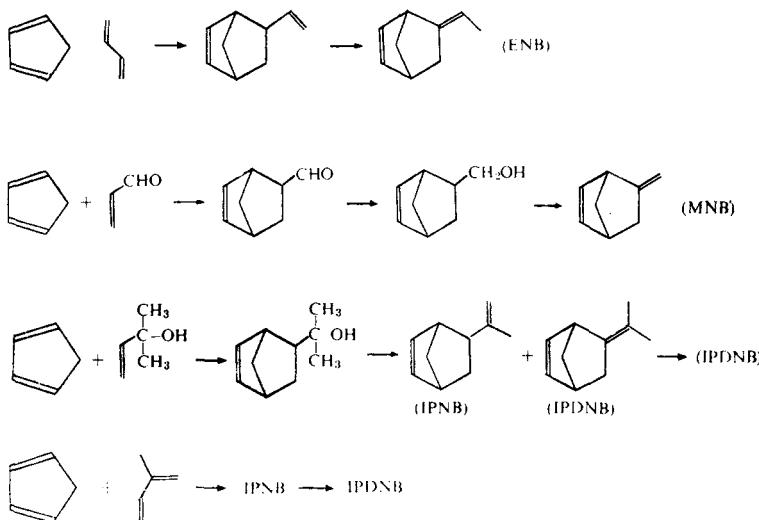
6. Dialkenyl Cycloalkanes

Only *trans*-1,2-divinyl cyclobutane (DVCB), a dimer of butadiene produced in good yield through a photosensitized reaction (Hammond et al., 1961, 1963), has been investigated in this class of termonomers (Natta et al., 1965). However, little data are available on the synthesis of the corresponding EPDM. It was shown by IR spectroscopy that DVCB can react via a double bond opening (70–40% of the monomeric units, depending on the type of catalyst) and via cyclobutane ring cleavage (presence of *trans* double bonds in the polymer). The same behavior was found in homopolymerization reactions with Ziegler-Natta catalysts (Valvassori et al., 1963b). In comparison with the trimer of butadiene (trivinylcyclohexane, see Section III B 2) DVCB shows a higher reactivity during the polymerization reaction, according to a ratio of 3:1, whereas the rates of vulcanization of the corresponding EPDM's are similar, however lower than the curing rate of COD-based EPDM.

7. Alkenyl- or Alkylidene Norbornenes

As it can be seen in Table II, this class of dienes contains the largest number of termonomers investigated. The interest in this family of

compounds is based on the well-known high reactivity of norbornene double bond (Rodd, 1953) which is shown also toward Ziegler-Natta catalysts. Thus the driving force has to be considered of thermodynamic origin for relief of strain energy. As a consequence this class of dienes shows high termonomer utilization in the polymerization reaction and low interference with the catalyst species, because relatively low concentrations of termonomer are required in the feed. Moreover, the synthesis of this type of dienes is quite facile, since it can be accomplished through a Diels-Alder reaction between cyclopentadiene (which shows a strong tendency (Sauer, 1967) to behave as diene) and an appropriate diene or vinyl derivative (dienophile). The resulting adduct can be submitted to successive reactions or rearrangements (Belikova et al., 1961; U.S. Pat., 1967; 1970; Paris, 1969) to obtain the desired position of the second double bond as, for instance, in the case of ENB, MNB and IPDNB (Fr. Pat., 1966; Ger. Offen., 1967):



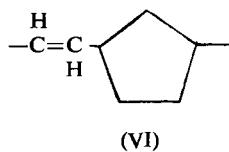
However, in the case of IPDNB synthesis the bottle-neck is the low yield in the Diels-Alder reaction, whereas the reaction of cyclopentadiene with isoprene occurs with relevant amounts of isomeric (C_{10}) side products (Plate and Belikova, 1961). According to the Alder rule (Sauer, 1967), it is highly probable that the resulting alkanyl norbornenes have the *endo* configuration; however, the behavior during the terpolymerization reaction of any *exo* isomer of this class of termonomer has

not been described so far. Only the vulcanization rate of EPDM's based on *endo*- and *exo*-IPNB was investigated (Table XIX) and the latter was found faster than the former.

The presence of a bulky group in position 5 of the norbornene molecule should increase the strain in the ring containing the double bond and hence its reactivity should be increased (Christman and Keim, 1968); actually only partial indications of this effect have been obtained (See Table II).

The selective high reactivity of norbornene double bond was still recognized during the early researches on EPDM synthesis (Gladding et al., 1962) by collecting IR spectroscopic evidences from dicyclopentadiene-based EPDM (see Section III A 9) and by comparing the reactivity of norbornene derivatives and aliphatic dienes. More direct evidence on the behavior of norbornene ring in the presence of typical terpolymerization catalysts have been successively obtained (Cooper et al., 1965) by using ^{14}C -labeled bicyclo-[2.2.1]-2-heptene derivatives in homopolymerization and terpolymerization experiments and by studying the resulting polymers through IR spectroscopy (Hank, 1965; German, 1966; De Kock and Veermans, 1966; Sartori et al., 1963).

Under particular conditions the norbornene ring may be opened to give repeating unit of type (VI):



which, however, is never present in EPDM chains. (Sartori et al., 1964; Truett et al., 1960; Tsujino et al., 1965). A similar anomalous reactivity is shown by MNB under homopolymerization conditions. The repeating unit (VII) has been observed (Sartori et al., 1963),



(VII)

but in terpolymerization processes only the regular opening of norbornene double bond takes place.

According to the relative reactivities of many termonomers (Table II), ENB shows the highest value. Its behavior is practically equal to 2-norbornene one (the parent monoolefin), whereas the isomer of ENB, 5-vinyl-2-norbornene, or other similar molecules (e.g., MNB or 5-(*cis*-2'-butenyl)-2-norbornene) show reactivities which are within 1/3-1/2 of ENB reactivity. The explanation of these results is not immediate; however they indicate a regular behavior, i.e., a minimum of secondary reactions, of ENB during the terpolymerization process. This inference has been recently confirmed (Duck and Cooper, 1971) by working with the system $\text{VOCl}_3\text{-Et}_3\text{Al}_2\text{Cl}_3$ at 20°C and in the presence of MW regulators. Under such conditions the incorporation of ENB is 90–100% for unsaturation ranging between 2 and 15%. Furthermore, the overall polymerization rate is slightly dependent on the termonomer concentration, thus confirming the existence of minimal interactions between ENB and catalytic centers.

The control of MW is obtained with H_2 , but high H_2 pressures reduce significantly catalyst activity; moreover, in the presence of H_2 the ethylene/propylene ratio and the termonomer incorporation can be adversely influenced. In contrast with what generally happens in this kind of polymerization, a small decrease in the ethylene content of the resulting EPDM, with respect to the corresponding EPM, was observed with ENB (Duck and Cooper, 1971).

The use of appropriate chlorinated compounds acting as catalyst activator and MW regulator (e.g., Cl_3CCOOEt , according to a molar ratio 4:1 with respect to the V compound), affect sharply and favorably both MW and polymer yield, while polymer branching is quite low. However, the degree of branching is independent of the type of V compound, whereas it is strictly dependent on the acidity, according to Lewis, of the alkyl aluminum halide (Easterbrook et al., 1971). For instance, when Et-AlCl_2 is used, extensive branching and gelation result. On the contrary Lewis bases act as catalyst modifiers and in their presence the amount of branching can be markedly reduced. Furthermore, at the end of the terpolymerization reaction, when the influence of acidic products derived from the quenching of the active species induces the formation of very high MW or gelled material, the positive influence of basic modifiers can be observed.

The examination of ENB-based EPDM properties, in particular during and after vulcanization, indicates the good behavior of the unsaturation sites introduced by ENB, e.g., high cure rates, heat stability, slow cure reversion. Similar good results have been obtained with IPDNB-based EPDM (cf. Table XIX). However, the behavior in covulcaniza-

tion with highly unsaturated elastomers (e.g., SBR or *cis*-1,4-polyisoprene) is not completely satisfactory, in particular when the content of ENB is lower than 10 wt %. Recently (Filburn and Spenadel, 1970; Samuels and Wirth, 1967b), ENB-EPDM has been extensively studied in comparison with other commercial EPDM's having similar features (Fujimoto and Nakade, 1969; Meulen, 1971; Satake et al., 1970; 1971a; Schnecko and Walker, 1971) in order to test its general properties and also its behavior as a general purpose rubber. The results indicate that ENB-based EPDM is certainly one of the best terpolymers produced so far.

Other dienes belonging to this class of termonomer have been described (Sartori et al., 1965); the feature of the secondary unsaturation is to be vinylidenic or internal. The products are 5-(2'-methylallyl)-2-norbornene, 5-(2'-butenyl)-2-norbornene (which exists as *cis* and *trans* isomers) and 5-(4'-cyclohexenyl)-2-norbornene (CHN). They can be obtained via Diels-Alder reaction between cyclopentadiene and, respectively, 2-methyl-1,4-pentadiene, 1,4-hexadiene, and 4-vinyl-cyclohexene. Little has been reported on the EPDM's based on the aforesaid dienes; the second and the third compound have been evaluated for their reactivity in comparison with propylene (Table II) and show the good utilization typical of norbornene derivatives. The presence of the secondary double bond in a six-membered ring gives CHN a slow-curing rate, as it has been observed in the case of THI and EHN (Duck and Cooper, 1971; Cameli et al., 1968; Van Schooten and Evehniis, 1965) (cf. Sections III A 5 and III A 9).

8. Alkyl Norbornadienes

The simplest compound of this class, i.e., 2-methyl-2,5-norbornadiene, was studied in the first paper devoted to EPDM synthesis (Gladning et al., 1962) and it showed apparent high utilization during the terpolymerization process.

Despite this interesting initial information, relatively little work has been carried out on this group of termonomers which could be prepared according to Diels-Alder reaction between cyclopentadiene and acetylene derivatives (Onischchenko, 1964). However, also the parent compound, i.e., 2,5-norbornadiene (NBD), has been investigated using the catalyst systems $VCl_4-n\text{-}Hex_3Al$ or $VAcac_3-Et_2AlCl$, but the properties of the corresponding EPDM have not been reported (Sartori et al., 1964). Only by IR has the absence of *trans* double bonds and of unstrained cyclopentene-rings in the chains been shown, and this result was taken

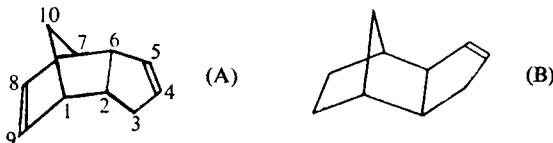
as an evidence of the regular opening of only one double bond present in the NBD molecule during the terpolymerization reaction.

On the contrary, during the homopolymerization of NBD, in the presence of V- or Ti-based Ziegler-Natta catalysts, the ring cleavage (see the next section) is the prevalent pathway of reaction of the diene.

9. Polycyclic Diolefins

A number of possible termonomers may be ascribed to this class and also some of the previous classes might be included in it. In order to treat separately the large amount of work devoted to dicyclopentadiene (DCP), we consider the subdivision adopted as useful.

DCP (tricyclo-[5.2.1.0^{2,6}]-4,8-decadiene) is of historical importance because after its use in EPDM synthesis (Brit. Pat., 1956b, 1957a, b), there was noticeable effort in the research in this field. This diolefin in the past was obtained in the distillate from coal tar as monomeric cyclopentadiene (CP) which easily dimerizes exclusively to the *endo*-DCP isomer (A), according to the *cis* addition rule of Alder (Sauer, 1967). Today CP is obtained in large quantity from the C₅ fraction produced in naphtha steam cracking and extraction processes used for the production of isoprene (Kirk and Othmer, 1960). The second stereoisomer of DCP, i.e., *exo*-DCP (B)



is obtainable as highly pure stereoisomer (Cesca et al., 1965b) through a Meerwein-Wagner rearrangement (Meerwein and Emster, 1920; Bruson and Riener, 1948) which requires the addition of electrophilic reagents on the bicycloheptene double bond of *endo*-DCP and subsequent regeneration of the unsaturation. Also the action of temperature can induce the formation of *exo*-DCP (Alder and Stein, 1934) since it is the thermodynamically more stable isomer (Becker and Roth, 1934).

Both the epimeric forms of DCP have been used in terpolymerization researches, but the largest part of work has been carried out with *endo*-DCP.

The first paper devoted to EPDM's synthesis (Gladding et al., 1962) was concerned also with *endo*-DCP and the excellent way it inserted into polymer chains was evidenced. However, the double bond in position

4,5 is not completely unreactive, as it has been proved by using 8,9-dideutero-8,9-dihydro-DCP and successive IR analysis of the polymer obtained. This early result was confirmed by successive papers devoted to the terpolymerization of *endo*-DCP in different solvents (Cunnigham, 1965) or with different catalysts (Cunnigham, 1966) and also to the study of the course of terpolymerization or the modality of feeding the termonomer (Cunnigham, 1967).

The facility of formation of insoluble material, as true crosslinked gel and not blocks of crystalline insoluble polymers, was found dependent on the type of solvent according to the order; *n*-heptane > tetrachloroethylene > benzene, the catalyst used being VOCl_3 or VCl_4 and $\text{Et}_3\text{Al}_2\text{Cl}_3$. The same order resulted with vanadium-tris-acetylacetone- or vanadyl-bis-acetylacetone-based systems; however, the tendency to give insoluble material is less enhanced with V organic salts. No difference in the yield exists when $\text{Et}_3\text{Al}_2\text{Cl}_3$ is used as cocatalyst in aromatic solvents and in union with different V compounds.

With a single initial addition of DCP to the feed, the catalysts obtained from VCl_4 , VOCl_3 , or V ($\text{C}_5\text{H}_7\text{O}_2$)₃ and $\text{Et}_3\text{Al}_2\text{Cl}_3$ in benzene give EPDM with similar unsaturation. The terpolymer yield increases quickly in the early stages of reaction and then slowly, because of deactivation of catalyst. MW shows a steady increase throughout the course of the reaction carried out in benzene and reaches a moderate final value. In *n*-heptane, the intrinsic viscosities grow very rapidly reaching a high value in a few minutes.

The formation of gelled EPDM can be avoided in part, even when *n*-heptane is used, by feeding DCP continuously instead of adding all the termonomer at the start of the reaction. This technique furnishes EPDM with constant level of unsaturation at different times of reaction and the highest final content of DCP. Thomalla et al. (1973) have found that relevant amounts of gel (up to 88 % of EPDM) are formed when the terpolymerization is carried out in liquid propylene at 20°C and with the catalysts $\text{VOCl}_3\text{-Et}_2\text{AlCl}$ or $\text{VO}(\text{OC}_8\text{H}_{17})_{1.7}\text{Cl}_{1.3}\text{-Et}_2\text{AlCl}$ ($\text{DCP} = 12 \text{ g/l}$). In the presence of H_2 (0.42 mole % in the feed) the supposed gel is almost eliminated with the latter catalyst, whereas the former yields still 23 % of insoluble (in toluene at 80°C) material.

The existence of long chain branching in EPDM containing *endo*-DCP has been ascertained from maximum relaxation time measurements (Easterbrook et al., 1971). Highly gelled EPDM, containing a low amount of unsaturation, was obtained carrying out the terpolymerization reaction at -60°C with the system $\text{VOCl}_3\text{-Al}(i\text{-Bu})_3$ in *n*-heptane

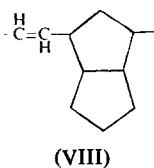
(Zavorokin and Matkovskii, 1967). Under more usual conditions, i.e., by working near room temperature, the catalyst $\text{VOCl}_3\text{-Et}_3\text{Al}_2\text{Cl}_3$ gives rise to a degree of branching which is 7.5 times higher when DCP is used instead of ENB, the content of termonomer being the same, i.e., 5.5 wt %. However, an EPDM containing 9.0 wt % of ENB has about the same content of branching as one containing 5.5 wt % of *endo*-DCP (Easterbrook et al., 1971).

A quantitative evaluation of unsaturation consumption has been carried out using tritium-labeled *endo*-DCP and comparing radiometric with iodometric values of unsaturation (Dolinskaya et al., 1969). The difference of titers, in EPDM prepared at room temperature with the catalyst $\text{VCl}_4\text{-R}_2\text{AlCl}$, is significant after 5 min of polymerization and after 30 min the chemical value is lowered ca. 25%. Moreover, large amounts of insoluble material, an increase in MW and of the rigidity of terpolymer appear when the concentration of DCP increases, when the temperature of polymerization is lowered, or when EPDM is treated with the components of the catalytic system.

Recently, a systematic investigation of several parameters, regulating the terpolymerization process of DCP, has been carried out (Easterbrook et al., 1971). The results obtained are common to EPDM synthesis with other termonomers and are summarized in Section IV. Sometimes, however, differences are encountered using different catalysts. For instance, in contrast with the behavior of the catalyst $\text{VOCl}_3\text{-Al}(i\text{-Bu})_3$ (Tosi et al., 1972), the system $\text{VOCl}_3\text{-Et}_3\text{Al}_2\text{Cl}_3$ gives EPDM whose ethylene content is not influenced by concentration of DCP in the polymer up to 10 wt % (Easterbrook et al., 1971).

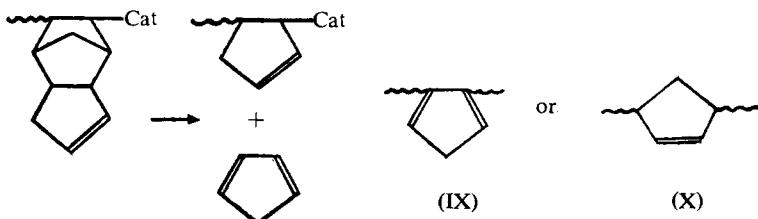
Much work has been devoted to defining the mode of reaction of DCP during the terpolymerization process, mainly by IR spectroscopic analyses (Cooper et al., 1965; De Kock and Veermans, 1966; Gladding et al., 1962; Sartori et al., 1964).

The prevalent opening of norbornene double bond has been proved, whereas the cleavage of bicyclo-[2.2.1]-2-heptene system, observed in the case of some norbornene derivatives (Truett et al., 1960) and giving, in the case of DCP, the structure (VIII),



can be excluded on the basis of the absence of the absorption due to *trans*-double bond. Moreover, the use of 4,5-dihydro-DCP as termonomer yields a completely saturated EPDM.

The use of DCP labeled with ^{14}C in both rings and the comparison of radiochemical and iodometric dosages has ruled out the possibility of the existence of structures such as (IX) or (X):



both containing one double bond for one cyclopentene unit (Cooper et al., 1965).

A careful comparison of IR absorptions obtained from cyclopentene and dicyclopentadiene derivatives, ethylene-DCP copolymers, and dihydro-DCP-based EPDM, has confirmed the absence of the structure (VIII) and strongly supported the reactivity of DCP through its unsaturation in position 8,9. The same conclusion has been reached with the aid of several model compounds, derivatives both of *endo*- and *exo*-DCP, which has also made possible the determination of DCP content in EPDM by using the band at 3045 cm^{-1} . This band characteristic of *endo*-cyclic double bond in five membered rings (De Kock and Veermans, 1966). In the same paper the configuration of DCP in EPDM was considered *exo* but, recently (Cesca et al., 1973a) this conclusion has been revised.

In fact, on the basis of IR examination of many EPDM samples, produced with different catalyst systems and containing either *exo*- or *endo*-DCP, it has been possible to identify the presence of *exo*-DCP in terpolymer. The absorption at 784 cm^{-1} (typical of *exo*-DCP derivatives) and also the ratio of optical densities measured at 690 and 719 cm^{-1} were used

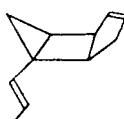
The most important conclusion of that work (Cesca et al., 1973a) is the absence of epimerization from *endo* to *exo* form of DCP during EPDM synthesis, also when the acidic character of the catalyst is enhanced. In fact, the possibility of such a rearrangement is related to the presence of strong electrophilic agents which, via attack of norbornene unsaturation, induce a Wagner-Meerwein isomerization (Meerwein and Emster, 1920; Bruson and Riener, 1948).

Recently the epimerization of *endo*-DCP has been reported during its homopolymerization with BF_3OEt_2 , whereas a mild initiator as $\text{PdCl}_2(\text{PhCN})_2$ is unable to give any rearrangement (Capito et al., 1968). However, also the system $\text{VOCl}_3\text{-Et}_3\text{Al}_2\text{Cl}_3$ and other acidic Ziegler-Natta catalysts are able to yield poly-*exo*-DCP starting from *endo*-DCP; this fact can be taken as the evidence of the existence in the catalyst of some species having a strong cationic character. At the same time EPDM prepared with *endo*-DCP and $\text{VOCl}_3\text{-Et}_3\text{Al}_2\text{Cl}_3$ catalyst shows no evidence of epimerization.

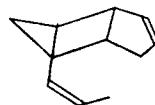
These results suggest at least two possibilities: (a) active centers acting through a coordinate mechanism have an intrinsic strong acidic character; (b) by-product, acting as strong Lewis acids, are originated by the interaction of coordinate catalyst components.

The data collected (Cesca et al., 1973 a) seem to better support the second hypothesis. Obviously, only in the presence of appropriate monomers can the initiating species, acting through a specific mechanism be active (cf. Section II D). These results are evidence that the polyfunctionality of Ziegler-Natta systems is another aspect of their heterogeneity. The implications of this conclusion in terpolymerization mechanism will be discussed in Section V.

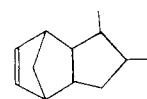
As far as the reactivity of *endo*-DCP is concerned under homopolymerization conditions with Ziegler-Natta catalysts obtained from transition metals compounds of the groups IV, V, VI, and VIII of the periodic table, seven repeating unit (XI)-(XVII) have been evidenced by IR spectroscopy (Dall' Asta et al., 1972):



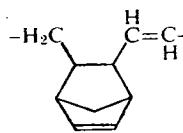
(XI)



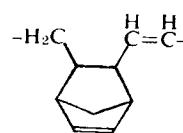
(XII)



(XIII)



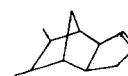
(XIV)



(XV)



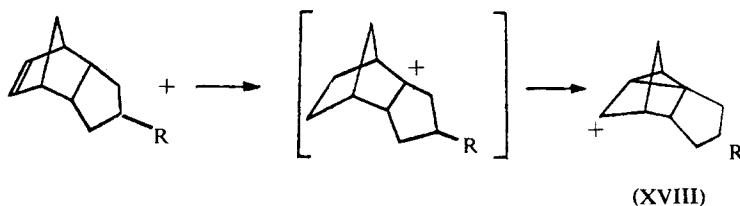
(XVI)



(XVII)

In particular, the vanadium-based catalyst system investigated ($\text{VCl}_4\text{-AlEt}_3$ in a molar ratio of 1:1.6 at 20°C) has only given structures (XVI), (XIII), and (XV) in the ratio 80:15:5.

In consideration of the facility of secondary reactions observed during the terpolymerization of DCP and cited above (see also Section II D), it is worth noting that *endo*-DCP can be homopolymerized by cationic initiators (e.g., EtAlCl_2 , TiCl_4) under relatively mild conditions (Cesca et al., 1970c). It has been shown, via copolymerization experiments between 4,5-dihydro-*endo*-DCP and 8,9-dihydro-*endo*-DCP, that the norbornene unsaturation is about twice more reactive than the cyclopentene double bond. However, in the case of polymer, obtained with cationic initiators from *endo*-DCP, less than one double bond for one structural unit was found. The properties of the polymer studied agreed with the presence of about 30% of nortricyclene units (XVIII):



resulting from a hydride shift and subsequent attack of norbornene unsaturation.

These results evidence once again (Pasquon et al., 1967) the complicated pathways of reaction shown by some diolefins when they are subjected to homopolymerization rather than terpolymerization conditions. Furthermore, in the case of DCP it has been proved that an initiation mechanism, which is different from the terpolymerization one, can attack the pendant unsaturation of the corresponding EPDM.

The quantitative evaluation of the reactivity of *endo*-DCP during the insertion into polymer chains indicates that it is 7.5 times more active than propylene (Table II) and the *exo* isomer is nearly twice as reactive as the *endo* isomer. Qualitatively the same results have been obtained in terpolymerization experiments at -60°C (Zavorokin and Matkovskii, 1967).

Hence, *exo*-DCP is, according to Table II, one of the most active dienes studied, similar, for instance, to ENB. Unfortunately the influence of *endo* and *exo* forms of norbornenic termonomers in polymerization has not been extensively investigated. It has been suggested

that *exo* isomer should be less reactive in post-polymerization reactions than the *endo* isomer, providing that no rearrangements take place during the terpolymerization (Christman and Keim, 1968). On the contrary, there is some information on the vulcanization behavior of EPDM's containing both *endo*- and *exo*-DCP or *endo*- and *exo*-5-isopropenyl-2-norbornene; in both the cases EPDM's containing *exo*-isomer are nearly twice more reactive (Ghetti et al., 1969; Kodama, 1968).

In this context it is interesting to recall that torsional angle effects (eclipsing strain energy) have been invoked, instead of remote steric effects, to account for the observed preference for reactivity of *exo* norbornyl and norbornenyl systems in the case of several reactions (Von Schleyer, 1967). Such an effect dominates also the stereochemistry of attack of some reagents to substituted cyclohexene (Pasto and Gontarz, 1971).

In the case of coordination catalysis in EPDM synthesis, the configuration of the *endo* form seems more suitable than the *exo* form to coordinate preferentially to catalytic centers and hence, a reduction of the efficiency of the active species may be expected.

Such a conclusion is in agreement with what has been observed in the metathesis reaction of norbornene derivatives carrying different substituents ($-COOH$, $-OH$, $-COOR$, $-CH_3$, $-Cl$) in position 5. In fact, even though the metathesis catalysts are based on transition metal atom derivatives (W, Rh, Ir) different from typical Ziegler-Natta ones (mainly Ti and V), it has been found that only the *exo*-derivatives of norbornene are subjected to the ring opening reaction, the norbornene coordination to the catalyst center being rather *endo* than *exo* (Michetti and Carter, 1965).

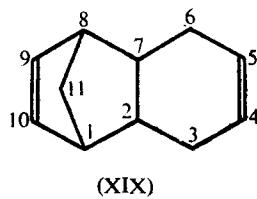
The properties of vulcanized EPDM containing *endo*-DCP have been extensively investigated (Draexler, 1970; Fujimoto and Nakade, 1969; German et al., 1966; Murakami and Tamura, 1971; Satake et al., 1971a; Schnecko and Walker, 1971; Singer et al., 1971). Relatively slow curing rates have been confirmed; on the other hand, there are practical limits beyond which is not convenient to increase the proportion of diene in the polymer (cf., also Fig. 1). In fact resistance to thermal oxidation has been found dependent on the amount of unsaturation remaining in the vulcanizate. The extent to which unsaturation is used for crosslinking decreases with increasing DCP content, with decreasing MW, and depends strictly on MWD. A noticeable decrease of the crosslinking density was found when the propylene content increased and the termonomer content was constant.

The crosslinking processes are markedly affected by the temperature of vulcanization, the activation energy being near to 25 kcal/mole. However, it is difficult to achieve a steady modulus value on prolonged curing, whereas, no reversion reactions have been detected up to 160°C. Stress relaxation mechanism were investigated on samples of *endo*-DCP-based EPDM differing for the structure of the crosslinkage, i.e., containing carbon-carbon bond, polysulfide or monosulfide linkage. The oxidative cleavage of monosulfide linkage was invoked to explain the results obtained, whereas a physical flow of the chains seems likely in the case of peroxide-cured EPDM.

The oxygen uptake of low-molecular weight DCP-EPDM was examined with the aim of both investigating the use of EPDM as paint films and of testing, in comparison with other kinds of unsaturation, the behavior of cyclopentene double bond under oxidation conditions catalyzed by Co salts (cf. Section II D and VI A).

Much comparative work has been done to study EPDM as general purpose rubber, in particular for tire manufacturing. It is now generally accepted that *endo*-DCP-EPDM shows much poorer behavior than that observed on more recently developed terpolymers, especially in co-vulcanization processes with highly unsaturated elastomers.

Other interesting termonomers studied more recently (Van Schooten and Evelmis, 1965; Cameli et al., 1968; Duck and Cooper 1971) are the methyl derivatives of the superior homolog of DCP, i.e., tricyclo-[6.2.1.0^{2,7}]-4,9-undecadiene (XIX)



or endomethylene-1,2,3,6,8, 8-hexahydronaphthalene (EHN). They can be obtained via Diels-Alder reaction from 2,5-norbornadiene (a product obtainable in good yield (Onischchenko, 1964) from another Diels-Alder condensation between cyclopentadiene and acetylene) and methyl derivatives of butadiene (Sartori et al., 1964). The use of isoprene in this reaction allows one to obtain 4-methyl-derivative of (XIX) (MEHN) which has the cyclohexene double bond hindered by the pres-

ence of the methyl group. On the other side, the allylic hydrogen atoms of the same substituent should improve the behavior of the resulting EPDM during the vulcanization process. Analogously to DCP, EHN and its derivatives exist as *endo* and *exo* isomers, the latter being prevalent (about 85%) in the case of the sample used in one of the paper under consideration (Duck and Cooper, 1971). Furthermore a small amount of the isomer of MEHN containing the double bond in position 5 was also present. When the catalyst used was $\text{VOCl}_3\text{-Et}_3\text{Al}_2\text{Cl}_3$, the MEHN utilization during the polymerization reaction was 95–75% for unsaturation levels ranging between 5–25%. Under the adopted conditions, the terpolymerization rate was nearly independent of termonomer concentration. Polymer branching was minimal.

The curing rate of EPDM containing MEHN is higher than 1,4-HD but lower than ENB-based terpolymers. EPDM's containing MEHN and dimethyl-EHN vulcanize more readily than those containing EHN (Cameli et al., 1968). The reversion reaction is the highest among the EPDM's studied. The behavior in covulcanization processes with SBR is rather poor, even with a high level of MEHN.

10. Acetylenic Hydrocarbons

A unique paper, dealing with the use of acetylenic hydrocarbons in the synthesis of EPDM, describes (Matkovskii et al., 1966) the terpolymerization of acetylene using the system $\text{VOCl}_3\text{-Al (i-Bu)}_3$. Although polymerization runs were carried out with high α -olefin concentrations (pressure up to 3.6 atm), the yield of polymer was poor and MW low. Both the parameters were markedly dependent on the acetylene concentration. The strong interaction of the third monomer with the catalyst centers was proved furthermore by the presence of a low degree of crystallinity in the polymer obtained. However, when the concentration of acetylene in the feed was increased, correspondingly the absorbance of vinylidene and vinyl bonds of the polymer increased. The polymer was soluble in tetraline at 135°C, although colored solutions (black-violet) were obtained. The color has been attributed to the presence of sequences of conjugated double bonds (blocks of acetylene units). The presence in IR region of the band of polyacetylene and the removal of it (and of the color) by reacting the polymer with strong dienophiles (maleic anhydride or tetracyanoethylene), supports the existence of acetylene blocks in the chains. Furthermore, the formation of macro-molecular Diels-Alder adducts was confirmed by IR analysis. The ab-

sence of ESR signals in the polymer and the complete solubility of it, suggests that it does not contain acetylene homopolymer. However, since fractionation data have not been reported, some uncertainty exists on the exact nature of the polymeric material obtained.

Other acetylenic hydrocarbons have been used in EPDM synthesis (Sonnenfeld et al., 1969); however, since they carry an ethylenic unsaturation conjugated with the triple bond, they will be discussed in Section III B 3.

11. Monoolefins with a Strained Ring

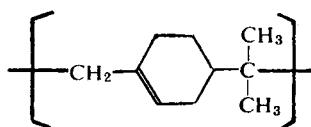
Molecules having a saturated strained ring are known to behave, in some reactions, as olefins (cf. for instance, cyclopropane and its derivatives; Lishanskii et al., 1965). The polymerization of cyclic olefins, through the ring cleavage and by retention of the unsaturation in the chains, is a recent result obtained by using particular coordination catalysts based mainly on tungsten or molybdenum halides (Dall'Asta et al., 1972). These catalyst systems, however, do not give useful results in EPDM synthesis, but can be used to prepare mixtures of polyenic hydrocarbons which have been proposed for synthesizing EPDM (cf. Section III A 2).

In previous sections some examples have been cited for diolefins reacting in the presence of Ziegler-Natta catalysts via ring-cleavage, both in terpolymerization and homopolymerization reactions (cf. Section III A 6); in these cases two double bonds for a repeating unit are present.

This section is concerned with monoolefins containing a strained saturated ring, but despite the elevated number of potential terminomers, only β -pinene has been reported (Magin et al., 1965). This fact is not surprising if one bears in mind that only radical or cationic initiators are able to cleave, for instance, the cyclopropane ring (Takahashi et al., 1964, 1965, 1968) according to the scheme: $n\text{CH}_2=\text{CH}-$

$$\begin{array}{c} \diagup \text{CH}_2 \\ \text{CH} \quad | \\ \diagdown \text{CH}_2 \end{array} \rightarrow (-\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_2-)_n$$
 which, in the case of cationic catalysts, is complicated by cyclized structures. The results obtained are quite similar to those collected by using dipentene (Section III A 4), i.e., the presence of unsaturation has been ascertained by titration with perbenzoic acid, but the polymer was found unable to crosslink.

The expected structure of β -pinene in what was supposed to be EPDM was assumed to be



(XX)

on the basis of homopolymerization (Marvel et al., 1959) and copolymerization (Kennedy, 1969) experiments carried out with cationic initiators. Since in the attempted EPDM there is no direct evidence of the existence of structure (XX) and in the absence of fractionation data, it may be suggested that β -pinene was not randomly present in the polymer obtained. Also, perhaps, the ring cleavage of the terpene derivative might have occurred under the action of adventitious cationic species through uncontrolled reactions which, actually, have also given significant amount of gel.

B. EPTM

Two potentially broad groups of trienes have been explored to find new termonomers; the former includes triolefins containing unconjugated unsaturations, the latter is related to trienes having at least two conjugated double bonds (cf. Table XVII).

The larger amount of work has been carried out on termonomers of the second group, the interest resting on the possibility of producing, with good yield, EPTM's characterized by a statistical distribution of the monomeric units, i.e., of conjugated dienic groups. In fact, in the literature the poisoning effect of conjugated double bonds on terpolymerization catalyst centers is frequently reported (Cesca et al., 1968a, b, 1971a). Furthermore, the perturbing action of conjugated dienic systems on the uniformity of composition and on MWD of the resulting EPDM is known (Capito et al., 1968; Christman and Keim, 1968; Natta et al., 1963; Phung et al., 1967; Samuels and Wirthik, 1967a; Seidov et al., 1966).

Recently, the utilization of several trienes, having two conjugated double bonds, has been attained and the synthesis of EPTM's characterized by unusual properties, since they contain as pendant groups a system of two conjugated double bonds, has been possible (Arrighetti et al., 1971).

1. Linear Nonconjugated Trienes

No paper has been published so far on EPTM's containing a termonomer belonging to this class although 1,4,9-decatriene has been cited in some reviews dealing with ethylene-propylene-based elastomers (Pasquon et al. 1967; Valvassori and Cameli, 1969).

2. Trialkenyl Cycloalkanes

The most studied compound of this class is 1,2,4-trivinylcyclohexane (TVC), a product of thermal isomerization of cyclo-1,5,9-dodecatrienes, existing as *cis-trans-trans*, *trans-trans-trans* and *cis-cis-trans* isomers, which are obtainable from the catalytic trimerization of butadiene (Wilke, 1963). On the basis of IR evidence, collected from EPTM containing TVC, the triolefin enter into polymer chains via vinyl double bond opening, the ring cleavage being excluded.

There are different isomers of TVC which show a marked difference in their reactivity during the terpolymerization reaction with ethylene and propylene. However, the overall utilization of TVC is not high, about 50% of the utilization of the dimer of butadiene DVCB (cf. Section III A 6) and in the range of 1-4 wt % of termonomer. The behavior of TVC-based EPTM in vulcanization has been investigated to a limited extent; however the 300% modulus increases regularly as the triene concentration increases, but the vulcanization rate is lower than the corresponding rate of COD-based EPDM (Natta et al., 1965c).

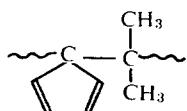
3. Trienes Containing Only Conjugated Unsaturation

Besides true trienes, acetylenic hydrocarbons having a conjugated double bond are also included in this class (cf. Section III A 10). Actually, in an unique paper, fulvene and acetylene derivatives have been described as termonomers (Sonnenfeld et al., 1969). EPTM's containing vinylacetylene (VA) or isopropenylacetylene (IPA) show, by IR analysis, the absence of triple bond and the presence of pendent vinyl and branched internal double bonds.

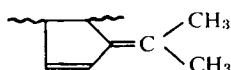
The presence of conjugated double bonds is shown by an absorption maximum in the UV spectra near 220 m μ . Therefore, the triple bond is the preferred center of reactivity with Ziegler-Natta catalyst, even though the yield data are quite poor owing to the strong poisoning effect of the acetylenic hydrogen. However, EPTM's containing VA or IPA, probably in the range 0.1-0.2 mole/kg (iodometric determination of

this kind of unsaturation is affected by anomalous and extended side reactions) give vulcanizates with fair properties. This result suggests a prevalent random incorporation of unsaturation. A similar result has been obtained from EPTM-based on 6,6-dimethylfulvene, a triene obtainable with good yield from the condensation of acetone with cyclopentadiene in the presence of basic agents (Freiesleben, 1963).

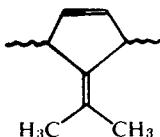
Some uncertainty exists on the type of termonomer unit of this EPTM; the following possibilities are to be taken into account:



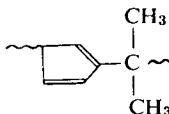
(XXI)



(XXII)



(XXIII)



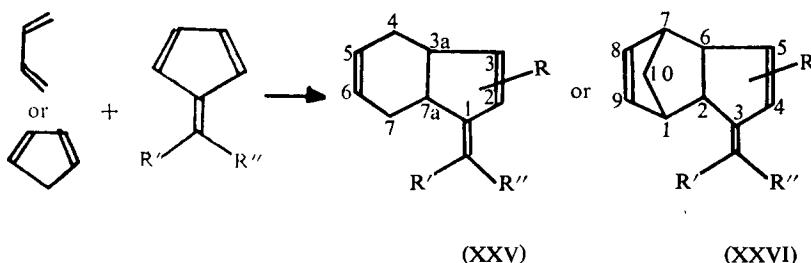
(XXIV)

On the basis of some IR bands, the structure (XXI) is considered prevalent, but also the repeating unit (XXII) is present; less probable the 1,4-opening (XXIII, XXIV). IR and UV spectra agree with the presence of conjugated double bonds.

4. Trienes Containing a Conjugated Diene System with Transoid Conformation

A thorough investigation has been devoted to several termonomers of this class (Arrighetti et al., 1971). The separation of the double bond involved in the terpolymerization reaction from the curing site (conjugated diene system) was projected in order to minimize the interfering effects of the dienic system with the active centers during the polymerization stage.

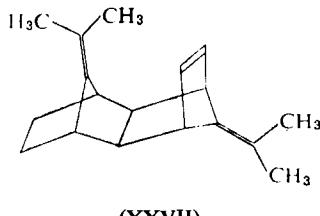
An obliged transoid conjugation of two double bonds can be accomplished by reacting a diene with a fulvene derivative. Diels-Alder adducts of type (XXV) or (XXVI) account for the behavior as dienophile shown by the fulvene derivative, because only with the strongest dienophile reacts as a diene (Alder and Ruhrmann, 1950).



(where $R' = R'' = \text{alkyl groups}; R = \text{H or alkyl group}$)

Good yields have been reported for the synthesis of 2-isopropylidene-bicyclo-[4.3.0.0¹⁵]-3,7-nonadiene (1-isopropylidene-3a,4,7,7a-tetrahydroindene, abbreviated as IPTHI), i.e., adduct (XXV) where $R = \text{H}$ and $R' = R'' = \text{CH}_3$ as the result of systematic investigations (Cesca et al., 1967). Several homologs of IPTHI have been prepared by reacting the appropriate dienophile with butadiene or its homologs. In the case of cyclopentadiene adducts of type (XXVI), the simplest derivative, 3-isopropylidene-tricyclo-[5.2.1.0^{2,6}]-4,8-decadiene (also called 1-isopropylidene dicyclopentadiene, viz., IPDCP) results.

Incidentally, it can be recalled that ethylene also reacts with 6,6-dimethyl fulvene, under severe conditions, to yield several adducts among which three products are prevalent. On the basis of mass spectrometry fragmentation data, they contain two fulvene and one ethylene molecule (two isomers) and two ethylene and one fulvene molecule, but the definitive structures have not been ascertained. However, only the former adduct (probably structure XXVII) having three double bonds for every molecule (one of which being norbornenic), can be a potential termonomer, but EPTM based on it has not yet been described.



On the contrary much work has been made on IPTHI-based EPTM, using different catalysts and different experimental conditions (Cesca et al., 1968 a,b,c,d, 1970a).

Preliminarily the random insertion of the triene into chains has been shown by fractionation and successive fraction analysis. The conjugated diene system is not attacked by Ziegler-Natta catalyst; in fact, when the cyclohexene double bond of IPTHI is hindered by the presence of one or two methyl groups, or when the cyclohexene ring is replaced by a benzene ring, no unsaturation is present in the resulting polymer. Furthermore, homopolymerization attempts with IPTHI and several Ziegler-Natta catalysts were always unsuccessful. Only cationic initiators are able to give homopolymer of IPTHI, with high yields, by attack of the dienic system (Cesca et al., 1970b).

Spectroscopic evidences (UV, IR, NMR) collected on EPTM containing IPTHI show the selective reactivity of the isolated double bond of the triene (Cesca et al., 1970a).

The concentration of IPTHI in the feed affects markedly the overall polymerization rate which is, in the case of $\text{VCl}_4\text{-Et}_2\text{AlCl}$ system, nearly inversely proportional to the termonomer concentration.

The content of unsaturation (within the range of 1–6 wt %) increases linearly with the concentration of IPTHI in the feed, whatever is the catalyst used. The content of termonomer was determined iodometrically (absorption of IBr) adopting the reference of radiochemical standards obtained with ^{14}C -labeled IPTHI (Fig. 22).

The interfering influence of IPTHI with active centers shows peculiarities depending on the type of catalyst used. The principal evidences are:

1. The lack of linearity in the plot of polymer yield vs. catalyst concentration (system $\text{VCl}_4\text{-AlEt}_2\text{Cl}$) at high IPTHI concentration. On the contrary, the system $\text{VAcac}_3\text{-Et}_2\text{AlCl}$ shows a first order dependence of the overall polymerization rate on VAcac_3 concentration. This dependence is only partly valid for the system $\text{VOCl}_3\text{-Et}_3\text{Al}_2\text{Cl}_3$.

2. The increase of yield and the modification of overall kinetics when monodentate Lewis bases are added to VCl_4 -based catalyst, whereas bidentate Lewis bases yield negligible amounts of EPTM. The positive effect is maximum when the molar ratio Al/base is 2 and is independent of Al/V molar ratio. This influence has not been observed with the system $\text{VAcac}_3\text{-AlEt}_2\text{Cl}$, whereas in the case of VOCl_3 -based system a negative influence on the yield and IPTHI utilization is exerted by Lewis bases.

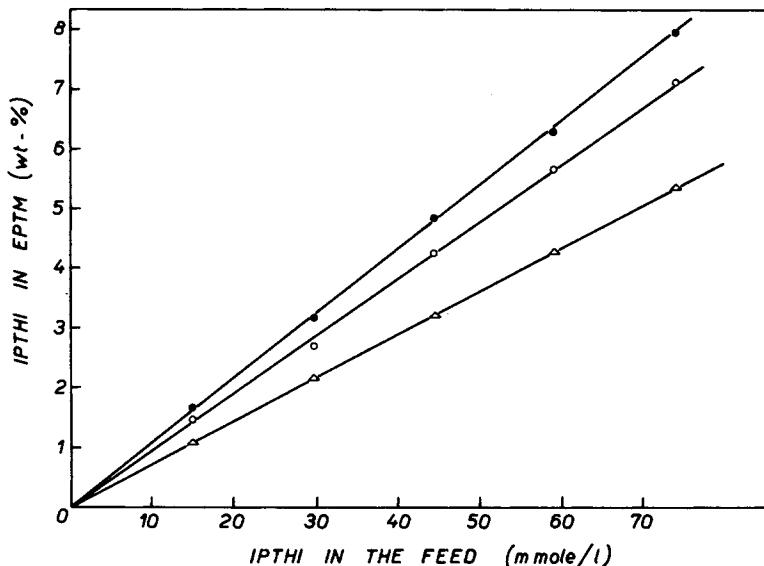


Fig. 22. Dependence of the content of IPTHI (cf. Section III B 4) in the polymer on the initial concentration of the triene in the feed: (●) = ICl total titer; (○) = ICl corrected titer; (△) radiochemical dosage. From Cesca et al., 1968b with permission of the Editrice di Chimica, S.p.A., Milan.

3. The increase of ethylene content in EPTM when the concentration of IPTHI in the feed increases. On the contrary, the systems based on VOCl_3 or VAcac_3 give EPTM with constant levels of ethylene.

4. The decrease of MW and of polydispersity index (\bar{M}_w/\bar{M}_n) when the termonomer concentration increases (Table V). In the case of $\text{VCl}_4\text{-Et}_2\text{AlCl}$ system the plot of $1/[\eta]$ vs. the square root of IPTHI concentration is linear, whereas for the system $\text{VAcac}_3\text{-AlEt}_2\text{Cl}$ linear correlations were found between $1/\text{MW}$ and IPTHI concentration at different polymerization temperatures.

5. The insensitivity of EPTM MW to the concentration of the catalyst components ($\text{VCl}_4\text{-Et}_2\text{AlCl}$), whereas the overall polymerization rate shows order 0.5 with respect to the concentration of Et_2AlCl for molar ratios $\text{Al}/\text{V} < 10$. For the system $\text{VAcac}_3\text{-Et}_2\text{AlCl}$ a zero order was found for the dependence of the overall polymerization rate on the concentration of Al derivative. Furthermore, MW is dependent on Et_2AlCl , but independent of VAcac_3 concentration.

6. The influence of the polymerization temperature; higher yield and

MW, but lower termonomer utilization, are observed at lower temperatures in the range 30 to -30°C . However, the system VAcac₃-Et₂AlCl shows a maximum efficiency between 0° and -10° .

7. MW's are continuously increasing with the polymerization time and with the concentration of α -olefins, provided the concentration of IPTHI is constant (Fig. 23).

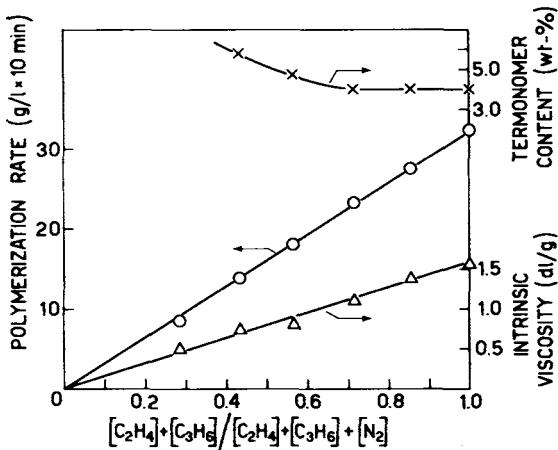


Fig. 23. Influence of the gaseous monomers concentration in $\text{C}_2\text{H}_4\text{-C}_3\text{H}_6\text{-IPTHI}$ terpolymerization. Initial concentration of IPTHI = 29.5 mmole/l; catalyst VAcac₃-Et₂AlCl. Reproduced from Cesca et al., 1968c with the permission of the Editrice di Chimica, S.p.A., Milan.

8. The overall polymerization rate is first order with respect to α -olefins concentration when their molar ratio and IPTHI concentration are constant.

9. Whatever the catalyst system used, a sharp decrease of the catalytic activity, measured by the overall kinetic curves, is exerted by IPTHI concentration (cf. Figs. 4 and 24). The systems based on vanadium halides are more sensitive than vanadium organic salts (e.g., acetylacetones or alcoholates) to the presence of termonomer.

In attempting to describe quantitatively the results observed with the system VCl₄-Et₂AlCl used at -20°C , a simplified kinetic treatment was proposed (Cesca et al., 1968c) on the basis of two reactions specific of IPTHI, namely: (a) chain termination activity (inhibition), according to which two end growing chains are stopped by one IPTHI molecule; (b) chain transfer efficiency.

To develop the proposed scheme several assumptions are necessary

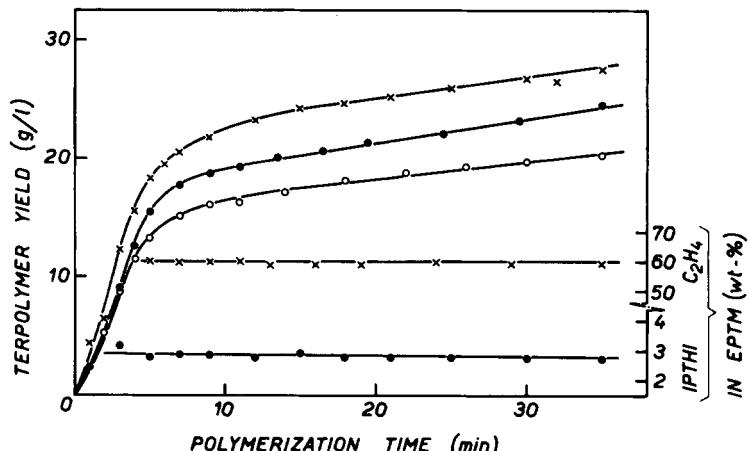


Fig. 24. Kinetic curves for $C_2H_4-C_3H_6$ -IPTHI terpolymerization and main properties of the resulting EPTM. Unaged catalyst: $VAcac_3-Et_2AlCl$ (1:6); $T = 0^\circ C$; solvent = *n*-heptane; $VAcac_3 = 0.875$ mmole/l; C_3H_6/C_2H_4 molar ratio = 2.5 in the gaseous feed. IPTHI: (x) = 13.3 mmole/l; (●) = 17.7 mmole/l; (○) = 22.2 mmole/l. Reproduced from Cesca et al., 1968b with the permission of the Editrice di Chimica, S.p.A., Milan.

to simplify the complicated system of terpolymerization. The more relevant are: the knowledge of the concentration of active catalytic species; the qualitative changing of active centers with time; the extention of relationships valid for α -olefin homopolymerization to terpolymerization. In part these difficulties were overcome by making reference to very short polymerization times. Within these limits the kinetic scheme was checked by the application of the relationship describing \overline{DP}_n as function of the polymerization time; both the methods gave values of the same order of magnitude for the rate constants assumed to describe, in first approximation, the terpolymerization process:

$$K_p \text{ (overall propagation reaction)} = 0.7-1.9 \times 10^3 M^{-1} \text{ min}^{-1}$$

$$K_t \text{ (inhibition reaction)} = 2.5-7.8 M^{-1} \text{ min}^{-1}$$

$$K_t \text{ (transfer reaction)} = 9.1-24.7 M^{-1} \text{ min}^{-1}$$

In the presence of anisole the system VCl_4-Et_2AlCl shows the same K_p value, whereas K_t is about 50% of the value observed in the absence of the Lewis base.

The dependence found for $1/MW$ on IPTHI concentration in the case of the system $VAcac_3-Et_2AlCl$, indicates that one end chain growing is terminated by one molecule of IPTHI. This result, associated with the

fact that the VAcac₃-based system is not sensitive to Lewis bases, suggests that this system is more stable than the VCl₄ one toward molecules (e.g., conjugated dienes) capable of interacting with the catalyst centers. The ratio $(K_t + K_t)K_p$ is an index of the interference of termonomer in the propagation reaction and its values have been calculated, respectively, for the systems VCl₄-Et₂AlCl, VAcac₃-Et₂AlCl, and VOCl₃-Et₃Al₂Cl₃, as: 1.7×10^{-2} (at -20°C); 1.2×10^{-2} (at 0°C), and 3.2×10^{-3} (at 20°C).

The superior homolog of IPTHI, having a methyl group in position 2 or 3 in formula (XXV) (actually it is obtained as a mixture of isomers), shows an interesting behavior both during terpolymerization and vulcanization processes. In fact, under comparable conditions its utilization is higher than IPTHI one, whereas the interference with the catalyst centers is lower (Fig. 25); furthermore, EPTM containing methyl-IPTHI has an elevated vulcanization rate (Ghetti et al., 1969), superior for instance to the curing rate of EPDM containing the same amount of ENB (cf. Table XX).

It is interesting to observe in Figure 26 that EPTM based on methyl IPTHI shows a good degree of covulcanization with SBR rubber, in particular in the critical region EPTM/SBR = 75/25.

The terpolymerization of IPDCP with ethylene and propylene has been investigated by using the system VAc₃-Et₂AlCl (Cesca et al.,

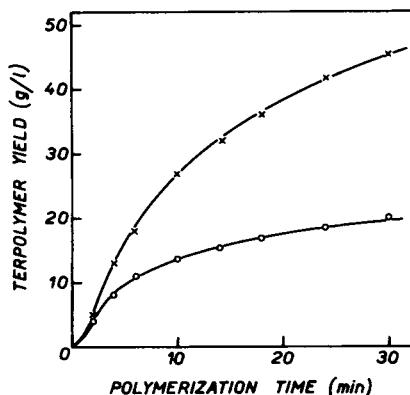


Fig. 25. Dependence of the yield of EPTM's on the polymerization time: (○) = IPTHI, (×) = 2 and 3-methyl-IPTHI. Unaged catalyst system VAcac₃-Et AlCl (1:6); T = 0°C; solvent = toluene; VAcac₃ = 0.25 mmole/l; C₃H₆/C₂H₄ = 2.0 in the gaseous stream; initial concentration of the triene in the feed = 7.74 mmole/l.

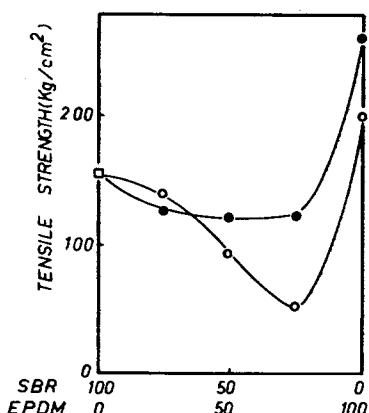


Fig. 26. Covulcanization of methyl-IPTHI-based EPTM (0.46 mole/kg of triene) (○) with SBR (reference to ENB-EPDM (○) containing 0.63 mole/kg of diene). Recipe: polymer = 100; HAF = 50; Circosol-4240 = 5; ZnO = 5; TMTD = 1.5; S = 1.5; MBT = 0.5.

1971b). The inhibition of catalyst centers by the triene was still observed, however, IPDPCP displayed an utilization (95% for ca. 5 wt % of triene) about fivefold higher than IPTHI, thus EPTM having a relatively high content of unsaturation (IPDPCP ≈ 15 wt %) can be obtained with relatively low concentration of triene in the feed. Also with cationic initiators, which give the selective 1,4-opening of the conjugated double bonds system of the triene, IPDPCP was found more reactive than IPTHI by means of copolymerization experiments (Cesca et al., 1971a). Therefore, the enhanced reactivity of IPDPCP appears to be a peculiar characteristic of the molecule, present both in the isolated double bond and also in the conjugated dienic system.

The selective reactivity of norbornene double bond of IPDPCP toward terpolymerization catalysts was shown by using 8,9-dihydro-IPDPCP as the termonomer (Cesca et al., 1945a); in these experiments unsaturation was never observed in the resulting polymer. On the other hand, the random distribution of IPDPCP in the EPTM chains was proved by fractionation analysis (Table XXII).

The dependence of termonomer concentration in EPTM on the feed concentration is linear up to 12 wt % of IPDPCP; the dosage has been carried out with ¹⁴C-tagged triene (Figs. 27, 28) and via UV measure-

TABLE XXII
Fractionation^a of C₂H₄-C₃H₆-IPDCP Terpolymer^{b,c}

Fraction	Weight (%)	[η] (dl/g) ^d	C ₂ H ₄ (wt %)	IPDCP (wt %) ^f
1	8.2	3.62	63	4.7
2	8.3	3.46	63	5.3
3	15.6	3.20	62	5.0
4	15.4	2.90	64	5.3
5	12.2	2.91	63	5.2
6	13.2	2.80	62	4.9
7	7.5	2.82	58	4.7
8	11.8	1.84	58	4.4
9	7.8	0.61	n.d. ^e	n.d. ^e
Initial EPTM	100.0	2.92	62	4.90

^aBy precipitation.

^bPrepared with catalyst VAcac₃-Et₂AlCl in toluene at 0°C.

^cReproduced by permission from Cesca et al., 1971b.

^dFrom toluene, at 30°C.

^eNot determined.

^fBy UV measurements.

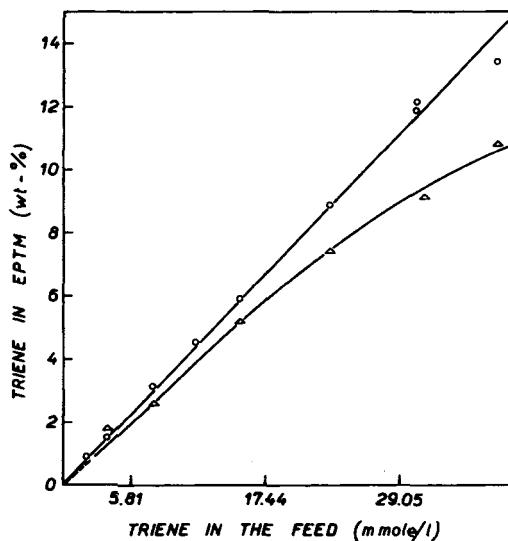


Fig. 27. Dependence of the content of IPDCP (cf. Section III B 4) in EPTM on the total concentration in the feed: (○) chemical method; (△) spectroscopic (UV) method.

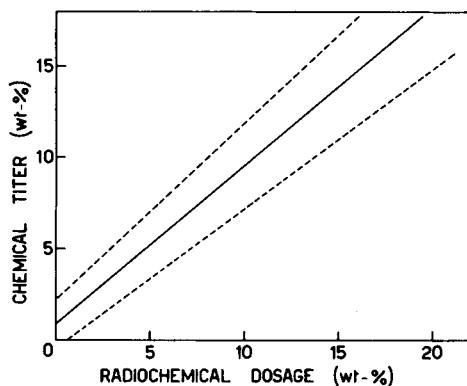


Fig. 28. Correlation between radiochemical and chemical dosage (IBr absorption) of IPDCP in the corresponding EPTM with 95% confidence limits. Reproduced by permission from Cesca et al., 1971b.

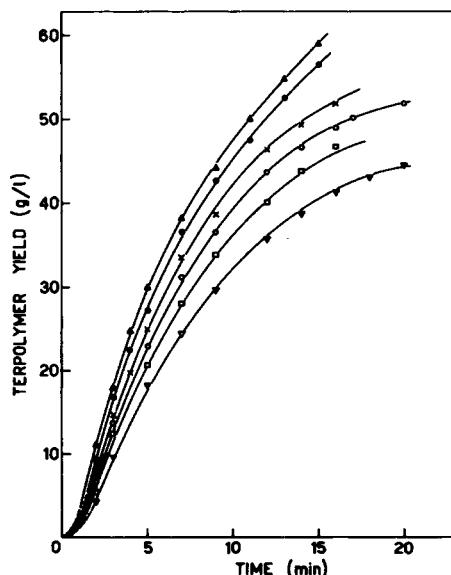


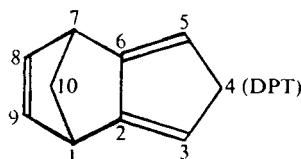
Fig. 29. Influence of the concentration of IPDCP on the overall terpolymerization kinetics. Termonomer concentration: (\blacktriangle) = 0.335 g/l; (\bullet) = 0.671 g/l; (\times) = 1.342 g/l; (\circ) = 2.681 g/l; (\square) = 4.020 g/l; (\triangledown) = 5.360 g/l. VAcac₃ = 0.174 g/l; other conditions as in Fig. 25. Reproduced by permission from Cesca et al., 1971b.

ments. At more elevated concentration of IPDCP (> 5 wt %) the UV dosage is lower than radiochemical one and this difference could mean that some branching starts from the diene system, since the polymer is completely soluble.

The influence of IPDCP concentration on the kinetic curves (Fig. 29 and cf. Fig. 4) and on MW, indicates that chain-breaking processes (termination and, perhaps, transfer to monomer) are operating during the terpolymerization stage. On the other hand, the absence of chain transfer reactions to the catalyst components and the fact that the increase of MW and the change of EPTM composition with time are limited to a shorter polymerization period with respect to corresponding EPM, suggest that IPDCP exerts a partial stabilizing effect on the catalyst centers. In the case of IPDCP the presence of a methyl group on the dienic system (XXVI where $R = \text{CH}_3$) furnishes a triene which shows nearly the same interference with active species as the parent molecule (XXVI, $R = \text{H}$).

5. Trienes Containing a Conjugated Diene System with Cisoid Conformation

The presence of two conjugated double bonds in a ring realizes an obliged cisoid conformation of the diene system. Therefore, taking into account the relative unstability of cyclobutadiene ring, the most simple termonomer of this class having also the favorable norbornenic unsaturation, is dehydro-iso-dicyclopentadiene, i.e., tricyclo-[5.2.1.0^{2,6}]-2,5,8-decatriene or dicyclopentatriene (DPT):



which is obtained from DCP via hydroxylation with SeO_2 and successive dehydration (Alder and Floch, 1954 and 1956). The reactivity of bis-allylic hydrogens of DPT allows the metallation of the triene and the introduction of alkyl groups on the cyclopentadiene ring. However, independently of the alkylation reaction conditions a mixture of mono-, di- and trialkyl-derivatives of DPT was always obtained. The result can be explained (Cesca et al., 1974a) by assuming the existence of thermodynamic equilibria between the hydrogen atoms of the alkyl cyclo-

tadiene derivatives, both in the presence (Rybinskaya and Korneva, 1971) and in the absence (Mironov et al., 1963) of ionic species. The alkylation of DPT is useful to reduce the reactivity of the diene system toward terpolymerization catalyst. However, soluble EPTM containing up to 2 wt % of DPT (UV dosage, Fig. 30, and radiochemical titer, using ^3H -labeled DPT) can be obtained with typical vanadium-based catalysts containing also a weak Lewis base.

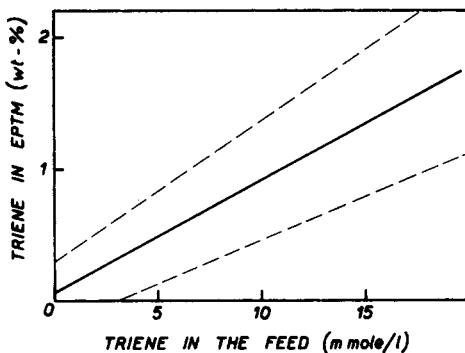


Fig. 30. Concentration of DPT (cf. Section III B 5) in the corresponding EPTM, determined by UV spectroscopy at $245 \text{ m}\mu$, vs. its concentration in the feed with 95% confidence limits.

Despite the low levels of unsaturation introduced in DPT-based EPTM, very high curing rates and also excellent behavior in covulcanization experiments with *cis*-1,4-polyisoprene have been observed. When methyl or dimethyl derivatives of DPT are used (they are obtained as a mixture of positional isomers) instead of the parent triene, higher unsaturation levels can be introduced in the resulting EPTM, up to 40% of utilization for levels of termonomer near to 2 wt %. At the same time the terpolymerization kinetics are perturbed in somewhat higher degree with respect to DPT (Fig. 31).

Despite the high reactivity shown by DPT, even toward electrophilic species, it enters randomly into EPTM chains, as it has been proved by fractionation experiments (Table XXIII). Moreover, a linear relationship was found between DPT concentration in the feed and in the polymer (cf. Fig. 30).

Another series of termonomers, belonging to this class, has been obtained (Cesca et al., 1974b) by reacting 2-norbornene-5-*endo*-methylene

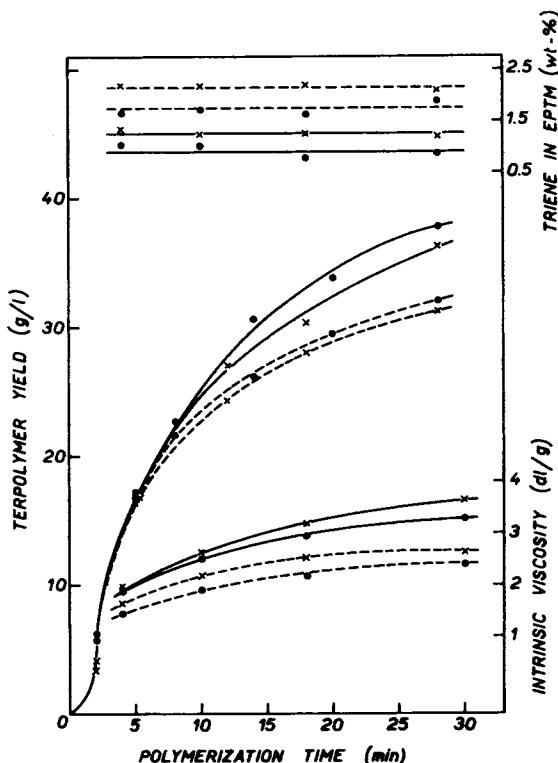


Fig. 31. Influence of the polymerization time on the yield and some main properties of EPTM's containing DPT (full line) and its methyl derivatives (broken line). Conditions: unaged catalyst, $\text{VAcac}_3 = 0.15 \text{ mmole/l}$ (●) or 0.18 mmole/l (×); $\text{Et}_2\text{AlCl}/\text{VAcac}_3 = 8.0$; $T = 0^\circ\text{C}$; solvent = toluene; $\text{C}_3\text{H}_6/\text{C}_2\text{H}_4 = 2.0$ in the gaseous phase; DPT and methyl derivatives of DPT = 10.0 mmole/l (●) or 15.0 mmole/l (×).

halide (XXVIII) with the alkali metal derivative of cyclopentadiene (XXIX) or its superior homologs:

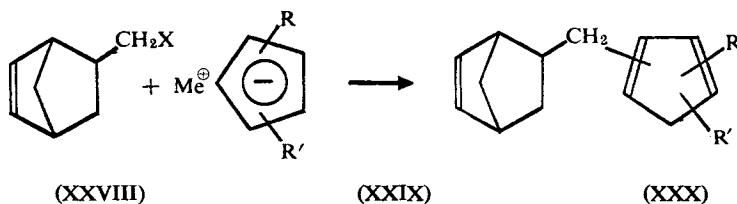
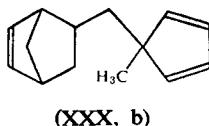


TABLE XXIII
Fractionation^a of DPT-Based EPTM^{b,c}

Fraction	Weight(%)	$[\eta]$ (dl/g) ^c	$\bar{M}_{osm} \times 10^{-5}$	DPT (wt %) ^d
1	7.4	2.31	1.30	1.2
2	9.0	2.20	1.29	1.1
3	6.9	2.13	1.21	1.2
4	10.8	1.92	1.18	1.1
5	8.4	2.22	1.11	n.d.
6	8.4	2.19	1.06	1.0
7	8.2	1.44	0.57	1.1
8	10.8	0.91	0.53	1.3
9	10.6	0.32	n.d.	n.d.
10	12.1	n.d.	n.d.	n.d.
Initial EPTM	100.0	1.65	n.d.	1.3

^aBy precipitation.^bPrepared with VAcac₃-Et₂AlCl catalyst system in toluene at °C.^cReproduced from Cesca et al., 1974a with permission. Hüthing and Wepf, Basel, Switzerland.^dFrom toluene at 30°C.^eBy UV measurements.

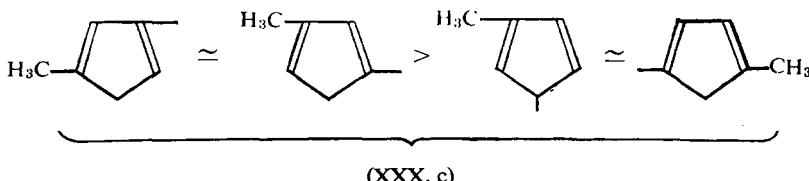
where R, R' = H or CH₃, Me = Na or K, X = Cl or Br. The resulting trienes are cyclopentadienyl-5-*endo*-norborn-2-enyl-methane derivatives (CNM). For the same reasons reported above in the case of DPT, the more interesting trienes having the general formula (XXX) possess at least one methyl group on the cyclopentadiene ring. When R=CH₃ and R'=H the triene (XXX, a), or MCNM, is obtained as a mixture of at least five isomers containing the substituting groups in different positions of the cyclopentadiene ring. The isomer containing both the substituents on the methylene group of the cyclopentadiene ring (XXX, b) can be separated by distillation, whereas some other isomer can be obtained through preparative gas chromatography.



The isomer (XXX, b) is present for 10–15% of the total mixture, depending on the preparation conditions.

However the components (XXX, c) present in more elevated concentration in the reaction mixture (ca. 70–80%) as evidenced by GC analyses, are made up by more than one isomer which carry the substituents

mainly on the double bonds of the cyclopentadiene ring, in agreement with the data obtained by Mironov et al. for dimethylcyclopentadiene (Mironov et al., 1962, 1963; Rybinskaya and Korneva, 1971). The more probable isomer structures (XXX, c), on the basis of spectroscopic investigations, are in the order:



Some vanadium-based catalysts have been used in synthesizing EPTM based on (XXX, a) under constant conditions (Fig. 32) for comparative purposes which, of course, are not the best conditions for every catalyst system.

The use of compounds (XXX, a) labeled with ³H, allows the observance of a linear dependence of the unsaturation in EPTM on its con-

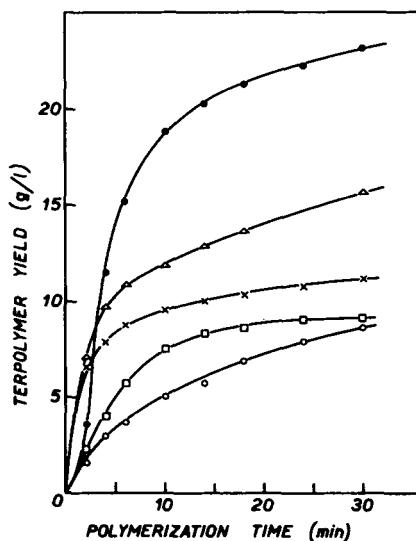


Fig. 32. Yield-time curves with different catalyst systems for terpolymerization based on triene (XXX, a) (cf. Section III B 5). Conditions: vanadium derivatives = 0.25 mmole/l; triene = 7.74 mmole/l; (●) = VAcac₃-Et₂AlCl (1:5); (Δ) = VCl₄-Et₂AlCl-anisole (1:5:2.5); (×) = VCl₄-(iBu)₈ Al(1:5); (□) = VOCl₃-Et₂AlCl (1:10); (○) = VO(O-n-Bn)₃-Et₂AlCl (1:10). Other conditions as in Figure 31.

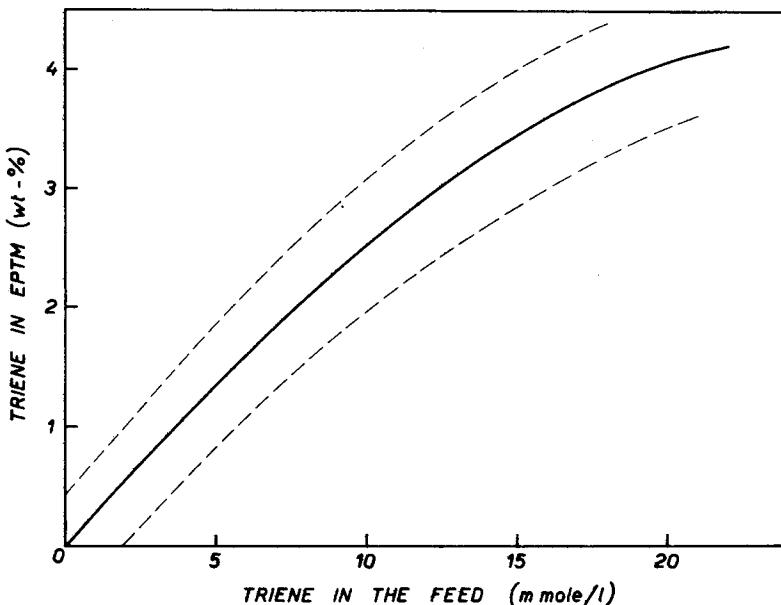


Fig. 33. Concentration of (XXX, a) in the corresponding EPTM (radiochemical dosage) vs. its concentration in the feed with 95% confidence limits. Catalyst system $\text{VAcac}_3\text{-Et}_2\text{AlCl}$ used in toluene at 0°C . Reproduced from Cesca et al., 1974b with permission.

centration in the feed (Fig. 33), for low levels of triene. Furthermore, excellent agreement has been found between UV and radiochemical dosage of unsaturation (Fig. 34). Fractionation analysis proved a random distribution of the triene in the chains (Table XXIV).

The selective reactivity through norbornene unsaturation of compounds (XXX, a) in typical terpolymerization runs, has been checked by using the norbornene-dihydro-derivative, i.e., methylcyclopentadienyl-2-*endo*-norbornanyl-methane, as termonomer. The polymers so obtained were found without any unsaturation and unable to vulcanize.

A marked difference of reactivity was found between (XXX, a) and (XXX, b), the latter yielding an utilization which is two times higher than the former, whereas the interference reactions with the catalyst have the opposite trend (Fig. 35). Therefore the behavior of (XXX, a) is averaged by the contribution of single isomers (XXX, c); these isomers are more sensitive to reacting with catalyst species and are less prone to enter EPTM chains.

Undoubtedly, the behavior of termonomers containing the cyclopenta-

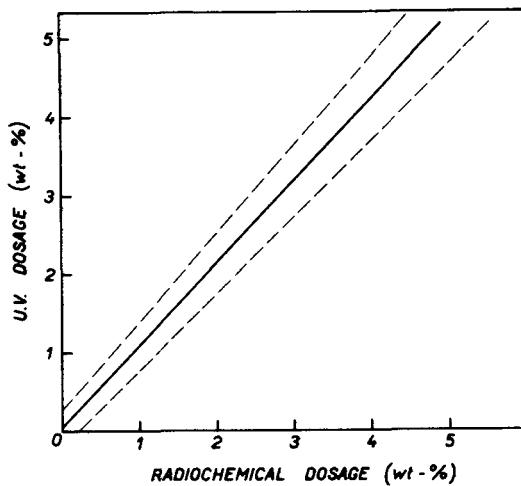


Fig. 34. Relationship between UV and radiochemical dosage of (XXX, a) in EPTM with 95% confidence limits. Reproduced with permission from Cesca et al., 1974b.

TABLE XXIV
Fractionation^a of an EPTM^b Containing the Triene (XXX, a)^e

Fraction	Weight (%)	$[\eta]$ (dl/g) ^c	C ₂ H ₄ (wt %)	(XXX, a) (wt %) ^d
1	2.23	3.92	n.d.	1.9
2	7.40	3.18	64	2.0
3	10.78	3.70	66	1.8
4	6.67	3.56	67	1.8
5	10.25	3.38	65	2.0
6	10.65	2.95	65	2.0
7	17.63	2.57	65.5	2.0
8	10.38	2.50	63	2.0
9	16.67	2.12	66	2.0
10	7.97	1.55	61	1.8
Initial EPTM	100	2.81	63	2.1

^aBy precipitation.

^bCatalyst system: VAcac₃-Et₂AlCl in toluene at 0°C.

^cFrom toluene.

^dBy UV measurements.

^eReproduced with permission from Cesca et al., 1974b.

diene ring is markedly influenced by the presence of bis-allylic hydrogens of the ring, whose enhanced reactivity is often invoked in ionic and radical reactions (Baird, 1971; Kennedy, 1972).

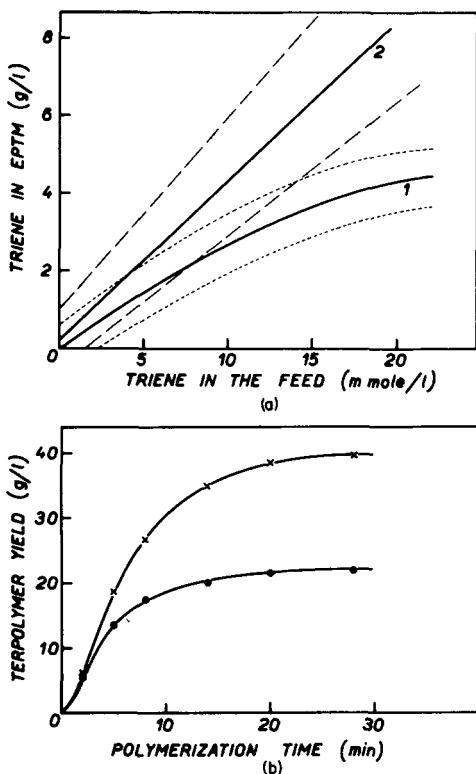


Fig. 35. (a) Relationships between the concentration of triene (XXX, a) = (1) or (XXX, b) = (2) in EPTM (UV dosage) and their concentration in the feed with 95% confidence limits. (b) Yield-time curves (b) for the EPTM's based on (XXX, a) = (●) or (XXX, b) = (×). Catalyst system: $\text{VAcac}_3\text{-Et}_2\text{AlCl}$ in toluene at 0°C ; triene concentration 7.74 mmole/l.

However, as a matter of fact, the utilization of (XXX, a), when the system $\text{VAcac}_3\text{-Et}_2\text{AlCl}$ is used at $-10^\circ/0^\circ\text{C}$, ranges between 35–65%, depending on the experimental conditions adopted and for levels of triene ranging between 0.8–3.5 wt %.

The most interesting result observed with EPTM's containing a cyclopentadienyl ring as pendant group, is their ability to covulcanize with highly unsaturated elastomers (Figs. 36, 37, and 38), also when the content of unsaturation is about five or tenfold lower than the one of typical EPDM used for the same purpose (cf. Section III B 7). As a con-

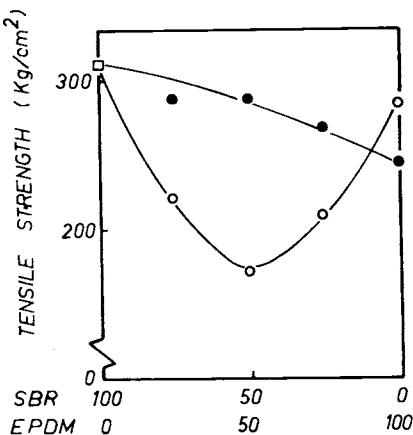


Fig. 36. Covulcanization of EPTM based on (XXX, a) (●) (0.32 mole/kg of triene) with SBR (reference to ENB-EPTM (○) of Fig. 26). Recipe as in Figure 26, except S = 1.7 and CBS (*N*-cyclohexyl-2-benzothiazole sulphenamide) = 1.

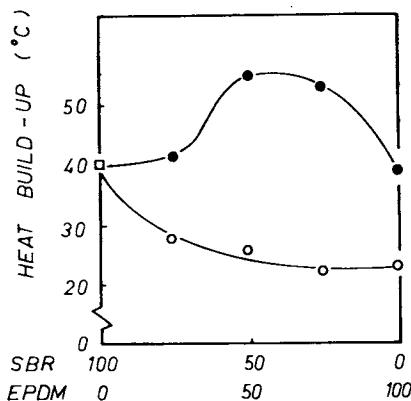


Fig. 37. Heat build-up of covulcanizates based on SBR and (XXX, a)-EPTM (○) or ENB-EPDM (●). Starting materials and recipe as in Figure 36.

sequence some better properties of the resulting elastomer (for instance, lower T_g , better aging properties of vulcanizate, better behavior of vulcanizate at high temperatures, etc.) and some advantages in the terpolymerization process can be foreseen and, actually, have been found, since significant low quantities of termonomer are involved.

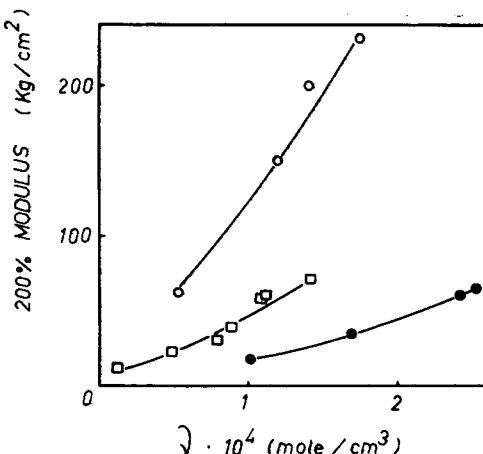
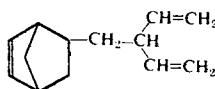


Fig. 38. 200% Modulus vs. network chain density for EPTM (○), EPDM (□), and SBR (●) of Figure 36.

The particular reactivity of cyclopentadienyl ring cited above, is responsible for the interesting properties shown by EPTM's containing DPT or CNM derivatives. In fact 5,6-dimethylene-2-norbornene (XXXI) or 5-(2-vinyl-3-butenyl)-2-norbornene (XXXII), which have some structural features common to DPT and to CNM, do not give to the corresponding EPTM's the noticeable properties observed in EPTM's containing the cyclopentadienyl ring as pendant group.



(XXXI)

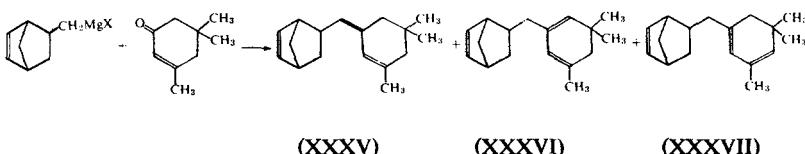
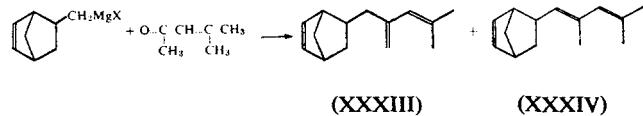


(XXXII)

6. Trienes Containing a Conjugated Diene System without Unique Conformation

In this class are included trienes having the conjugated diene system in a chain or, in part, even in a ring. In the first case a cisoid-transoid equilibrium exists, and also in the second case the two double bonds cannot be considered in an obliged situation (transoid or cisoid) because, actually, a mixture of isomers exists. Examples of these situations are the trienes (XXXIII-XXXIV) and (XXXV-XXVII) obtainable by

reacting the Grignard derivative of 5-halomethyl-2-norbornene with unsaturated ketones, e.g., the dimer (mesityl oxide) or the trimer of acetone (isophorone), and successive dehydration:



Recently, an easy preparation of the parent compound of (XXXIV), i.e., 5-butadienyl-2-norbornene (BNB), has been reported starting from 2,5-norbornadiene and butadiene (Takahashi and Inukai, 1970; Carbonaro et al., 1971), but the reaction furnishes an irrelevant yield with superior homologs of butadiene. However, BNB is able to enter into EPTM chains, but with low utilization and elevated consumption of catalyst. In addition, the butadienyl cure site reacts slowly and incompletely during the vulcanization process. Similar results have been observed with linear trienes containing a butadienyl tail as, for instance, 1,3,7-octatriene or 3-methyl-1,4,6-heptatriene, both obtainable from dimerization of butadiene (Otsuka et al., 1963; Takabashi et al., 1967) as pure products. IR analysis indicates that both the trienes have a prevalent transoid conformation. Anyway, terpolymerization experiments have evidenced that the polymer obtained contains low levels of unsaturation, even when elevated concentration of triene is present in the feed; frequently a low MW polymer is obtained under such circumstances.

On the contrary compounds (XXXIII-XXXIV) and (XXXV-XXXVII), obtainable as equimolar mixture of single components, have been found highly efficient in terpolymerization process (Figs. 39, 40), the utilization being between 40-65% for levels of termonomer (XXXIII, XXXIV) ranging between 5-15 wt % (UV titration). Fractionation data (Table XXV) have also demonstrated the statistical distribution of monomeric units in EPTM containing (XXXIII-XXXIV)

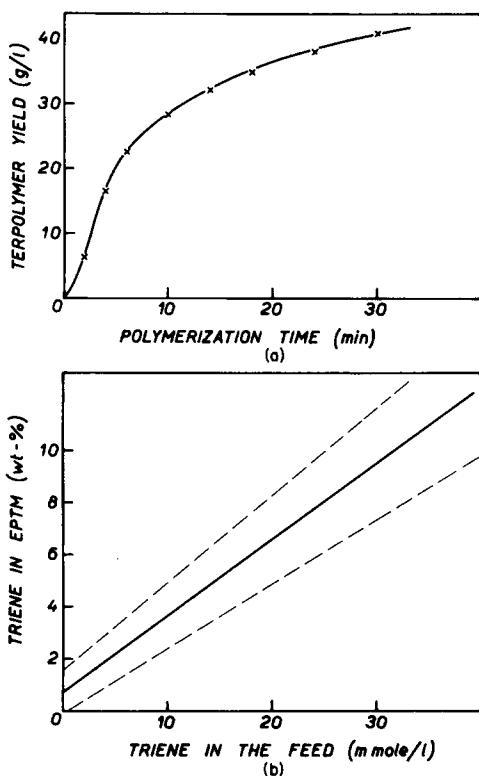


Fig. 39. Yield time curve (triene concentration = 7.74 mmole/l.) (a) and relationship between the concentration of termonomer in EPTM and in the feed (b) obtained for the trienes (XXXIII-XXXIV) (cf. Section III B 6) under the conditions reported in Figure 25.

For the mixture of isomers (XXXV-XXXVII) the utilization is (UV dosage, Fig. 40) between 40 and 75% when the content of termonomer is in the range of 4-15 wt % and the polymer is obtained under mild conditions (total pressure of monomers less than 1 atm). Only at high levels of unsaturation does some gelled material appear during the terpolymerization stage. However, the behavior under normal terpolymerization conditions is excellent. Once again, the analysis of the fractions obtained from fractionation experiments (Table XXVI) indicates that unsaturations are distributed at random.

The results reported above suggest that the butadienyl residue, when it

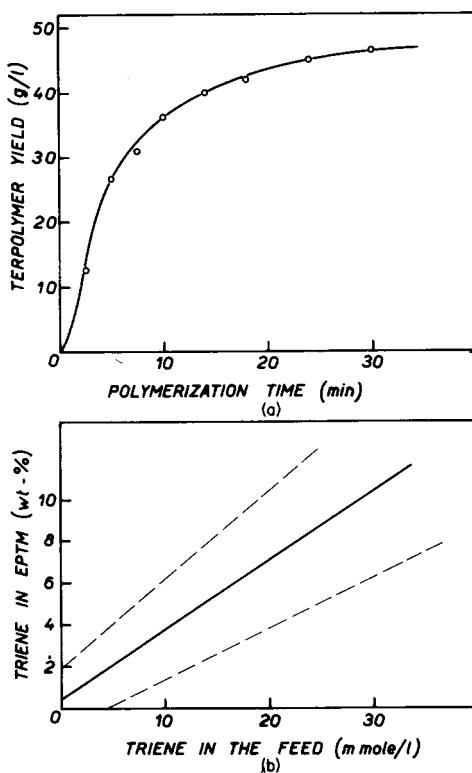


Fig. 40. Yield-time curve (triene concentration = 7.74 mmole/l.) (a) and relationship between the concentration of termonomer in EPTM and in the feed (b) obtained for the trienes (XXXV-XXXVII) (cf. Section III B 6) under the conditions reported in Figure 25.

does not contain substituting alkyl groups, causes the inability of the corresponding triene to enter easily into EPTM chains. This happens because a very stable complexation of the deshielded dienic system with the active catalytic species takes place. The effect does not depend on the type of the common catalysts used, although it has been observed, with other dienes still containing a conjugated diene system, that the presence of bulky groups on a vanadium atom (bonded or coordinated) partly prevents the poisoning effect of conjugated double bond system.

The presence of methyl groups on the butadienyl system favorably affects the behavior of EPTM during the vulcanization process, both for

TABLE XXV

Fractionation^a Data of an EPTM^b-Based on Trienes (XXXIII-XXXIV)

Fraction	$I(M)^c$	$[\eta]$ (dl/g) ^d	(XXIII-XXXIV) (wt %) ^e
1	1.33	0.227	9.03
2	4.56	0.565	n.d.
3	10.63	0.636	n.d.
4	18.97	0.781	11.4
5	29.15	0.950	10.6
6	41.66	1.23	10.3
7	53.75	1.42	11.1
8	65.09	1.70	10.3
9	76.35	1.84	10.6
10	83.80	2.10	9.9
11	89.28	2.52	9.0
12	95.87	2.97	8.6
13	99.45	2.99	n.d.
Initial EPTM	—	1.47	10.7

^aBy column elution.^bPrepared with VAcac₃-Et₂AlCl catalyst system.^c $I(M) = (\Sigma_i w_{i-1}) + w_1/2$.^dFrom toluene at 30°C.^eBy UV measurements.

the presence of a more elevated number of allylic hydrogens and for a regular distribution of the triene into chains. Probably the unsatisfactory behavior of BNB-based EPTM during the curing process may be attributed to relatively large unvulcanizable portions consisting of fractions with little unsaturation.

7. Behavior in Vulcanization of EPTM Containing a Conjugated Diene System

Terpolymers of the type described in Sections III B 4, 5, 6 have been vulcanized according to recipes normally used for EPDM. The general properties of typical EPTM's containing a system of conjugated double bonds, before and after vulcanization are reported, respectively in Tables XXVII and XXVIII; other preliminary data are in Table I. Vulcanization properties vary according to unsaturation levels and type of unsaturation introduced. The way the double bonds of the dienic system are linked markedly influences their behavior during the curing process. As it could be expected, also the type and number of alkyl groups substituting the hydrogen atoms belonging to the diene system, exert a

TABLE XXVI
Fractionation^a Data of an EPTM-Based on Trienes (XXXV-XXXVII)

Fraction	$I(M)^b$	$[\eta]$ (dl/g) ^c	(XXXV-XXXVII) (wt %) ^d
1	2.6	n.d.	n.d.
2	17.9	0.88	4.7
3	37.6	2.18	2.8
4	47.3	n.d.	3.5
5	53.2	n.d.	2.7
6	58.9	2.82	3.9
7	63.7	3.05	3.9
8	68.2	2.37	3.6
9	73.1	3.62	3.6
10	78.6	4.04	3.3
11	84.0	4.49	3.3
12	88.9	4.92	3.2
13	92.9	5.43	3.0
14	95.8	5.56	2.6
15	97.6	n.d.	n.d.
16	99.2	n.d.	n.d.
Initial EPTM	—	2.79	3.6

^aBy column elution.

^b $I(M) = (\Sigma w_{i-1}) + w_i/2$.

^cFrom toluene at 30°C.

^dBy UV measurements.

noticeable influence on the reactivity of unsaturated systems involved in crosslinking reactions.

Sometimes long range effects, induced by strained rings to contiguous ones, or the existence of preferred conformations (e.g., of type cisoid-transoid, *exo-endo*) which the secondary center of unsaturation of termonomer belong to, may be noted in studying the vulcanization process of unsaturated terpolymer.

However, as it has been stressed in Section III A, the exact definition of the chemical behavior of the unsaturated system (i.e., the double bond and its surrounding allylic hydrogens) responsible for the crosslinking reactions, is quite impossible at present for lack of basic knowledge about the complex system of successive and competitive reactions governing the vulcanization process.

Despite the unfavorable situation just summarized, the exceptional reactivity of the cyclopentadienyl ring can be easily observed, even at low levels of unsaturation (for instance near 0.1 mole/kg of termonomer) both

TABLE XXVII
General Properties of Some EPTM's

Sample	Termonomer (type)	Termonomer concentration (mole/kg)	[η] (dl/g) ^a	Ethylene (wt %)
1	methyl-IPTHI ^d	0.457 ^b	2.60	55
2	IPTHI ^d	0.484 ^b	2.08	47
3	IITHI ^d	0.395 ^b	2.50	55
4	IPTHI ^d	0.250 ^b	2.13	48
5	IPDCP ^d	0.310 ^c	2.11	62
6	IPDCP ^d	0.240 ^c	1.97	54
7	(XXXIII-XXXIV) ^e	0.292 ^c	2.11	—
8	(XXXV-XXXVII) ^e	0.194 ^c	2.28	49
9	(XXX, a) ^f	0.320 ^c	1.51	60
10	(XXX, a) ^f	0.104 ^c	1.46	50

^aFrom toluene at 30°C.

^bBy IBr absorption (Cesca et al., 1968b).

^cBy UV spectroscopy.

^dCf. Section III B 4, p. 135.

^eCf. Section III B 6, p. 154.

^fCf. Section III B 5, p. 146.

TABLE XXVIII
General Properties of Vulcanizates

Sample ^a	4	3	6	5	10
Termonomer					
Type	IPTHI	IPTHI	IPDCP	IPDCP	(XXX, a)
Concentration (mole/kg)	0.250	0.395	0.240	0.310	0.104
Technological properties					
Modulus 300%					
(kg/cm ²)	84	124	50	70	180
Tensile strength					
(kg/cm ²)	253	270	241	230	230
Elongation at break (%)	620	485	700	650	375
Heat build-up (°C)	35	31	37	33	32
Curing recipe:	polymer 100, stearic acid 1; ZnO 5, HAF 50;				
	Naphtha Oil 5; TMTD 1.5; MBT 0.5;				
	sulfur 1.5; curing time, 60 min; curing temperature, 153°C.				

^aCf. Table XXVII.

in vulcanization and covulcanization processes with highly unsaturated elastomers (Figs. 41 and 42). The enhanced reactivity of bis-allylic hydrogens of cyclopentadienyl ring are very likely responsible for the

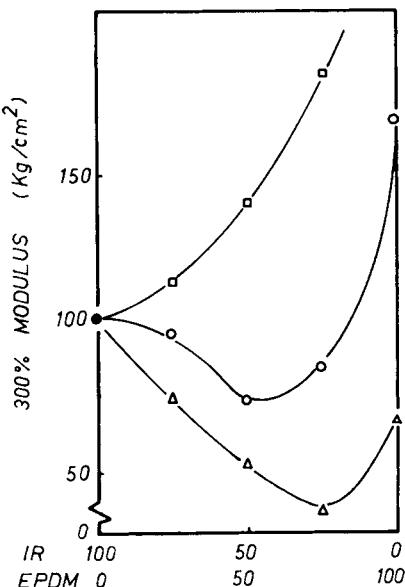


Fig. 41. Covulcanization of *cis*-1,4-polyisoprene (IR) with EPTM based on (XXX, a) (0.124 mole/kg of triene) or with EPDM's based on 1,4-HD (0.77 mole/kg of diene), and ENB (1.08 mole/kg). EPTM = (\square); 1,4-HD-EPTM = (\triangle); ENB-EPDM = (\circ). Recipe: polymer = 100; HAF = 50; Circosol-4240 = 5; ZnO = 5; S = 1.7; CBS = 1; AO-2246 = 1; stearic acid = 1.

results observed as suggested by the comparative evalutaion of other EPTM's having either the analogy of two conjugated double bonds in an obliged *cis* position (cf. triene (XXXI) reported in Section III B 5) or the distribution of the two unsaturations on a system of five carbon atoms (cf. structure (XXXII)). Also the mild reactivity shown by EPTM based on the triene (XXX, b) (cf. Section III B 5), which has no bis-allylic hydrogens, supports the previous conclusion.

The crosslinking rate for terpolymers containing different termonomers has been evaluated according to a method previously described (Ghetti et al., 1969). The polymers have been vulcanized at 145°C, in an oscillating disc curometer, following the recipe reported in Table XXVIII. The experimental data have been treated according to a second order reaction with respect to double bond concentration. The results are reported in Table XX. They show, clearly, that in some cases, particularly high vulcanization kinetics are obtained, superior to those

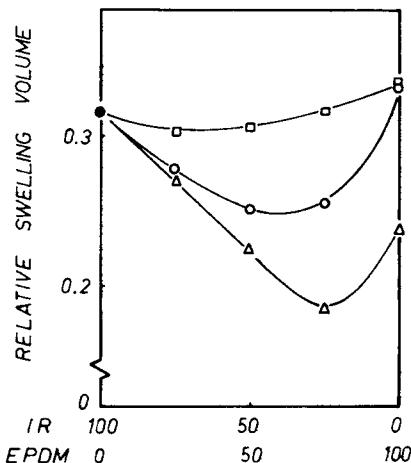


Fig. 42. Swelling of covulcanizates from IR and EPTM or EPDM. Starting materials and recipe as in Figure 41.

normally observed with conventional termonomers. In Figure 20 experimental and theoretical curves have been reported, as an example, for an EPTM-based on methyl-IPTHI and fairly good agreement can be seen.

Another interesting feature is shown by some EPTM based on trienes studied by us, as far as the dependence of the network chain density on the termonomer concentration is concerned. The data, plotted in Figure 43, indicate for instance, a noticeable different trend for terpolymers based on triene (XXX, a) or on ENB. The same network chain density, shown by a typical ENB-based EPDM, is obtained with an EPTM containing a fivefold lower concentration of termonomer (XXX, a).

IV. SOME COMMON TERPOLYMERIZATION RESULTS

Some common features encountered during the synthesis of EPDM's or EPTM's are summarized in this section. The generalization of these results is assumed in first approximation since, from a rigorous standpoint, every system shows specific characteristics. Furthermore, it is well known how difficult it is to correlate or compare results coming from different laboratories and pertaining to these types of catalysts.

Very recently, the most important variables involved in the terpolymerization kinetics and the control of the polymer structure, with par-

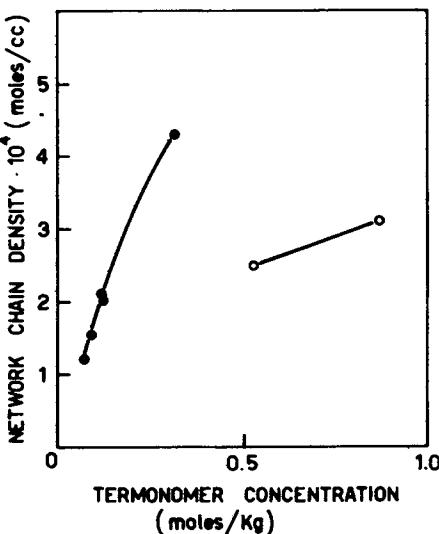


Fig. 43. Network chain density vs. termonomer content; (●) = EPTM based on (XXX, a) and (○) = EPDM based on ENB.

ticular reference to a continuous-flow stirred tank-reactor, have been reviewed (Ver Strate et al., 1973).

Details of some terpolymerizations, not given in previous sections or described as "regular", are reported here.

1. The presence of a third monomer reduces the catalyst efficiency and modifies the kinetic curves according to behavior which depends on the type of termonomer, catalyst and, in general, on the experimental conditions.

2. The catalyst activity and its intrinsic features (e.g., degree of heterogeneity, average lifetimes of active centers, etc.) depends markedly on the modality according to which the components of the system interact (e.g., catalyst formation *in situ* or through partial addition of components, temperature of interaction, etc.).

3. Any aging time reduces the number of active species but, frequently, gives higher homogeneity to catalyst centers.

Therefore many nonaged catalysts show a continuous decreasing activity during the polymerization time, even when the third monomer is absent.

The system $\text{VOCl}_3\text{-EtAlCl}_2$ or $\text{Et}_3\text{Al}_2\text{Cl}_3$ have been reported to lose activity and decrease in valence more rapidly when they are in the pres-

ence of monomers than when under nitrogen (Junghanns et al., 1962). The activity of depleted catalysts can be regenerated by adding appropriate compounds (among which halogenating molecules are the best known; Belg. Pat. 1965, 1967; Easterbrook, 1971) to the polymerization medium, even several times, provided that they are in a defined ratio with the transition metal compound.

4. The best catalysts are prepared starting from hydrocarbon soluble vanadium compounds and from alkyl aluminum halides. EPM's having a narrow distribution of the average composition, of MW and a high sequential homogeneity are obtained in the presence of homogeneous catalysts. Furthermore, they show a syndiospecific catalytic activity, whereas systems based on AlR_3 and on soluble V compounds are aspecific, yielding EPM's with medium sequential homogeneity. Systems based on Ti compounds furnish copolymers with low sequential homogeneity, i.e., with relatively long sequences of monomers. Careful investigations have been carried out on the catalyst activity of typical systems as function of the monomer composition of feed, both in EPM (Valvassori et al., 1963a), and in EPTM synthesis (Cesca et al., 1968a) and it has been concluded that most of the initiating species come from ethylene units.

5. The overall terpolymerization rate increases when the value of the following variables increases: (a) catalyst concentration; (b) α -olefins concentration; (c) molar ratio $\text{C}_2\text{H}_4/\text{C}_3\text{H}_6$; (d) molar ratio Al/V (the importance of this ratio depends on the particular catalyst considered); (e) reciprocal of the polymerization temperature (at constant concentration of monomers); (f) reciprocal of the concentration of MW regulators; (g) reciprocal of the concentration of termonomer; (h) presence of catalyst activator (within defined ratio with V compound).

6. The incorporation of α -olefins is slightly modified by the presence of termonomer; an increase of ethylene content is generally observed with respect to corresponding EPM. The quantitative treatment of this influence has been recently proposed (Askerov, 1973; cf. also p.12). An analogous result has been observed in the presence of H_2 , a MW regulator (see below, point 13 and also p. 71). However, by varying the concentration of α -olefins in the feed, a corresponding modification of the EPDM composition results.

7. As in the case of EPM, the EPDM composition depends mainly on the type of V compound and is independent of the polymerization time and of the molar ratio Al/V. Significant increase of temperature implies, when the catalyst is prepared *in situ*, a modification of the catalytic species which yield, generally, EPDM's having higher ethylene content.

8. The relationship between the content of termonomer in EPDM and in the feed is nearly linear for low levels of unsaturation (generally less than 5 wt % of termonomer for dienes which interact slightly with active centers). For high contents the relationship is more complicated, depending, once again, on the specific reactivity of termonomer toward catalytic species.

9. The utilization of termonomer increases with the temperature of polymerization. Generally an optimum range of temperature exists for each couple of catalyst-termonomer in order to avoid undesirable side reactions leading, sometimes, to too extended chain-breaking reactions or, in other cases, to long branching or gelled polymers.

10. Termonomers containing a norbornene unsaturation, as reactive double bond for the terpolymerization, are ten to twenty times more reactive than termonomers having vinylic or cyclic unsaturation.

11. Trienes, having two double bonds conjugated and separated from the third unsaturation, behave excellently in a terpolymerization reaction, provided that some alkyl groups are present on the pendant diene system and an elevated termonomer concentration is avoided.

12. Higher MW are obtained in aliphatic solvents, which favor also "jumping" reactions, with respect to aromatic solvents or having, however, a basic character. The presence of Lewis bases reduced the "jumping" reactions (see next point) and within defined ratios with transition metal compound enhances catalyst efficiency (catalyst modifiers). However, Lewis bases can play various roles in the polymerization process since they are able to interact with both the transition metal halide and the metal alkyl component and hence to enter catalyst complexes (cf. Section V A). Therefore, donor molecules can compete with monomers in the coordination or adsorption steps to active centers by reducing their number (i.e., influencing the polymerization rate) or modifying their function (e.g., by influencing the copolymer composition or the chain transfer efficiency) and also, by contrast, activating the efficiency of the active sites in dependence of the donor molecule basicity and/or concentration. The latter case may involve the removal of more acidic sites or of the excess of alkyl Al derivative coordinated by the transition metal atom. Acidic centers are more catalytically efficient in the presence of basic dienes or trienes and certainly are responsible for side reactions of the cationic type. However, for a detailed discussion which gives references to experimental evidences and mechanistic considerations, see Section V A.

13. The control of MW of EPDM can be achieved with some chain-transfer regulator, for instance with H_2 , ZnR_2 , etc. However, the intrin-

sic viscosities of EPDM are found increasing when: (a) α -olefins concentration in the feed increases (provided a constant termonomer content is considered); (b) the molar ratio C_2H_4/C_3H_6 in the polymer increases (at constant termonomer concentration); (c) the polymerization time increases (in particular in the first polymerization stage); (d) the concentration of aluminum compound decreases; (e) the polymerization temperature decreases; (f) the concentration of catalyst activator increases (within certain limits).

An accidental increase of MW, sometimes up to gel formation, takes place as a consequence of "jumping" reactions, i.e., of every reaction which implies an attack of secondary diene unsaturation. Very fast cationic reactions occur during the stopping stage of the terpolymerization process, as a consequence of the interaction between Brönsted acids and alkyl aluminum halides. However, the influence of termonomer on MW can have opposite effects depending on its ability to induce prevalent chain-breaking reactions (reduction of MW) instead of "jumping" reactions (increase of MW).

14. The presence of methyl groups as substituents of the pendant unsaturation of EPDM reduces the interference effects with the catalytic species and enhances significantly the curing rate of terpolymer (within certain limits).

15. Slow curing EPDM's are almost completely unable to covulcanize in the presence of different amounts of natural rubber or SBR, whereas terpolymers containing sufficiently reactive unsaturation (among which EPTM's carrying very low amounts of alkyl substituted cyclopentadienyl ring as curing sites) succeed in covulcanization over the whole range of compositions.

16. There are only preliminary indications about the possibility of terpolymerizing a conjugated diene (i.e., butadiene) with C_2H_4 and C_3H_6 , provided appropriate catalyst systems are used. However, the resulting EPDM incorporates blocks of diene and shows poor properties.

V. TERPOLYMERIZATION MECHANISM

A tremendous effort has been made to elucidate the polymerization mechanism of α -olefins with Ziegler-Natta catalysts, but so far there is not conclusive evidence to completely define this peculiar type of polymerization.

In the past some authors considered the mechanism as anionic-coor-

dinate, in particular when ethylene-propylene copolymerization was taken into account (Natta et al., 1969).

This conclusion rested mainly on the low value of the reactivity ratio shown by propylene, in comparison with the ethylene reactivity ratio; this trend was found for all the catalyst systems able to yield EPM.

A different explanation of these results, invoking steric effects due to methyl group, was set forth some years ago (Karol and Carrick, 1961) and seems more correct on the basis of successive kinetic results (Natta et al., 1961b) and also of homopolymerization studies carried out with other olefins (Pino et al., 1960). In fact, activation energies of ethylene and propylene homopolymerization were found to have the same value (ca. 6.6 kcal/mole) for the system $\text{VCl}_4\text{-Al}(n\text{-C}_6\text{H}_{13})_3$, hence the relevant difference in reactivity between these two monomers has to be ascribed, mainly, to steric effects, i.e., to the preexponential rate factor. Furthermore, the reactivity is markedly reduced when bulky alkyl substituents are present in α -olefin molecules (e.g., 1-pentene > 4-methyl-1-pentene > 4,4-dimethyl-1-pentene), and in these cases electron releasing effects on the double bond can hardly be invoked.

As far as the subject of this review is concerned, few papers deal, unfortunately, with the mechanistic aspects of α -olefins copolymerization or terpolymerization.

Recently an old suggestion (Wesslau, 1958; Overberger and Ang, 1960; Carrick et al., 1960; Muharashi et al., 1960; Phillips and Carrick, 1962; Lukach and Spurlin, 1964; Baker and Tait, 1967) concerning Ziegler-Natta systems has been confirmed (Belov et al., 1967; Cozewith and Ver Strate, 1971; Meshkova et al., 1969), i.e., also in ethylene-propylene copolymerization with colloidally dispersed or soluble catalysts (cf. also Section II B) there is more than one type of active center; therefore, the reactivity ratios found previously refer, in many cases, to average values derived from several individual reactivity ratios pertaining to individual catalytic species.

More recently (Zambelli et al., 1972) a complicated situation has been found in the microstructure of EPM obtained with syndiospecific catalysts. The detection of irregular enchainment (tail-to-head: cat- $\text{CH}(\text{CH}_3)\text{-CH}_2\sim$) of propylene units to catalyst centers, associated with the "normal" one (head-to-tail: cat- $\text{CH}_2\text{-CH}(\text{CH}_3)\sim$), indicates that propylene reacts in two ways, depending on the influence of the last unit of the growing chain. This means that ethylene-propylene copolymerization is rather a terpolymerization and, once again, the meaning of the reactivity ratios is doubtful. In this context some conclusions previ-

ously retained as firm have to be considered with caution as obtained on grossly heterogeneous copolymers containing, probably, a mixture of copolymeric fractions having different composition, different sequence distribution and, perhaps, small amounts of homopolymers (Carrick, 1967). Evidences of heterogeneity can be found, more clearly, in EPM produced with heterogeneous catalysts (cf. Fig. 2).

In conclusion, it is easy to foresee that the mechanistic aspect of EPDM synthesis can be depicted, at present, only in a first approximation by referring to some results obtained in the field of α -olefins homopolymerization.

A. Coordinative Aspects

Recent results, obtained using ^{13}C -NMR spectroscopy and carried out with the aim of elucidating the stereochemistry of ethylene-propylene copolymers, have confirmed previous conclusions on the action mechanism of iso-, syndio- and aspecific catalysts (Crain et al., 1971; Zambelli, 1971). In the case of isospecific polymerization of α -olefins the interaction of the monomer with the catalytic center, which should be dissymmetric, is considered the driving force in obtaining a stereospecific polymer containing sequences having the configurations of type mmmmm (Crain, 1971). Heterogeneous catalysts, based on titanium halides, give the best isospecific activity; they work, generally, at relatively high temperature, i.e., between 50 and 100°C.

On the contrary, when syndiospecific catalysts are considered (they are soluble and give the best results at low temperatures, i.e., near to -70°C; moreover, they are able to yield EPM with enhanced tendency to alternate the monomeric units), the interaction of the monomer with the asymmetric configuration of the last unit of the growing chain is invoked to explain the formation of syndiotactic sequences of type rrrrr (Crain, 1971). The structure of the catalytic syndiospecific centers, which are probably dissymmetric, exerts a cooperative effect by orienting the monomer molecules. It is worth noting that stereoregularity is detectable also in EPM (cf. Section II H 3); actually, a regular alternating arrangement of methyl groups induced by syndiospecific catalysts or the constant configuration originated by isospecific catalysts in EPM have been shown by ^{13}C -NMR investigations (Crain, 1971; Zambelli et al., 1971). When catalytic complexes are not able to orient the approaching molecules, they are aspecific and the resulting sequence distri-

butions, both of the α -olefin unit in poly- α -olefin or in EPM, and of the two monomeric units in EPM, become random.

It is also worth noting that a perfectly alternating EPM, i.e., having the structure of hydrogenated *cis*-1,4-polyisoprene, has not yet been obtained, neither from direct synthesis nor from fractionation of whole copolymer. However, in the case of ethylene-*cis*-2-butene copolymers (Natta et al., 1962b) there is a high tendency to yield an alternating structure, i.e., crystalline copolymer of erythrodiisotactic type, which arises from steric interactions between the incoming bulky internal olefin and the growing chain.

This means that the control of syndiospecific catalyst is limited prevailingly to the stereochemistry of the olefinic unit and is partial in this respect because frequently tail-to-head insertion of propylene unit occurs (see below), whereas the distribution of ethylenic unit takes place at random or with some tendency to alternation. This conclusion is not surprising because, according to recent views (Gaylord and Takahashi, 1969), the possibility of obtaining perfectly alternating copolymers comes from the existence of peculiar interactions between the monomers (formation of acceptor-donor-like complexes), rather than from specific interaction monomer(s)-catalyst. The former is certainly the case of perfectly alternating copolymers produced spontaneously, i.e., in the absence of any type of initiator (Cesca, 1973b; Gaylord, 1971). The existence of interaction between monomer and comonomer seems related to differences of bulkiness or of polarity between them or to the ability of forming true complexes with a constant structure which may include also the catalyst species. Alternatively, the alternating coordination of two kinds of monomer to transition metal active center has been proposed in the case of propylene-butadiene copolymer (Furukawa, 1972). Up to now alternating copolymers of low olefins have been obtained only with conjugated diolefins (Natta et al., 1964 c; Furukawa, 1972) and with some internal olefins (Pasquon et al., 1967). However, in the case of EPM abundant irregularities have been found in the structure of olefinic unit (cf. Section II H 3); namely, the inversion of propylene repeating unit takes place under the influence of penultimate effects due both to the type and the structure of the last unit of the growing chain. Moreover, these results seem to suggest that the normal way of insertion of propylene into EPM chains is tail-to-head (Zambelli et al., 1972).

Whenever the general validity of these results were confirmed, the stereochemical configuration of catalyst centers hardly could be involved to induce, even though cooperatively, the structure of the resulting

copolymer and, probably, the discussion of the asset of ligands around the vanadium atom (see below) might scarcely be important.

Despite the criticism which may be subjected to the interpretation of results of previous mechanistic researches in the light of more recent results hereinbefore summarized, it is always interesting to examine the formation and the general features of catalytically active vanadium species as they have been represented up to now. In particular, syndiospecific catalysts use some soluble vanadium compounds (e.g., VCl_4 , $VAcac_3$, etc.) and alkyl aluminum halides, i.e., the same catalyst systems which yield EPM's having narrow distribution of composition and MW, high sequential homogeneity and also EPDM's with a random distribution of termonomer.

ESR analysis shows that the valence of active vanadium is formally 3. The result is independent of the presence or absence of monomers, type of solvent, and type of ligands of V, whereas it depends on the type of alkyl aluminum derivatives (with AlR_3 vanadium compounds are generally reduced to V(0)), on the molar ratio Al/V (when Et_2AlCl is used), on the temperature of interaction, and also on the reaction time (Natta et al., 1965b). However, when the temperature of interaction is raised to room temperature, a progressive reduction of V(III) to V(II) is observed, the rate of depletion depending on the factors just mentioned. The resulting systems, containing V(II), are inactive in α -olefins copolymerization and in α -olefins syndiotactic homopolymerization, whereas the homopolymerization of ethylene is still attained. The rate law of catalyst decay is approximately the same as the decrease of concentration of V(III) in the catalyst solution. However, the presence of V(III) does not assure the catalytic activity, since an Al-V(III) complex has been found inactive when originated from $VO(OC_2H_5)_3$ and Et_2AlCl (Collamati and Sartori, 1965). Similar results have been obtained by Lehr (1968) studying the VAc_3-Et_2AlCl system.

On the other hand the same system $VAcac_3-AlEt_2Cl$ shows a catalytic behavior quite similar to the corresponding VCl_4 -based catalyst, thus eliminating V(IV) as the active valence.

A detailed discussion of the mechanism of interaction between VAc_3 and Et_2AlCl at low and room temperature has been reported (Khartonova, 1972), but more recent investigations have shown that the Acac ligands of $VOAcac_2$ are rapidly substituted by chlorine ligands exchanged with alkyl aluminum chlorides; hence vanadium active centers should contain low amounts of Acac ligands (Henrici-Olivé and Olivé, 1971).

On the basis of kinetic studies it was also evidenced that active vanadium species constitute a small fraction (less than 1%) of the total

vanadium present in the polymerization medium, the catalytic centers being continuously destroyed when relatively high temperatures (0–20°C) are adopted, whereas at –78°C a steady state can be attained.

All the evidence collected on the VCl_4 and VAc_3 -based systems suggest that the catalytically active vanadium contains $VC_2(C_2H_5)$ as part of the catalytic complexes, having a more complicated composition, through the formation of complexes having a chlorine bridge more stable than an alkyl one (Boor and Youngman, 1966). Weak Lewis bases, e.g., anisole, can enter into catalytic complexes, but they are very similar, from a steric standpoint, to the complexes formed in the absence of base.

Organometallic Al derivatives are components of the catalytic complexes which should have the octahedral coordination of V(III) (Boor's model; Boor and Youngman, 1966). However, they are considered able to exchange their ligands with the components of the reaction medium. This is an important assumption because when the substitution of a ligand or the partial dissociation of the catalytic complexes takes place, the number and the type of coordination vacancies change and hence both the stereospecificity and the catalytic efficiency are modified. Actually, high concentrations of Lewis bases or alkyl aluminum halides have been found to influence negatively the crystallinity of syndiotactic polypropylene. The same results were observed when organometallic compounds, having a lower tendency toward complexation (e.g., gallium derivatives), were used (Zambelli et al., 1968a, b).

Catalytic complexes should have at least a coordination vacancy for the coordination of the monomer since, on the basis of kinetics schemes, this early stage has been postulated. However, according to some authors, there is no direct experimental evidence to support monomer coordination (Chirkov, 1971; Burfield and Tait, 1972). Alternatively, the olefin might be adsorbed on the solid phase in the case of heterogeneous systems or, perhaps, interpose directly into the metal-carbon bond site. The necessity of a heterogeneous phase or the assumption that bimetallic complexes are necessary in order to have isospecific catalysts have been ruled out by recent results (Ballard, 1973; Giannini et al., 1970) carried out with soluble Zr or alkyls alone.

The propagation step takes place by inserting the monomer, coordinated or not, at the V–C bond. NMR and IR studies have allowed the conclusion that both in syndiotactic and isotactic homopolymerization or copolymerization of propylene the double bond addition is *cis* (Natta et al., 1960d; Zambelli et al., 1968c).

The results now summarized are partly confirmed and integrated with

other data obtained during the study of EPM and EPDM syntheses. Unfortunately, the results are sometimes not very meaningful since they are derived from unfractionated samples and obtained by different authors. However:

1. The system $\text{VAcac}_3\text{-Et}_3\text{Al}$ is unable to produce any EPM, EPDM or polyethylene.

2. The systems based on different V compounds (e.g., VOCl_3 , VCl_4 , VAcac_3) are less efficient when are associated with EtAlCl_2 than with Et_2AlCl .

3. The isospecificity of some catalyst systems, observed through IR spectroscopy in EPM, is in the following order: $\alpha\text{-TiCl}_3\text{-AlEt}_3 > \text{VCl}_3\text{-AlEt}_3 > \text{VOCl}_3\text{-Al}i\text{Bu}_3 > \text{VCl}_4\text{-Et}_2\text{AlCl} > \text{VAc}_3\text{-Et}_2\text{AlCl}$ (Kissin et al., 1967).

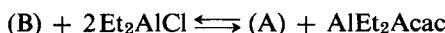
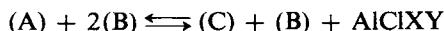
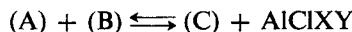
4. All termonomers have, to a different degree, an inhibiting effect toward catalytic species. The degree of inhibition depends also on the type of V compound used. For instance, VCl_4 -based systems are more sensitive to the termonomer than VAcac_3 -based systems.

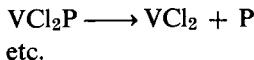
5. Weak Lewis bases increase, when present in significant concentration, the yield of EPDM obtained with the system $\text{VCl}_4\text{-Et}_2\text{AlCl}$. Bidentate bases (e.g., dioxane, diglyme, α,α' -dipyridyl, etc.), at the same concentration, inhibit completely any catalytic activity in the case of $\text{VCl}_4\text{-Et}_2\text{AlCl}$ system, but not with the system $\text{VAcac}_3\text{-Et}_2\text{AlCl}$.

6. Catalyst systems based on VAcac_3 or VOCl_3 and Et_2AlCl are not activated by Lewis bases.

7. Trienes containing a conjugated double bonds system were found more poisonous than termonomer containing isolated double bonds. For instance, one molecule of IPTHI (see Section III B 4) was found to terminate two EPTM end-growing chains.

All the data above cited enables one to depict catalytically active centers as octahedral structures of type (A)-(F) (Fig. 44) which have to be considered as species undergoing competitive equilibrium reactions with different molecules of the medium. For instance:





where the symbols used are those of Figure 44.

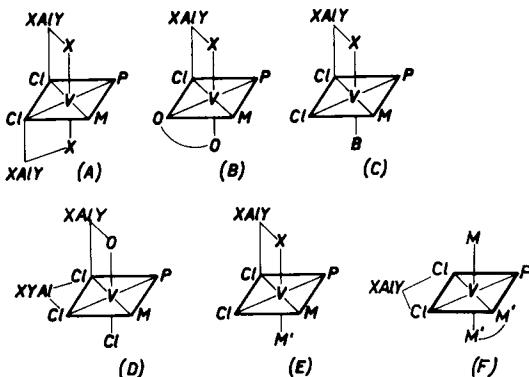


Fig. 44. Representation of coordination complexes as possible active species of vanadium-based Ziegler-Natta catalyst. X, Y = Et or Cl; O²⁻O = bidentate ligand; B = Lewis base or monodentate ligand; P = polymer growing chain; M = olefin monomer; M' = diolefin (or polyene) monomer.

Structures of catalyst complex containing the V=O group are unlikely, since the IR band at 1009 cm⁻¹ (Andreieva et al., 1970) is absent in the final products of the reaction between the catalyst components, i.e., Et₂AlCl and VO(OEt)₃ (molar ratio Al/V ≥ 2). On the other hand, ethoxyl groups are transferred from V to Al atom (a new band at 895 cm⁻¹).

The number of possible catalytic complexes is relatively elevated as a consequence of the postulated reactions, even though it might be possible to put forth a rough priority of stability between the structures invoked. The foregoing representation of catalysts centers and the examples of equilibria involved between them take into account a number of experimental evidences found by several authors in studying Ti- or V-based coordinated catalysts; they have been collected in a previous review (Boor, 1969). Besides the results previously cited, we can mention other data to account for the complex situation concerning this type of catalyst. For instance: the formation of complexes is suggested also by the low solubility of V(III) derivatives in hydrocarbon solvents; dif-

ferent types of alkylaluminum halides are bonded to V centers; at least two types of V(III) species have been observed; one very active but unstable, the other less active but more stable, the former coming from an inactive V(III) precursor and the latter having an uncertain origin (Lehr, 1968; Lehr and Corman, 1969); the fast alkylation reaction of transition metal compounds and also the facile decay of labile alkylated derivatives has been widely described (De Vries, 1961); the existence of different oxidation states has been recognized in systems based on V(V) or V(IV) derivatives (Junghanns et al., 1962; Obloj et al., 1965); the possibility of dismutation of alkyl aluminum halides under the action of Lewis bases has been reported (Zambelli et al., 1963); etc.

A rigorous description of the geometry of the active centers and of the factors controlling the stereospecificity of Ziegler-Natta catalysts has been given by Cossee on the basis of quantum-chemical and crystal-chemical considerations and is reported in detail elsewhere (Cossee, 1967). The representation of catalytic centers above depicted takes qualitatively into account Cossee's main statements. However, it should be noted that the scheme proposed by Cossee implies the complicated step of alternating the positions where the monomer is coordinated and the polymer chain is growing. Recently, such a representation has been refined and the previous assumption of Cossee has been shown to be (Allegra, 1971) unnecessary for the mechanism action.

When it is assumed that such a mechanism regulates also the copolymerization of dienes (or polyenes) with α -olefins, EPDM synthesis studies suggest another refinement of the Cossee's scheme. In fact, the bifunctionality of termonomer and its enhanced coordination ability, with respect to the monoolefin monomers, imply the occupation of two coordination positions in the octahedral spatial arrangements of the active center (cf. Fig 44 E-F, Section II A and V D). Even though the presence of termonomer reduces the overall kinetics of polymerization (due to its tendency to occupy a higher number of vacancies and to coordinate to active sites more stably than α -olefins), however, the diene (or triene) enters $C_2H_4-C_3H_6$ enchainment. This means that, very likely, there is more than one vacancy in the octahedral coordination of every transition metal atom which can be occupied by π electrons of more than one double bond. Probably, the vacancies allow the change of the type of ligand through equilibrium reactions similar to those reported above. Such a situation involves different catalyst complexes just the ligands coordinated by the transition metal atom are different.

The incidence of possible ligands, having different basicity and coor-

dination ability, on the catalytic activity of the transition metal, has been evidenced by the introduction of Lewis bases in the terpolymerization medium (Cesca et al., 1968a, 1974b) and also by quaterpolymerization studies involving a diene and a triene, other than ethylene and propylene (Cesca et al., 1974c). Comparable experiments have shown that during the synthesis of EPDM the C_2H_4/C_3H_6 ratio in the terpolymer increases by increasing the termonomer (e.g., DCP, COD) concentration in the feed. By contrast, the introduction of an α -olefin (e.g., 1-butene) as termonomer does not modify the composition of the resulting $C_2H_4-C_3H_6-C_4H_8$ terpolymer (Natta et al., 1963a). This result points out the relevant modification of the active centers when they are in the presence of bidentate olefinic ligands. However, the conclusions of these papers agree qualitatively with the previous postulate even though some result, encountered in those investigations, are still obscure.

It is worth noting that the existence of more than one vacancy for the monomer coordination to active centers seems supported also by results obtained in the case of the homo- and copolymerization of conjugated diolefins in the presence of V- or Ti-based catalyst systems (Furukawa, 1972; Porri and Pini, 1973).

B. Cationic Aspects

The foregoing discussion has been developed referring to coordinate mechanism, the most widely accepted interpretation of Ziegler-Natta catalysis, but it should be pointed out that other mechanistic interpretations have been proposed.

It is proper to mention some of them, because in EPDM synthesis the reactivity of secondary double bond of termonomer (cf. Section II D) or its structural rearrangement (cf. Section III A 9) have been explained in terms of cationic mechanisms. Furthermore, some recent findings (Zambelli et al., 1972) can hardly be explained on the basis of any significant action exerted on the growth reaction by the configurational characteristic of the catalyst, at least in the case of homogeneous systems. Hence, there is the opportunity of emphasizing some aspects of Ziegler-Natta catalysts not involved in the previous discussion.

As a matter of fact, it is significant that among the more recent and authoritative reviews on Ziegler-Natta catalysis (Boor, 1969; Hoeg, 1967; Reich and Schindler, 1966) no mention has been made of any presiding mechanism having a cationic character. Some data, reported in the literature, have been obtained under particular conditions or, in other

cases, their meaning is not of facile interpretation. For instance, the rate of EPM formation has been found directly proportional to the conductivity of the systems based on Al-*i*-Bu₂Cl and some alkyl chlorovanadate (Bushick and Stearns, 1966), in the order VOCl(OEt)₂ > VOCl₂OEt > VO(OEt)₃. These experiments can indicate only the existence of ionic species in the catalyst solution. Their concentration depends on the reaction time, catalyst/cocatalyst molar ratio and the interaction temperature, according to diagrams which show a maximum of conducibility at 30°C after ca. 20 min of reaction, whereas the polymerization rate (of ethylene with the catalyst system VO(OEt)₃-Et₂AlCl) is continuously decreasing since the early minutes of polymerization (Andreieva et al., 1970).

Also the interesting electrodialytic studies of Shilov et al. (1962; Dyachkowskii, 1965), which suggest the presence of cationic species containing Ti(III) in the electrodic zone where active centers of Ziegler-Natta type are operating, should be restricted within the limits of the specific conditions adopted. In fact, it can be noted that: (a) the experiments were carried out in an unusual solvent (dichloroethane). (b) the polymerization of ethylene occurs in the cathodic zone of the dializer under the action of electric fields having high strength (i.e., > 1 kV). This highly reactive olefin can be polymerized with radicals under mild conditions, provided that appropriate salts, which are able to increase its concentration in solution, are present (Bier and Messwarb, 1962). (c) Products derived from the reaction of α -decene with the ion, which is probably [Cl₂TiCH₃]⁺, have not been investigated.

Another argument subjected to contradictory interpretations is the dependence of the value of the propylene reactivity ratio as function of the transition metal valence. Since $r_{C_3H_6}$ increases when the halides of Ti or V pass from the oxidation state (IV) to (III), it has been deduced that propylene polymerization requires more cationic catalyst than ethylene (Karol and Carrick, 1961). Also the presence of nucleophilic dienes in EPDM synthesis, which generally depress the propylene reactivity, has been considered as evidence of the ability of the electron-rich diene system in reducing the electrophilicity of the active centers, whereby ethylene reactivity will be enhanced with respect to propylene.

In reality, the situation appears more complicated and alternate explanations may be suggested (e.g., steric effects) to account for the influence of the diene in EPDM synthesis (cf. Section II D). As Karol et al. (1961) suggested, there is certainly a decrease in electronegativity when the valence state diminishes (e.g., V(IV) = 1.8 and V(II) = 1.2),

thus the resulting metal-carbon bond is more polar and the incorporation of any polarized monomer should be favored. But there is also the contrasting effect of the reduction of the electron acceptor character of the metal, due to the filling of d-orbital when the valence decreases, and this means a reduction of catalytic activity toward α -olefins.

Furthermore, an increase in propylene reactivity has been observed when $\text{Et}_3\text{Al}_2\text{Cl}_3$ or EtAlCl_2 was used with VOCl_3 or VCl_4 instead of Et_3Al or Et_2AlCl . These results reflect, probably, another order of phenomena, i.e., the facile and diversified reducibility of superior V halides to lower V(II) (considered unable to yield active centers for EPM synthesis (Lehr, 1968; Lehr and Corman, 1969)), which takes place also as a function of the alkylating ability of the organometallic Al compound. It is very likely that several types of active centers, differing in both the valence state of the transition metal compound and the type of catalytic action promoted (Junghanns et al., 1962; Obloj et al., 1965), coexist simultaneously in the systems cited.

For instance, the system VCl_4 – EtAlCl_2 yields negligible amounts of solid EPM (and also EPTM (Cesca et al., 1968a)) under typical copolymerization conditions, i.e., $T = -20/20^\circ\text{C}$ in toluene, $\text{Al}/\text{V} = 5-50$, overall pressure of monomers = atmospheric. Only, a significant yield of wax-like and oleous products, having an elevated content of propylene and aromatic structures, have been observed; very likely, they originated from cationic alkylation processes prevalent with respect to a coordinate copolymerization mechanism (see below).

Another interesting example of concurrent reactions, acting, very likely, through a cationic mechanism, is offered by several reactions (oligomerization, isomerization, cyclization, and alkylation) which take place during olefin metathesis reaction in the presence of acidic catalysts (WCl_6 or MoCl_5 – ROH and $\text{Et}_3\text{Al}_2\text{Cl}_3$ or EtAlCl_2). Also in these cases, the presence of Lewis bases reduces undesired side reactions and a stereospecific methatetic polycondensation of α,ω -dienes is obtained (Dall' Asta et al., 1972b).

The association of tetrahydrofuran (THF) to the system VOCl_3 – $\text{Et}_3\text{Al}_2\text{Cl}_3$ has been investigated in the case of EPM synthesis (Karasev and Minsker, 1971) in order to ascertain some cationic activity of the catalyst. According to the behavior of cyclic ethers, the formation of telomers by addition of THF (through ring opening of the ether) to eventual cationic species and, perhaps, the modification of the EPM structure (IR investigation), as a result of chain transfer with scission, would be expect-

ed. Neither of these two events was observed, thus it has been concluded that no cationic species are originated from $\text{VOCl}_3\text{-Et}_3\text{Al}_2\text{Cl}_3$.

As it will be discussed below (cf. also Cesca et al., 1973a) such a conclusion depends markedly on the electrophilicity of the monomers involved. In the presence of strong nucleophilic and unsaturated species not containing an oxygen atom, e.g., conjugated dienes, catalyst systems based on VOCl_3 or VCl_4 and EtAlCl_2 or $\text{Et}_3\text{Cl}_2\text{Cl}_3$ give a significant amount of crosslinked EPDM and the formation of oligomers of the diene used.

The cationicity of several coordinate catalysts can be increased by the presence of protogenic molecules, used usually for destroying catalytic activity (Cesca and Priola), when definite ratios exist between the Lewis acid and the Brönsted acid. For instance, the cationic activity of the system $\text{TiCl}_4\text{-}(i\text{C}_4\text{H}_9)_2\text{AlCl}$ ($\text{Al/Ti} = 0.7$) exerted toward toluene solutions of propylene (Kudashev et al.) is markedly increased by the presence of CH_3OH ($\text{CH}_3\text{OH}/\text{Ti} = 0.3$). The yield of propylene oligomers and alkyl derivatives of toluene is increased manyfold by the presence of CH_3OH in the system.

Clearly, these results point out the necessity of using short-stopping agents and very efficient conditions for quenching Ziegler-Natta catalysts having acidic character in order to minimize "jumping" of MW or branching in EPDM (cf. Section II D).

The existing literature and several excellent reviews allow one to omit a recapitulation of the different mechanism put forth to explain Ziegler-Natta catalysis (Boor, 1969; Hoeg, 1967; Reich and Schindler, 1966). Probably, one of the most interesting conclusions, reached after examining a number of papers, is the polyfunctionality of this kind of catalysts, i.e., the ability in initiating chain reactions with different mechanism. However, this is not the case of the initial step, characterizing Ziegler-Natta catalysis, which can be described as the coordination of monomer, through its π -electrons, to an electrophilic transition metal site before inserting at the metal-polymer bond of the growing chain. In fact, this electrophilic attack of the monomer, even though it has been called cationic initiation (Uelzmann, 1958), is considered, generally, a fundamental prerequisite without any direct influence on the nature of the propagating species. On the contrary the propagation step, depending on the way it is represented, diversifies the different mechanisms proposed.

Actually, noticeable differences have been collected (Novokshonova et al., 1967) between the initiation and propagation step; furthermore, the prior complexation of the monomer to the active centers is not the

rate-determining step (Ingberman et al., 1966). However, the agreement between different authors is not complete on this point.

From a general point of view, at least three different types of coordinated mechanisms can be foreseen, anionic, radical, and cationic depending, schematically, on: (a) the electrophilicity of coordination center; (b) the polarization of the active metal-carbon bond; (c) the polarizability of monomer involved.

Some attempts have been made to represent in an unified scheme all the principal mechanism derived from a gradual variation of the parameters cited above, in order to interpret the experimental evidences. Such a unified view (Kennedy and Langer, 1964) may help one to explain some ambiguous data.

In fact, when a Ziegler-Natta catalyst is formed by one or two strong electrophilic components, they can be sufficiently acidic, according to Lewis, to initiate a cationic polymerization. Of course, this potential attitude becomes actual only if monomer is able to stabilize the carbennium ion. On the contrary, in the case of ethylene, cationic systems such as $\text{EtAlCl}_2(\text{CH}_3)_3\text{CCl}$ yield, in low amounts, only branched saturated C_6 , C_8 , and C_{10} hydrocarbons (Priola et al., 1972).

Other supports can be found in the literature to confirm this interpretation; it is interesting to recall the work of Sinn et al. (1961) who used high vacuum techniques and exhaustive purification to demonstrate that traces of protogenic substances, acting as coinitiators, are necessary to polymerize typical cationic monomers in the presence of Ziegler-Natta catalysts or of simple alkyl aluminum halides. These results agree quite well with the behavior of many cationic initiators (Pepper, 1964). But when ethylene was used, polymerization was unavoidable in spite of any exhaustive purification. Furthermore, the quenching of catalyst ($\text{AlR}_3/\text{TiCl}_4$) with CH_3OH^3 yielded radioactive polyethylene but not when $^{14}\text{CH}_3\text{OH}$ was used (Ayrey, 1969).

Also the results obtained with well-defined crystalline, soluble bimetallic catalyst complexes are very informative (Natta et al., 1959b; Natta and Mazzanti, 1960). When alkyl groups (R_1 , R_2) are progressively replaced by chlorine atoms in catalysts of type $(\pi\text{-C}_5\text{H}_5)_2\text{TiCl}_2\text{AlR}_1\text{R}_2$, the activity in ethylene polymerization correspondingly decreases, whereas the stereospecific cationic polymerization of vinyl isobutyl ether, absent when $R_1 = R_2 = \text{Et}$, becomes quantitative for $R_1 = R_2 = \text{Cl}$.

The poly(vinylether) obtained did not contain any alkyl or cyclopentadienyl group of the initial complex, thus a cationic mechanism seems likely. On the contrary, polyethylene contained terminal ethyl groups

when $R_1 = R_2 = Et$ or $R_1 = Et$ and $R_2 = Cl$, but when $R_1 = R_2 = Cl$ cyclopentadienyl groups were found in the polymer, hence the polymerization mechanism involved metal-carbon bonds.

For the present discussion the behavior of a complex having $R_1 = Et$ and $R_2 = Cl$ is important, since it promotes either a cationic or a coordinate mechanism, depending on the tendency of the monomers to polymerize by one or the other mechanism.

Extreme care is therefore necessary in evaluating experimental results when two or more monomers, having different sensitivity to possible initiation mechanisms, are in the presence of polyfunctional catalysts which can change their method of action under slight modifications of the reaction medium. Certainly this situation applies to EPDM synthesis and is responsible for some uncertainties existing in the literature (cf. Section III A 9) and of the facile occurrence of side reactions (cf. Section II D). Our results, published recently (Cesca et al., 1973a) on DCP-based EPDM obtained with acidic coordinate catalysts, confirm the previous statement. We have found that *endo*-DCP can be homopolymerized with the system $VOCl_3-Et_3Al_2Cl_3$ and other acidic Ziegler-Natta catalysts through a Wagner-Meerwein rearrangement which yields the *exo* structure of the repeating unit. This epimerization occurs only in the presence of sufficiently strong cationic catalyst (Carner et al., 1969). This can be taken as the evidence of the type of mechanism governing the homopolymerization of DCP. On the contrary, *endo*-DCP, in the presence of the same catalyst system and under the same experimental conditions, except in the presence of ethylene and propylene, gives an EPDM which contains the diene exclusively as *endo*-DCP. The absence of isomerization suggests a terpolymerization mechanism different from the cationic one, typical of α -olefins, which we refer to as coordinate, without any specification.

No convincing answer has been given, up to now, to the problem of the simultaneous existence of cationic and coordinate mechanism. The experimental evidence so far collected and cited hereinbefore seems to exclude the coexistence of two mechanisms. Moreover, in view of the high value of the rate constants involved in cationic polymerization of olefins, it seems likely that cationic species are active, as a consequence of the presence of adventitious protogenic impurities, when coordinate mechanism is ineffective, e.g., in the earliest stages or at the end of polymerization (Cesca and Priola). However, on speculative ground there is no difficulty in admitting that an equilibrium exists (Kennedy and Langer, 1964) between an almost unpolarized metal-carbon bond

(presiding coordinate mechanism) and an intimate ion-pair (inducing a ionic mechanism), the equilibrium resulting regulated by the principal factors summarized earlier (p. 177) under (a)-(c).

C. Radical-Like Aspects

Recent data (Zambelli et al., 1972), obtained on EPM, induce the re-examination of the influence of the transition metal active center when ethylene and propylene are copolymerized in the presence of syndio-specific catalyst. In fact, the copolymers show a significant amount of irregularities in propylene enchainment (cf. Section II A 3) at level of repeating units (propylene inversion). The relatively low degree of regularity of these copolymers, having syndiotactic structure, may suggest a mechanism acting through almost-free propagating chain ends, where steric and electronic repulsions between approaching monomer and the chain end, particularly efficient at low temperatures, are the weak driving force which builds the syndiotactic structure of EPM chains.

This schematic representation is different only in part from a coordinate mechanism, as represented in the detailed description proposed by Cossee (1967), since the insertion reaction implies the homolytic cleavage of the Ti-alkyl group bond. From a formal point of view the transition state of coordinate mechanism resembles a coordinate-radical process, taking place as a four-center stage which, through a concerted process of breaking and reconstituting σ alkyl-metal and $\sigma\pi$ olefin transition metal bond, regenerates a new σ bond between the growing chain end and the transition metal.

Along these lines of reasoning and mainly on the basis of kinetic evidences collected with homogeneous systems, Chirkov (1971) attempted recently to define the mechanistic character of Ziegler-Natta catalysis. Ziegler-Natta catalysts would act through a radical pair, namely by a pair of weakly bound radicals in a manner similar to classical catalysis description. This would occur because a radical bound to a transition metal behaves as a pseudo-radical as far as its reactivity is concerned, although there is no convincing evidence of the existence of free radicals in this type of catalysis. Depending on the strength of the metal-carbon bond in the complex, two limiting mechanisms would define Ziegler-Natta catalysts: ionic and radical.

Alkyl radicals, weakly bound to the metal by a covalent link, would be involved in all the principal steps of polymerization.

This interpretation did not consider adequately some important

features of Ziegler-Natta catalysis, for instance: (a) the preliminary co-ordination of the monomer, about which there is general agreement, even though this statement is considered rather a postulate from kinetic results than direct experimental evidence; (b) the role exerted by d-orbitals of transition metal compounds; (c) the stereoregulating action of stereospecific catalysts, which is their most prominent property; (d) the elevated efficiency of Ziegler-Natta catalysts in the presence of a low concentration of α -olefins; (e) the absence of negative influence exerted by radical scavengers; (f) the efficient action of hydrogen, or its isotopes, as transfer agent.

Thus the picture proposed by Chirkov, who invokes a radical mechanism for initiation, propagation, and termination, differing from a free radical one only in quantitative aspects, seems unable to describe adequately the complex phenomenology offered by Ziegler-Natta catalysts.

In particular, two different orders of behavior are offered by heterogeneous and homogeneous Ziegler-Natta systems, mainly from the kinetic point of view. But also their stereospecificity is completely different since, in a first approximation, the former are generally isospecific and the latter syndiospecific.

Chirkov's conclusions, referred above, better approximate the evidence collected from syndiospecific catalysts, which he studied in ethylene homopolymerization and in EPM synthesis. As far as heterogeneous systems are concerned, their stereospecific mechanism and the chemical structure of the active sites have been described, more recently (Kissin et al., 1970; Kissin and Chirkov, 1970), on the basis of the Arlman-Cossee model (Arlman and Cossee, 1964).

Attempts to determine radiochemically the polarization sign of active centers producing syndiotactic polypropylene by using CH_3OH^3 or $^{14}\text{CH}_3\text{OH}$ as quenching agents, gave results which have been considered inconclusive (Zambelli et al., 1972) since, in both the cases, low amounts of very radioactive polymers were collected. These data show that in some cases they can be misleading (Childers, 1963; Cooper et al., 1963), as there is not the certainty that the quenching agent is able to react directly and selectively with true active sites. However, this conclusion overestimates some contradictions encountered in labeling polydienes (Childers, 1963; Cooper et al., 1963) and forgets that many authors successfully used the quenching methods for determining the concentration of active centers in α -olefin homopolymerization studies (Feldman and Perry, 1960; Bier et al., 1962; Burfield and Tait, 1972). Whenever the aforesaid am-

biguous labeling data were confirmed, an alternate explanation might invoke the absence of polarization in metal-polymer bond and in this case (syndiospecific catalysts) Chirkov's views would find partial support.

In reality, in the case of isoprene-propylene cooligomerization (Furukawa et al., 1973b), in the presence of V-based catalyst (cf. Section VI A), the initiation reaction takes place by propylene addition to active sites through both primary and secondary insertion. Their relative occurrence is in the range 1-6/1 and depends on the propylene content in the feed; the mechanism is considered to be anionic coordinate.

Very recent results indicate that when $-O-H^3$ Brönsted acids stronger than methanol are used as terminating agents in propylene polymerization, a radioactive polymer is obtained (Zambelli and Tosi, 1974). Indeed such evidence suggests that at least a weak anionic character is associated with the polypropylene growing-chains. On the other hand, the alternating copolymerization of ethylene with internal olefins (e.g., 2-butene, cyclopentene, etc.) which is achieved with typical EPDM catalysts under very mild conditions (Dall'Asta and Mazzanti, 1963) can be accounted for by a coordination mechanism which does not involve, necessarily, any polarization of the growing chain.

In this context mention might be made of the formation, under radical initiation, of syndiotactic polymer from vinyl monomers carrying bulk substituents on the double bond; the stereoregulation is considered to be derived from the steric repulsion between substituents. However, this argument is outside the purpose of the present work, while the investigations concerning the possibility of polymerizing radical sensitive monomers with Ziegler-Natta catalysts have been so far inconclusive with regard to defining, indirectly, the α -olefin polymerization mechanism. Since radical fragments are generated from the interaction of Ziegler-Natta catalyst components, the situation is similar to the case of cationic species discussed in the previous section. But as far as the reactivity of α -olefins with radical is concerned, there is little probability that, in the absence of a radical sensitive comonomer and under the mild conditions of EPDM synthesis, a chain reaction occurs. Only within a condensed ethylene phase, made with an aqueous solution of silver salt, has it been possible to obtain low yields of linear polyethylene in the presence of redox systems and under mild conditions (5 kg/cm^2 , 40°C) (Bier and Messvarb, 1962). However, aside from the possibility of obtaining a increased concentration of α -olefin in the presence of metal compounds which can complex the monomer, the role of α -olefin coordination is to

reduce the stability of the transition metal-carbon bond which accounts for the relatively small nuclear translations involved in coordinated mechanism.

Actually, α -olefins polymerization proceeds well with Ziegler-Natta catalysts in the presence of many free radical scavengers as amines, ethers, etc.; moreover, a number of these compounds can accelerate the EPDM reaction formation also.

In the case of vinyl chloride or vinylidene chloride copolymerization with ethylene, in the presence of systems based on $TiCl_4$ or $Ti(OBu)_4$ and Et_2AlOEt , the possibility of producing a true copolymer occurs only for Al/Ti ratios lower than one, but, generally, a mixture of copolymer and polyethylene is observed (Ulbricht, 1971).

However, the action of Ziegler-Natta catalysts in this kind of copolymerization has been shown to occur through radical mechanisms (Ulbricht, 1971, p. 401), even though the efficiency is low (0.8% of the alkyl groups of the system $TiOBu_4$ - $AlBu_2Cl$ change into free radicals) (Budanova and Mazurek, 1967).

The capability of modified Ziegler-Natta catalysts to promote the ionic-coordinated polymerization of vinyl chloride was inferred from the possibility of copolymerizing it with propylene (Razuvayev et al., 1965). This conclusion disagrees with the results collected by Matsuoka et al. (1965) who found that propylene can copolymerize with vinyl chloride also in the presence of typical radical initiators (AIBN). The ambiguity of these data can be accounted for by admitting the existence of two processes: one based on a coordinated mechanism capable of yielding polypropylene, and the other based on the formation of free radicals which involve the participation of vinyl chloride.

However, the possibility of existence of more than an unique polymerization mechanism is not characteristic of only Ziegler-Natta systems (modified or not). Certainly the high reactivity of organometallic Al compounds are responsible for several side reactions, in particular when there are molecules containing heteroatoms in the reaction medium. In reality, it seems essential that two monomers having different polarity are allowed to interact between them or with some component of the catalyst system in order to yield two different polymerization mechanisms.

The role played by organometallic Al derivatives in producing effective radical initiation has been shown recently during the copolymerization of ethylene with vinyl acetate in the presence of equimolar amounts of $AlEt_3$, $ZnCl_2$, and CCl_4 (Saegusa et al., 1970). A dual site character of the catalyst system has been inferred since a random co-

polymer (typical of radical initiation) and a 1:1 alternating copolymer (typical of a charge-transfer polymerization mechanism involving the complexation of VA with $ZnCl_2$) have been obtained simultaneously.

The data now cited are other examples of the formation of a mixture of products through two different mechanisms acting, perhaps, simultaneously. Further experiments are needed to elucidate them. However, in a few cases, involving nonhydrocarbon monomers and particular conditions of synthesis, the existence of simultaneous and, sometimes, antithetic mechanisms has been proved (Gilbert et al., 1956; Hayashi et al., 1973; Irie et al., 1973); in other case the opposite was found true. For instance, the cationic homopolymerization of a cyclic ether can occur in the same medium after the rapid anionic homopolymerization of vinylidene cyanide (Oguni et al., 1973), the polymer of which is insoluble in the reaction solvent.

A recent paper of Zambelli and Tosi (1973) is very interesting in the context of the topics discussed in this chapter, since a four center complex has been proposed as the transition state presiding over the concerted action mechanism of α -olefin polymerization. The model is considered valid both in the case of iso- and syndiospecific catalysts because, in principle, the corresponding polymers can be formed by the same catalyst complex, depending on the type of monomer insertion which can be primary or secondary, i.e., with formation, respectively, of a new primary or secondary metal-carbon bond (see below).

The scheme proposed is only formally analogous to that depicted in the earliest part of this section, as it has been suggested independently by some analogies with the hydroformylation catalysts of α -olefins. However, the model accounts for the fundamental stereochemical requirements of iso- and syndiospecific polymerization mechanism, by assuming that the steric influence due to the bulkiness of the ligands on the transition metal-carbon bond determines the formation of an activated and stabler *trans*-complex (syndiotactic propagation) instead of a *cis*-complex (isotactic propagation). Whenever an environmental difference exists above and below the transition metal-carbon bond and the monomer approaches the active center from a constant direction, the primary insertion, which minimizes the interactions between monomer and growing chain, yields the isotactic propagation, whatever the last unit of the growing chain is. On the contrary, a secondary insertion from the same side of the substituted carbon of the last unit of the growing chain makes possible the steric control of the last unit of the chain on the monomer addition (syndiotactic propagation).

The mechanism proposed might seem, at first sight, rather unilateral

in the sense that is based essentially on a limited number of recent results obtained by the authors (Crain et al., 1971; Zambelli et al., 1971, 1972). However, this type of data, resulting from the investigation of the stereochemical situation of the polymer obtained with different types of catalysts (i.e., syndio-, iso- and aspecific systems), are very coherent and self-consistent, since the microstructure of macromolecules may be regarded as a detailed recording of the action mechanism of the catalyst used (Zambelli, 1971). On the other hand, a number of data collected in the past by many researchers have evidenced that several factors regulate the mechanism of Ziegler-Natta polymerization (e.g., electronic, kinetic, physical factors besides stereochemical ones) but, unfortunately, the attempts made to unify in an unique scheme (Boor, 1969; Hoeg, 1967; Kennedy and Langer, 1964; Reich and Schindler, 1966) the data coming from the different approaches adopted have so far been unsuccessful.

D. Conclusive Remarks on Terpolymerization Mechanism

The mechanistic data summarized and discussed in previous sections evidence that, at present, there is no possibility of conciliating different findings, coming from different authors, in an unitary scheme which takes into account all the confirmed data collected so far.

Coordinate mechanism finds more support, but behind the nominalism of the definition there is a lack of conclusive evidence and the presence of contradictory data which are not reducible to classical interpretations.

The study of EPDM (and also EPM) synthesis affords some contributions to the general knowledge of Ziegler-Natta catalysts and, on the basis of what has been said in previous sections, can be evidenced as follows.

1. The existence of several catalyst complexes, derived from equilibrium reactions from a limited number of initial species, may account for the heterogeneity of V-based catalyst systems and for the imperfect control of the propagation step.
2. The presence of potential cationic initiators may be explained on the basis of catalyst complexes equilibrium dissociations induced by particular modifications of the reaction medium (e.g., presence of Lewis base or other nucleophilic molecules, presence of adventitious protogenic substance, etc.).
3. Since the molecule of termonomer compete with other ligands, for coordination to V atom, its bifunctionality induces behavior as a bidentate ligand.

In particular when the electron-donor ability of the secondary unsaturation of termonomer is high, it tends to occupy a coordination vacancy in a relatively stable fashion, i.e., it inactivates a catalytic center. Probably some catalytic species are preferentially inactivated; however, the reduction of the type of active species may account for a narrower MWD of EPTM with respect to the corresponding EPM when branching or other side reactions are avoided.

4. As far as the ionicity of the active vanadium-carbon bond involved in EPM synthesis is concerned, nothing can be said so far on the basis of polymerization termination experiments carried out both with CH_3OH^3 and with $^{14}\text{CH}_3\text{OH}$. In each case, a polymer very low in radioactivity was found. The ambiguity of this kind of experiments was already stressed, even though, in other cases (e.g., use of a sufficiently strong Brönsted acid), the data were interpreted without doubts.

A general cationic mechanism governing the synthesis of EPDM's, assumed previously to explain a supposed *endo-exo* rearrangement of DCP (Meerwein-Wagner isomerization), does not find support in more recent results obtained employing true *exo*-DCP and several catalyst systems. The presence in Ziegler-Natta systems of catalytic species potentially able to initiate polymerization reactions with a mechanism different from the coordinate mechanism, e.g., radical or cationic, has been previously recognized when appropriate monomers are present. This may be also the case of termonomers used in EPDM synthesis when they are involved in side reactions induced by electrophilic species, being active before or after the formation of EPDM chains (cf. Section II D), since, up to now there is no clear evidence that two different mechanisms are simultaneous in this kind of polymerization.

6. Probably an almost-neutral character is associated with the transition metal-growing chain bond when EPDM is formed in the presence of syndiospecific (and aspecific) catalysts. In this case the steric control of the chain growth by the stereochemical configuration of the transition metal complex is greatly depressed and is obtained through the interaction of approaching monomeric unit with the growing chain end. Since there is no reason to reject some features typical of coordinate mechanism, in particular: the coordination of monomer, the high catalytic efficiency, the relatively elevated chain growth lifetimes, etc., the similarity to a coordinate-radical mechanism should be accepted only in first approximation, as an inadequate description since there is an absence of more precise information.

7. In conclusion, despite the enormous work made so far in the field of Ziegler-Natta polymerization, it can only be said that syndiospecific

catalysts, i.e., the best catalysts for EPDM synthesis, and perhaps also vanadium-based aspecific catalysts, act through a coordinate mechanism. Other work is necessary to give more precise definition, since at present there are no results which can indicate unequivocally a specific mechanism.

VI. OTHER RESEARCH RELATED TO EPDM

Some results concerning both post-modification of EPDM's and the study of macromolecules similar to EPDM ones have been published and, even though the amount of data available at present is, sometimes, quite scarce, it is worthwhile to mention them in this review as they are a logical extension of the investigations started with EPM and continued with EPDM.

A. Ethylene-Diene (EDM) and Ethylene-Triene (ETM) Copolymers

This type of copolymer began to be studied only few years ago with the aim of confirming the structure and the polymerization mechanism of EPTM based on IPTHI and IPDCP (Cesca et al., 1971a, b) (cf. Section III D), and of finding new materials for practical utilization (Carbonaro and Greco, 1969; Cucinella and Mazzei, 1971; Schnecko et al., 1971; Singer et al., 1971; Wismer and Prucnal, 1971). Whereas previous investigations (Natta et al., 1961c, 1962, 1964a), carried out on copolymers of ethylene with olefins containing internal or cyclic double bonds, anticipate, in some way, the successive work with dienes or trienes often containing cyclic unsaturations, more recently the research has acquired a more systematic character (Schnecko and Walker, 1971; Schnecko, 1972; Schnecko et al., 1971).

Generally, the diene or the triene involved in the copolymerization with ethylene, under experimental conditions very similar to the corresponding ones for the EPDM synthesis, shows the same reactivity features observed in the terpolymerization process. For instance, the type of double bond involved in copolymerization and the structure of the repeating unit derived from the comonomer, are very likely the same as in EPDM, whereas the extent of utilization of the diene or the triene and of side reactions, e.g., chain transfer, inhibition of catalyst sites, etc., is comparable.

In the case of IPDCP-ethylene copolymer when the concentration of the triene increases (samples containing up to 35 wt% of IPDCP have

been prepared), correspondingly the quantity of gelled material increases. EDM's based on ENB, DCP, MEHN were obtained free of crosslinked material by using significant amount of H₂ in the entire range of possible compositions.

However, while the catalyst systems which can yield EPDM are also effective in synthesizing EDM or ETM, they fail to copolymerize propylene with the same comonomers. This result confirms previous observations (cf. Section IV) which have recognized that the largest amounts of active centers are originated from ethylene molecules.

The small tendency of propylene to homopolymerize under the mild conditions of terpolymerization is also typical of some termonomers studied so far. Furthermore the repeating units of the homopolymers however obtained show structural features completely different from the repeating unit observed in EPDM or EPTM based on the same diene or triene. In fact, in the case of IPTHI (Cesca et al., 1970a) and IPDCP (Cesca et al., 1971b) only the conjugated dienic system is selectively attacked by Ziegler-Natta catalyst when they possess some acid character (Cesca et al., 1970b); otherwise no polymer is observed. Analogously, *endo*-DCP is homopolymerized, under mild conditions (concentration lower than 0.8 mole/liter) only through a Meerwein-Wagner rearrangement to the *exo*-form which takes place only in the presence of cationic species (Cesca and Priola). The mechanistic implications of these observations support furthermore the previous conclusions reported in Section V.

EDM's and ETM's having a low diene or triene content show an X-ray crystallinity of the polyethylene type which tends to decrease when the concentration of ethylene diminishes; at about 40–50 wt % of ethylene (ca. 12–20 mole % of comonomer) the crystallinity disappears.

The same trend has been observed for the $[\eta]$ values, thus suggesting the existence of chain-breaking processes due to the polyene, whereas the solubility of copolymer in hydrocarbon solvent has the opposite behavior due to crystallization of polyethylene segments.

The roentgenographic data and the spectroscopic investigations (IR, NMR, and sometimes, UV) have confirmed, in the case of IPTHI-, IPDCP-ETM, and DCP-EDM, the copolymer composition (given also by careful elemental analyses of a sufficiently large sample population).

Rough fractionation data, performed by extraction with boiling solvent, have yielded fractions of ETM differing in composition, but the absence of trace of polyethylene homopolymer in the initial materials could not be excluded.

In the case of EDM based on ENB, DCP, and MEHN, the random

distribution of monomeric units in the entire range of possible compositions has been inferred (Schnecko and Walker, 1971) from physical investigations (DTA and modulus-temperature measurements). However, no confirmation has been given of this conclusion, in the case of ENB- and MEHN-EDM, through fractionation and structural investigations. Analogously to what happens in EPDM and also EDM synthesis, the catalyst consumption follows the order MEHN > ENB > DCP, while the utilization of DCP is close to 80%. Under the experimental conditions adopted, i.e., high conversion and nonequilibrium conditions, an enhanced catalytic efficiency with respect to both homopolymers has been surprisingly observed during the EDM synthesis.

Recently, Hofrek et al. (1973) have investigated from a kinetic point of view the copolymerization of ethylene with 1,5-hexadiene in the presence of $3\text{TiCl}_3 \cdot \text{AlCl}_3$, and Et_3Al . By adopting a computerized nonlinear least square method for interpolating the conversion data, they obtained at 50°C the following reactivity ratios: $r_{\text{C}_2\text{H}_4} = 81.59$ and $r_{1,5\text{HD}} = 0.064$. Unfortunately, the copolymer properties have been described generically (crystalline sample with $T_m = 140^\circ\text{C}$ and MW above 10^6). The material was found to crosslink with dicumyl peroxide at 160°C with a performance 30% better than polyethylene.

MWD of EDM is rather similar (i.e., broad) to polyethylene than that of the polydiene obtained under comparable conditions; the latter is somewhat narrower. This result, together with the structural information deduced from spectroscopic investigations, may be regarded as supporting a similar coordinate mechanism for the co- and terpolymerization of α -olefins with a diene. However, under similar experimental conditions, the homopolymerization of some diene or polyene can follow a different mechanistic path (Cesca and Priola).

The introduction of a diene, such as ENB, DCP, or MEHN, into polyethylene chains induce a noticeable increase in T_g since it is, respectively, for EDM's based on the foregoing comonomers, 5, 14, and 30°C for a polyene content ranging between 12 and 20 mole %. The results indicate a decrease of the chains flexibility proportional to the bulkiness of the polyene. However EDM's do not show good elastomeric behavior, because their hardness and glass transition are too high. On the other hand, these materials can be used in coating applications since they afford transparency, flexibility, good adhesion, high gloss, hardness, hydrophobicity, impact resistance, possibility of pigmentation and easy crosslinking in the air and in the presence of Pb, Cr- or Mn-based catalysts.

With respect to EPDM- or polybutadiene-based coatings, EDM's furnish interesting products since they do not contain tertiary carbon atoms. Therefore, their oxidative aging is improved with respect to EPDM, mainly below 60°C, despite the relatively high level of unsaturation introduced in polymers used as paint films (Schnecko et al., 1971; Singer et al., 1971). In fact, oxygen uptake is a complex function of the polymer composition and some synergism between propylene and DCP has been evidenced in the study of low-MW DCP-based EPDM as air-dried films.

While noticeable difficulties have been encountered in the synthesis of random EPDM based on butadiene (cf. Section III A 1), the study of BD-based EDM was relatively easier and new, interesting materials were produced.

Two types of random copolymers, based on ethylene and butadiene, have been obtained by using the system $TiCl_4 \cdot 2P(C_6H_5)_3 - Et_2AlCl$ (1:10–30) prepared *in situ* in toluene and at the temperature of polymerization (35–70°C) (Carbonaro and Greco, 1969). The first type contains low amounts of butadiene (0.3–2 mole % of *trans*-1,4-units), shows a crystallinity typical of polyethylene, high MW, and a broad distribution of both MW and unsaturations. The second type has higher contents of *trans*-1,4-butadiene (16–59 mole %), low MW (usually \bar{M}_v is lower than 2000), X-ray crystallinity of polyethylene type up to 30–35% of butadiene, whereas for diene levels ranging between 40 and 60% again a noticeable crystallinity is evident (angle of maximum diffraction $2\theta = 21^\circ 30'$, while for a highly crystalline polyethylene the 200 reflection occurs at $2\theta = 23^\circ 95'$, but it is not attributable to *trans*-1,4-butadiene sequences. The results have been explained by assuming a possible isomorphism between *trans*-1,4-butadiene and methylene sequences.

The content of vinyl groups is usually less than 5% of total unsaturation. Oxidative degradation of copolymers containing 40–60% of butadiene shows the existence of butadiene and ethylene blocks as supported also by some IR data (absence of crystallizable methylene sequences but the presence of *trans*-1,4-butadiene sequences).

The catalyst system $V[N(C_2H_5)_2]_4 - EtAlCl_2$ (1:5–10) prepared *in situ* in aliphatic or aromatic hydrocarbons is capable of yielding, at temperatures close to 110°C, an ethylene-butadiene copolymer whose composition ranges between 1 and 80 mole % of diene (Cucinella and Mazzei, 1971b). A marked decrease in copolymer yield and MW was found by increasing the diene content of the feed, while the butadiene (present as a *trans*-1,4-unit in the chains) content of copolymer increased. However,

when the concentration of ethylene was low (partial pressure less than 5 kg/cm²) only polybutadiene was formed. Fractionation data suggest a fair homogeneous distribution of monomers in single fractions, while IR spectra indicate the presence of crystallized methylene sequences (up to a butadiene content of 70%) and only low amounts of vinyl groups (less than 3%). X-ray investigations show the existence of polyethylene crystallinity for ethylene contents higher than 60%, while for butadiene levels ranging between 40–60% a *trans*-1,4-polybutadiene crystallinity accompanies the polyethylene one. At higher levels of diene the copolymer shows only a crystallinity of polybutadiene type. Copolymers with very low content of butadiene (ca. 1 mole %) can be crosslinked with conventional recipes based on sulfur to yield interesting materials (Bailey et al., 1967; Pritchard et al., 1965).

All the data suggest a higher degree of randomness in monomer distribution with respect to copolymer obtained with Ti-based catalysts.

B. α -Olefin-Diene Alternating Copolymers

Contrary to EDM's and ETM's, much work has been made by Furukawa and coworkers on alternating copolymers of linear α -olefins (mainly ethylene and propylene) and conjugated diolefins (mainly butadiene and isoprene). Starting from the investigations on catalyst systems useful for the alternating copolymerization of electron acceptor monomers (acrylates, acrylonitrile, etc.) and electron δ monomers (among which conjugated dienes are a noticeable class of monomers) (Furukawa and Iseda, 1969; Furukawa et al., 1970, 1971), the experimental conditions for obtaining new, interesting synthetic rubbers have been disclosed (Furukawa, 1972a,b).

The recent publication of two reviews (Furukawa, 1972c; 1973) on alternating copolymers of diolefins and olefinic compounds allows one to discuss briefly the argument in this context.

The first alternating ethylene-butadiene copolymer was obtained by Natta et al. (1964b; Pasquon et al., 1967, p. 219) by using the catalyst system $(i\text{Bu})_3\text{Al}-(i\text{Bu})_2\text{AlCl}$ –anisole– VCl_4 (2:2:2:1), but the yields and MW were quite low and the equimolar copolymer (containing, however, some irregularities, i.e., short homosequences) was only the minor component of a complex mixture of macromolecules containing mainly *trans*-1,4-polybutadiene and polyethylene. The result evidences the difficulty of obtaining random or alternating copolymer from olefins and conjugated diolefins, as stressed in Section III B. This conclusion has been

confirmed by the more recent work of Furukawa and Hirai (1972) who obtained copolymers whose composition and structure are not unique and, however, are strictly dependent on the feed composition, flow rate of monomers and molar ratio of catalyst components. For instance, by using the system $(i\text{Bu})_3\text{Al}-\text{TiCl}_4$ -benzoic acid (1:2.7:4.3) at -25°C , a mixture of alternating (86%) and random ethylene-butadiene copolymer is obtained; the former contains the diene monomer as a prevalent *trans*-1,4-unit besides some 1,2-units. MW's are, however, rather low.

More favorable is the case of the copolymer based on propylene and butadiene which can be obtained with an alternated structure (220 MHz NMR spectra and X-ray diffraction data) by different V- or Ti-based Ziegler-Natta catalysts (Kawasaki et al., 1969; Furukawa et al., 1969, 1972; Suzuki et al., 1971; Furukawa and Hirai, 1972a). The systems are generally based on three components in order to control the acidity of both the transition metal compound and the organometallic Al derivative, to increase the efficiency of the catalyst, to avoid the homopolymerization of butadiene to 1,4-*trans* or 1,2-polymers and to attain high MW's. Sometimes carbonyl compounds or Lewis bases are added to the catalyst. Typical examples of such systems are: $\text{VOAcac}_2-\text{Et}_3\text{Al}-\text{Et}_2\text{AlCl}$, $\text{VOCl}_3-\text{VO}(\text{OEt})_3-\text{Et}_3\text{Al}$, $\text{TiCl}_4-\text{Et}_3\text{Al}$ -benzophenone. However, the catalyst is prepared at very low temperatures (i.e., ca. -70°C) and the polymerization is also carried out at low temperature (between -30 and -40°C) in aromatic solvents. The copolymer prepared under such conditions is always equimolar, regardless of the feed composition, even though it is sometimes accompanied by small amounts (some percent) of polybutadiene. The copolymer contains *trans*-1,4-butadiene units and considerable amounts of vinylidene groups as evidenced by NMR and IR and are due, very likely, to hydride elimination from the propylene units of the chain ends and formation of metal hydrides. From these observations an anionic coordinate mechanism governing the copolymerization process has been inferred. The alternating coordination of propylene and butadiene depends on the availability of coordination sites which, alternately, are occupied by butadiene (bidentate coordination of monomer and π -allyl bonding of the last dienic unit of the growing chain) or propylene (monodentate coordination of monomer and σ -bonding of the last α -olefin unit of the chain). Such an interpretation is supported also by the type of products evolved from the hydrolysis of the catalyst ($\text{VOAcac}_2-\text{Et}_3\text{Al}$ -allyl bromide) treated with small amounts of monomers. In fact, the π -allyl group prefers propylene (formation of 2-methyl-1-pentene but not heptenes),

while the σ -bonded ethyl group (from the catalyst) prefers butadiene (formation of 1-hexene). Furthermore, since butadiene is much more reactive than propylene in the initiation, it is introduced first in the polymer chains.

The mechanistic conclusions cited above apparently do not hold when the catalysts are used at relatively high temperature (Furukawa et al., 1973a), as random butadiene-propylene copolymers, having a wide range of propylene content, are yielded by the catalyst system $TiCl_4-Et_3Al-COCl_2$ working at room temperature and in tetrachloroethylene. In reality, the randomness of the copolymer, evidenced by fractionation and degradation data, is in contrast with the value of the monomer reactivity ratios ($r_{C_4H_6}=6.36$ and $r_{C_3H_6}=0.42$) which may suggest some degree of blockiness when the active species were homogeneous.

The evaluation of the type of active centers might elucidate the behavior of these complex systems, whose activity and specificity was found markedly dependent on the valence of the transition metal atom present in catalyst complexes which, in turn, depends on the relative molar ratios of the catalyst components (cf. Table XXIX and Fig. 45).

TABLE XXIX

Structures of the Catalysts Obtained from the System $VOAcac_2-Et_3Al-Et_2AlCl$
Used in the Copolymerization of Propylene and Butadiene

ESR signal	Catalyst	Result of copolymerization	
		region ^b	type of copolymer
No signal	$V^{2+}-Cl-V^{2+}$	a	alternating
Eight-line	unassociated V^{2+}	b	containing 1,2-polybutadiene
Broadline	$V^{2+}-V^{3+}$	c	containing <i>trans</i> -1,4-polybutadiene
No signal	$V^{3+}-V^{4+}$	d	random

^aReprinted with permission from Furukawa et al., 1972.

^bWith reference to Figure 45.

However, by changing the type of diene and the molar ratio of the monomers in the feed, these ternary Ziegler-Natta systems show a polyfunctional character (cf. Sections II B and V D). In fact, when isoprene and propylene (ca. 1:1) are allowed to react in the presence of the system $VOAcac_2-Et_3Al-Et_2AlCl$ (1:5:5) at $-30^\circ C$, an alternating copolymer is formed (NMR and ozonolysis data), while no random copolymerization or homopolymerization of isoprene or propylene occurs (Furukawa, et al., 1973b). At the same time relevant amounts of isoprene dimer (3,7-

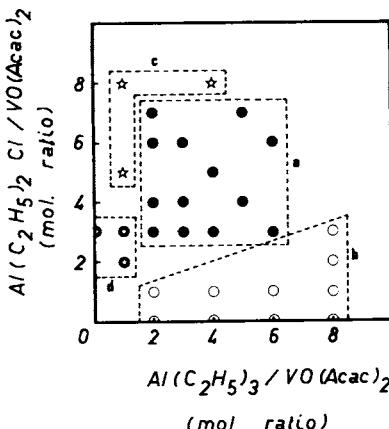


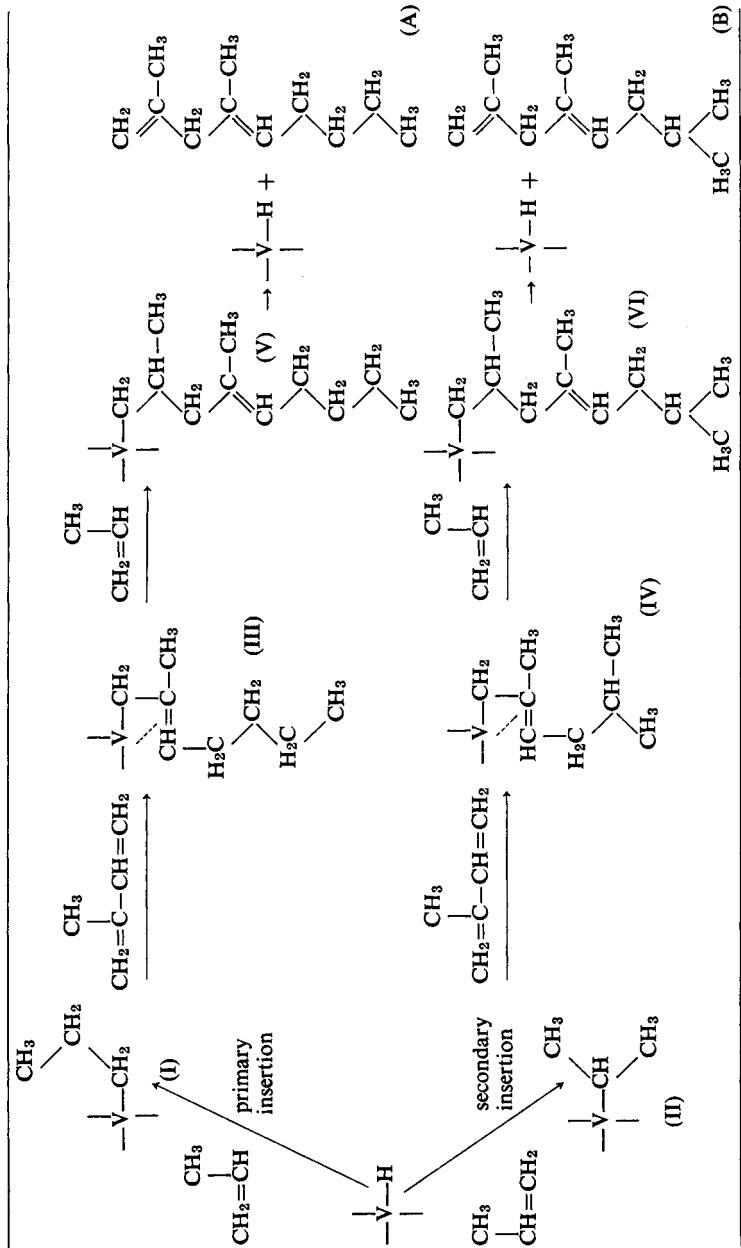
Fig. 45. Correlation of the type of copolymer obtained with a mixture of butadiene and propylene in the presence of the system $VOAcac_2-Et_3Al-Et_2AlCl$ ($Al/V = 6$). Cf. Table XXIX. (Reprinted with permission from Furukawa and Hirai, 1972a).

dimethyl-2,4,7-octatriene) and trimer are formed, whereas in the presence of an excess of propylene a noticeable quantity of new cooligomers has been observed. They are: 2,4,7-trimethyl-1,4-octadiene and 2,4-dimethyl-1,4-nonadiene (both *cis* and *trans* isomers).

Several interesting mechanistic conclusions can be drawn from these results. Namely:

1. At least two active species are formed and their relative amount is approximately comparable. One of them is effective for the alternating copolymerization of propylene and isoprene, the other for the oligomerization of isoprene.
2. Cooligomers composed of two propylene units and one isoprene unit are formed, in particular when the feed is richer in propylene. At the same time the formation of isoprene dimer and trimer decreases. The structure of the cooligomers gives an idea of the action mechanism of catalyst which firstly coordinates and inserts a propylene molecule on a $-V-H$ bond. This insertion can be primary or secondary (cf. Section II H 3 and Section V) leading, respectively, to intermediate (I) and (II) of Table XXX. Successively, an isoprene molecule always adds as 1,4-unit having the first carbon atom bonded to V and the fourth carbon to the propylene unit previously inserted on the catalyst site (intermediate (III) and (IV)). Finally, the second propylene unit always adds via primary insertion yielding intermediates (V) and (VI) which, through

TABLE XXX
Mechanism of the Cooligomerization Reaction of Propylene with Isoprene
 Et_2AlCl^*



^aFrom Furukawa et al., 1973a.

a hydride shift respectively, 2,4-dimethyl-1,4-nonadiene (A) and 2,4,7-trimethyl-1,4-octadiene (B) are formed.

The absence of other undecadienes, i.e., isomers of dienes (A) and (B), supports the reaction pathway of Table XXX which is in agreement with the data collected by Zambelli et al. (1972) in studying the microstructure of EPM. As stressed in Section V the formation of both the cooligomers (A) and (B) is due, probably, to steric effects rather than to different degrees of ionicity in the $\text{--V}^{\pm}\text{H}$ and $\text{--V}^{\pm}\text{C}^{\pm}\text{--}$ bonds. In fact, the first insertion of propylene on the $\text{--V}^{\pm}\text{H}$ bond does not occur selectively when the catalyst site can accommodate in its immediate proximity the methyl group of the propylene unit bonded through the tertiary carbon atom (intermediate (II) of Table XXX). Successively the presence of the growing chain favors the primary insertion of propylene. However, the primary insertion of the first propylene molecule is favored with respect to the secondary one.

3. Cooligomers higher than (A) and (B) have not been observed, hence it is not sure that the alternating copolymers are originated through the reaction scheme depicted in Table XXX.

4. The addition of Lewis bases (as $\text{P}(\text{C}_6\text{H}_5)_3$ or pyridine) to the catalyst system hinders the cooligomerization reaction, but not the oligomerization of isoprene which seems to occur at active sites different from those which are responsible for the alternating cooligomerization (and, perhaps, for the alternating copolymerization).

The copolymerization of butadiene with other linear α -olefins, i.e., 1-butene, 1-pentene, 1,7-octadiene, 1-dodecene, seems to proceed with a similar mechanism since, in some cases, an alternating copolymer has been isolated (1-butene-isoprene). On the contrary, 2-butene (probably a mixture of *cis* and *trans* isomers) did not enter *trans*-1,4-polybutadiene chains (Furukawa et al., 1972).

The difficulties encountered in copolymerizing acetylene with a conjugated diene instead of an α -olefin, are proved by the absence of data on this subject. Only very recently liquid-waxy copolymers have been obtained from acetylene and butadiene by using nickel carboxylates or nickel complexes in conjunction with Et_2AlCl , interacted at 20–30°C in toluene for 10–20 min and used at room temperature (Furukawa et al., 1973c). The copolymer composition and catalyst activity have been found dependent on the preparation conditions of catalyst. However, a linear copolymer can be obtained (IR and NMR data) which show

a prevalent unsaturation content of *cis*-double bonds (average 82%), *trans*-double bonds (11%) and vinyl-double bonds (7%). Analysis of NMR spectra indicates the presence of butadiene and acetylene dyads, acetylene-butadiene sequences, and acetylene isolated units. Long acetylene sequences, i.e., higher than triad, are substantially absent. The dyad fractions evaluated from NMR agree with those calculated according to Bernoullian statistics, hence these copolymers are mostly random; furthermore, rough fractionation data suggest a homogeneous composition.

C. Post-Modifications of EPDM's or EPTM's

While from the standpoint of EPDM's stability the reactivity of their unsaturations can be a shortcoming (cf. Section II B), the same property is very useful for post-modification reactions. They are, generally, carried out after the synthesis of terpolymers.

Two main types of post-modifications have so far been investigated, i.e., the grafting onto EPDM chains of radical initiated vinyl monomers (e.g., styrene and acrylonitrile) and the halogenation of the allylic positions of EPDM unsaturations. But other reactions can be feasible as, for instance, the introduction of appropriate functional groups or other types of additions or grafting reactions. Of course, these modifications depend on the reactivity of unsaturation present in EPDM; however the disclosure of new polymers or the improvement of older materials seems easily attainable through the appropriate use of post-modification reactions (cf. below Section VI C 2).

1. Grafting of Styrene-Acrylonitrile onto EPDM

The interest in ABS-like resins (Bamford and Eastmond, 1964) stems from their interesting property of shock absorbency obtained by producing materials which show a maximum of impact strength with a minimum loss of mechanical rigidity and processability. The polymeric systems proposed for this purpose have to possess the properties of plastic materials modified by an appropriate presence of an elastomeric phase.

Actually, due to incompatibility of such different polymers, a two-phase system is realized by utilizing either polar forces (as it happens, for instance, in the case of PVC and acrylic elastomers blends) or the graft of pendant rigid chains onto an elastomeric backbone. In this way it is possible to obtain a sufficient degree of compatibility through ap-

properite rubber particles size and distribution in the plastic matrix (Bender, 1965; Hageman, 1969; Keskkula et al., 1971).

The excellent behavior of ABS resins makes them suitable for outdoor applications, since the aging is markedly reduced under oxygen and UV radiations. It has been demonstrated that the unsaturation of polybutadiene chains are responsible for such degradation (Gesner, 1965) and on the basis of this conclusion the use of a more stable EPDM as rubber phase has been investigated.

As it will be seen below, the most interesting attempts at preparing ABS-like resins imply, as post-modification of EPDM, a real copolymerization reaction between styrene (S), acrylonitrile (AN), and the unsaturation of EPDM. From a general standpoint, grafting reactions are complicated by chain transfer and radical recombination reactions which have been evidenced also in the attempts of grafting EPM with several radical systems and monomers (Natta et al., 1968).

In the case of EPDM, some difficulties have been encountered at the synthesis level because of the low content of double bonds present in EPDM (generally 3–10 C=C per 1000 C atoms) in comparison with *cis*-1,4-polybutadiene (ca. 200 C=C per 1000 C atoms) or SBR copolymers, the elastomers normally used to prepare ABS resins.

However, by choosing an appropriate reactive unsaturation, for instance ethylidene introduced by ENB, it has been found that ca. 10–12 C=C per 1000 C atoms afford a sufficient amount of points to be attacked by grafting reaction, in order to prepare EPDM-SAN copolymers with well-balanced properties.

It is surprising that the unsaturation introduced by 1,4-HD, having the same number of allylic hydrogens as the ENB secondary unsaturation, has been found unable to yield copolymers with a good degree of grafting. Evidently the strain of norbornene structure also exerts its influence at a more distant range than that normally considered (Rodd, 1953), e.g., on the unsaturation partly outside the tricyclic structure. A similar indication has been found, in a different context, by studying the reactivity of the conjugated diene system of IPTHI and IPDCP (Cesca et al., 1971a). In fact, the latter triene shows a higher homopolymerization rate which has been attributed to a long range influence of the norbornene structure on the diene system.

Very high degree of grafting have been observed (Ital. Pat., 1973) with IPDCP-based EPTM; in fact, 0.7–1.0 wt % of triene is sufficient to obtain the same content of styrene-acrylonitrile copolymer grafted onto EPDM containing 8 wt % of ENB. Also the mechanical and some

general properties of these ABS-like materials based on IPDCP-EPTM are similar and sometimes better (e.g., accelerated and natural weathering) than EPDM-SAN copolymers. Very likely, the low content of unsaturation is responsible for such behavior. Furthermore, interesting features have been disclosed in this class of impact resistant materials when the ethylene content of the starting elastomer (other EPTM's can be used instead of IPDCP-based terpolymer) is increased and appropriate synthesis conditions are adopted.

The excellent behavior of ENB is confirmed by MNB which, however, furnishes a degree of graft always lower than the former diene at a given level of unsaturation. On the contrary, DCP has been found of little utility for this type of reaction.

Another difficulty has been encountered in the technique of graft polymerization since the usual emulsion technique of preparing ABS yields too low a degree of graft. This means the absence of the necessary compatibility between the elastomeric and the rigid phase when an EPDM latex is substituted for polybutadiene one.

Some attempts have been made to overcome this drawback, either by using multifunctional crosslinking agents in order to improve the grafting reaction (U.S. Pat., 1969) or by working with a bulk suspension technique (U.S. Pat., 1970e). But in the latter case the polymeric material becomes insoluble already after incorporation of only 1% of AN, and hence the distribution of the two polymeric phases is unsatisfactory.

More recently, it has been discovered (U.S. Pat., 1970d) that appropriate mixtures of aliphatic and aromatic solvents are an excellent medium for performing the graft reaction of S and AN onto EPDM chains with high yields and maintaining sufficiently low viscosities of the reaction mixture. This can be accomplished since the polymerization process does not take place in solution but is very similar to an emulsion technique. In fact, the SAN copolymer separates in the hydrocarbon medium initially as homogeneous, in the form of droplets, thus the kinetic features of the process allows quantitative conversions in a few hours at 70–80°C. Furthermore, the solution precipitation procedure assures a satisfactory dispersion of the rubber phase in the plastic matrix and hence well-balanced properties are observed in the resulting EPDM-SAN copolymers which compare very favorably with typical ABS resins.

A detailed investigation (Meredith, 1971) of main factors regulating technological and aging properties of EPDM-SAN copolymers has shown that the notched impact strength is proportional to the degree of grafting. While the evaluation of mechanical and rheological properties

of EPDM grafted copolymers containing 11% of EPDM evidences excellent performance both for extrusion grade materials and also for injection molding applications, the examination of aging properties clearly shows the superior behavior of EPDM-SAN in comparison with ABS. This superiority has been found effective under severe processing conditions, accelerated thermal treatment, and outside exposure. Due to the presence of both antioxidants and UV stabilizers in ABS, the resistance to aging observed in EPDM-SAN resins is not obtained with ABS.

2. *Halogenation of EPDM*

It is long since known that halogenation of butyl rubber (IIR) furnish a polymer with improved characteristics with respect to the parent material, thus some of its long-standing shortcomings have been overcome. Halogenated IIR shows, in fact, compatibility of curing with highly unsaturated elastomers, increased adhesion to natural rubber and metals, and also greater resistance to ozone (Morissey, 1958).

Despite the difference in structure, some analogy of behavior in technical applications exists between IIR and more common EPDM's, therefore is not surprising that attempts of halogenation and successive dehydrohalogenation have been carried out several years ago on EPM (Crespi and Bruzzone, 1961b). But the aim of those first researches was to make possible vulcanization of EPM by means of sulfur through the introduction of low amounts of unsaturations and not of ensuring cure compatibility. Only more recently the halogenation of EPDM (Belg. Pat. 1964) has been accomplished in order to introduce halogen atoms in allylic positions. Therefore, the situation of halogenated IIR has been simulated in this type of post-modified EPDM, whose resulting behavior is very similar to that observed in the former polymer (Dontsov, 1969; Morissey, 1971).

The best results have been obtained with bromine and chlorine, since fluorine is too reactive and apparently breaks the polymer chains, at least in the case of IIR, whereas iodine reacts very slowly. Also interhalogenic compounds, as ICl or IBr, afford an excellent halogenating ability. Just the knowledge of the mechanism of interhalogenic compounds in adding to double bonds (Gossl, 1960) has permitted the description of the pathway of introduction of a halogen atom in an allylic position. Initially the addition of the halogen derivative, e.g., ICl, to the double bond yields a dihalide derivative which, successively, decomposes by splitting out a molecule of HI and regenerating a "new"

double bond, since its position is shifted one C atom. As a consequence the "new" position of the halogen atom is allylic.

Alternatively, in the case of chlorinated IIR, Baldwin et al. (1961) have proposed a different mechanism, which is based on the proton abstraction by the chloride anion; the result is again a double bond shift, while the halogen cation substitutes in the α position of the unsaturation.

In the case of 1,4-HD-EPDM studied, and containing 10–20 C=C per 1000 C atoms, the splitting out reaction after the halogenation, carried out either with molecular halogens or halogenating agents, such as *N*-bromosuccinimide, etc., is not spontaneous and has to be catalyzed by UV radiations or by temperature (Morissey, 1971). However, the covulcanization tests of halogenated EPDM with natural rubber, indicate that both unsaturation (ca. 3–4 C=C per 1000 C atoms, according to iodometric titration) and halogen (ca. 5 wt %) are necessary to obtain the best results. Whenever either the halogen content or the unsaturation level are lowered, the covulcanization degree is also depressed. Evidently, these data support the proposed mechanism of the halogenation reaction and suggest also a complex vulcanization process in which the action of ZnO is decisive in forming the network by reacting with the halogen atoms (Dontsov et al., 1969).

Among the dienes investigated the best covulcanization results have been observed with ENB-EPDM; a fair behavior has been shown by 1,5-cyclooctadiene and 1,4-hexadiene, whereas DCP-based EPDM compares less favorably.

Brominated EPDM, in comparison with chlorinated samples having the same amount (wt %) of halogen and of unsaturation, shows clearly superior mechanical properties. Blends of highly unsaturated elastomers, containing 20–30 parts of brominated EPDM and cured with sulfur have shown excellent ozone resistance. Also the flexing properties of the blends were found very satisfactory for the best stress-strain properties; this happens for amounts of halogen near 5 wt %, in correspondence to the best compatibility. On the contrary, the heat build up shown by flexometer is significantly higher when it is compared with the components of the blend. It is felt that, by optimizing the curing system, the physical properties should result as better balanced.

Remarkable adhesion is introduced in blends based on natural rubber and brominated EPDM, in comparison with the same blends containing common EPDM's. The results concern adhesion to steel, adhesion to a natural rubber tire carcass compound and building tack, which is very poor in EPDM alone. This preliminary experimental evidence is more

significant if one bears in mind that previous attempts at improving EPM and EPDM tack, either by using plasticizers, tackifiers, adhesives or blends with other polymers, have yielded very poor results (Blümel, 1968).

It is worth noting that halogenated polymers can act as coinitiators of cationic systems when they are in the presence of alkyl aluminum halides (Kennedy, 1971; Kennedy and Smith, 1972; Thame et al., 1972). By using monomers capable of initiation by such a mechanism, e.g., olefins, vinyl ethers etc., new types of grafted polymers can be produced.

Finally, also anionic living polymeric systems, as for instance polystyryllithium, can graft onto halogenated chains, as it has been shown in the case of chlorinated EPM, (Ueno et al., 1968).

On the other hand, the metallation of EPDM's based on ENB, 1,4-HD, and methyl-EHN (cf. Section III A 9) has been attempted with some metallating agents (Hawkins et al., 1973). The best results have been obtained with the system *n*-butyl lithium plus *t*-butoxyl potassium. However, several difficulties have been encountered as, for instance, the purification of EPDM, the use of diluted solutions of elastomer (few percent of EPDM to avoid viscosity problems) and the small reactivity of the substrate. Therefore, even though in principle interesting modifications of the starting EPDM might be envisaged through the anionic grafting of carboxylic groups, rigid branching (e.g., polystyrene blocks), or elastomeric sequences compatible with highly unsaturated elastomers (e.g., polybutadiene branches), in practice the degree of grafting is rather low even after several hours of reaction. Furthermore, the number of side chains per macromolecule of starting elastomer reaches the average number of 2 with difficulty, so that the technological properties of the resulting modified EPDM are not fully satisfactory.

D. EBDM and Quaterpolymers

Almost all the work carried out on elastomeric olefins copolymers has utilized the two lowest olefins, i.e., ethylene and propylene. Aside from historical reasons, there are economical and chemical facts which can justify the present situation. The economical reasons are founded on the simplest method of separation of the olefin C₃ fraction, which comes from the steam cracking of virgin naphtha, with respect to the C₄ fraction which includes other two isomers besides the α -olefin; furthermore, the weight of one mole of 1-butene is 33% higher than that of propylene. But the chemical properties of 1-butene give the heaviest weight in deciding the opportunity of coupling this α -olefin with

ethylene. In fact, the reactivity of 1-butene in copolymerization with ethylene is more than one order of magnitude lower than that of propylene (Natta et al., 1963b; Zambelli et al., 1968a). This drawback might be counterbalanced by some properties due to the presence of the 1-butene molecule as, for instance, lower values of T_g and of the macroscopic density for EBM with respect to EPM having the same molar composition (Gromova et al., 1967; Seidov and Dalin, 1971); or by the necessity of lower amounts of α -olefin to make the resulting copolymer amorphous (Shirayama et al., 1972; Seidov and Dalin, 1971). Furthermore, the trend observed in poly- α -olefins for the tendency to crystallize or their tackiness when the number of C atoms of the side chains increase, might encourage the study of EBDM, since it is well known that in EPDM the tack property is largely unsatisfactory (Blümel, 1968).

Also terpolymers based on ethylene, 1-hexene, and ENB or DCP (EHDM) have been taken into account and prepared with the system VAcac₃-iBu₂AlCl (Seidov et al., 1972); only when the reaction temperature was low, i.e., in the range -10/-20°C, an elastomer soluble in *n*-heptane was obtained ($[\eta] = 2.7 \text{ dl/g}$). However, EHDM based on DCP has much lower solubility than ENB-EHDM. In any case EHDM's are vulcanizable with sulfur and accelerators, but their properties have not been compared with those of the corresponding EPDM or EBDM. Seidov et al. (1971) have synthesized DCP-based EBDM by working in liquefied 1-butene with VAcac₃-iBuAlCl, but they have not described the properties in detail.

Actually, EBDM's based on DCP or 1,4-HD and having low MW have been found (Blümel, 1968) very similar to corresponding EPDM's as far as the mechanical properties of vulcanizates are considered, whereas, a significant improvement (ca. 30-50%) of adhesion properties is observed when 10 parts of EBDM are added to 90 parts of EPDM. It is worth noting that blends of EPDM's yield a much lower increase in the same property.

The gain in the vulcanization rate of blends of EPDM's in which part of the slow curing terpolymer is substituted by a fast-curing EPDM is quite obvious. The result of quaterpolymerizing two α -olefins and two dienes is surprising. In fact, the resulting elastomer derived from the quaterpolymerization of ethylene, propylene, DCP and MBNB (cf. Table II) is faster curing than the mechanical blends of two EPDM's based on the same dienes (Blümel, 1968).

Some more interesting preliminary information is contained in some patents (Ital. Pat., 1972) concerning quaterpolymers utilizing moderate amounts, i.e., 5-8 wt %, of slow-curing and easy available diene (e.g.,

DCP) and very low quantities, i.e., ca. 1 wt %, of highly reactive trienes containing the cyclopentadienyl unsaturation as pendent group (cf. Section III B 5).

In fact, as is shown in Figure 46, some tensile properties of EPTM containing 0.12 mole/kg of MCNM are not fully satisfactory because of the too low levels of unsaturation. Such a drawback can be overcome by associating another diene, possibly very cheap but reactive in the polymerization step, as DCP does. The performance shown by such a class of quaterpolymers in the curing process is very interesting, as illustrated by Figures 47 and 48.

They have been found covulcanizable in all the range of mixing with highly unsaturated elastomers. The resulting vulcanizates show, practically, the same properties as EPDM's having high contents (ca. 10 wt %) of the best termonomers so far studied.

The mutual interference of two polyenes in quaterpolymerizing with ethylene and propylene has been observed (Cesca et al., 1974c), as expected. Generally, the more reactive polyene modified the usual percentage of utilization of the other polyene. However, the fractionation data show that true quaterpolymer are obtained with common catalysts and under normal conditions.

Recently, other patents have been published concerning quaterpoly-

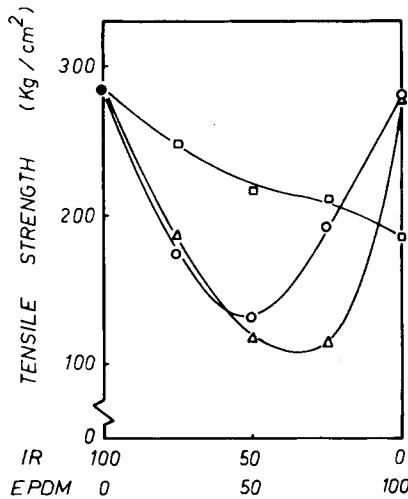


Fig. 46. Covulcanization of IR with EPTM or EPDM. Conditions and products same as in Figure 41.

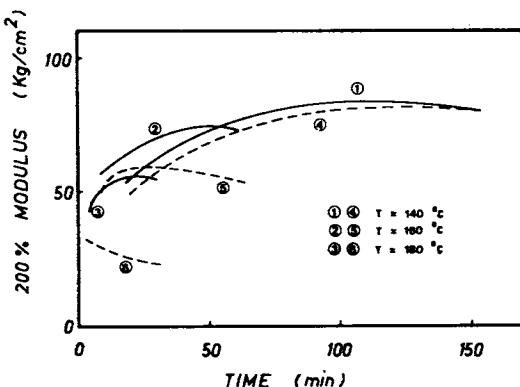


Fig. 47. Covulcanization kinetics at different temperatures of blends of a quaterpolymer containing *endo*-DCP and triene (XXX, a) (respectively, 10 and 0.96 wt %) and *cis*-1,4-polyisoprene (IR). Reference (broken lines) to 5-ethylidene-2-norbornene-based EPDM (ca. 10 wt % of ENB) IR blends. Recipe: quaterpolymer (or EPDM) = 75; IR = 25; HAF = 80; Circosol-4240 = 40; ZnO = 5; S = 2.1; AO-2246 = 1; stearic acid = 1; Vulkacit = 1.6 (at 140°C), 1.2 (at 160°C), 0.8 (at 180°C). Reprinted from Cesca et al., 1974c with permission of Marcel Dekker Inc., New York.

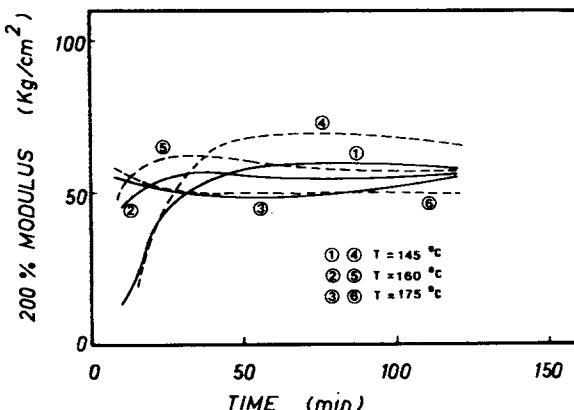


Fig. 48. Covulcanization kinetics at different temperatures of blends of IR and quaterpolymer containing *endo*-DCP and triene (XXX, a) (respectively, 3.4 and 0.70 wt %). Reference (broken lines) to IR/ENB-EPDM (ca. 10 wt % of ENB). Recipe; quaterpolymer (or EPDM) = 65; IR = 35; FEF = 45; Circosol-4240 = 18; S = 2.5; stearic acid = 1.7; ZnO = 5; BLE = 1.5; Vulkacit = 0.8; retarder W = 0.2. Reprinted from Cesca et al., 1974c with permission of Marcel Dekker Inc., New York.

mers containing ethylene-propylene and based, generally on two dienes having a different degree of efficiency during the vulcanization process (Germ. Offen., 1970). But, unfortunately, no characterization work on this kind of complex macromolecular structures has so far been published. Only an interesting paper (Solf and Herrmann, 1971), devoted to the synthesis, polymerization conditions, fractionation, and spectroscopic characterization of quaterpolymers based on ethylene, propylene, DCP and acrylic esters, has been recently reported. Despite the use of coordinate catalyst, the random enchainment of the four comonomers and the high conversion of acrylic esters involved (previously complexed with Lewis acids, e.g., AlCl_3), the type of polymer obtained is somewhat outside the purpose of the present review and hence they will not further discussed. The incorporation of small amounts of acrylic acid in EPM chains (and also in polyethylene and polypropylene) has been accomplished recently on industrial basis (*Mod. Plast. Int.*, 1973).

However, it is interesting to observe that mixtures of alkyl methacrylates or alkyl acrylates with 4-methyl-1-pentene in the presence of a $\text{VOCl}_3\text{-Et}_3\text{Al}$ system (3:1 and $T = 20$ or -78°C) do not yield random copolymers, suggesting that the polymerization of the two monomers takes place by different mechanisms (Chiellini and Nocci, 1973).

Indeed, a coordinate mechanism for methyl methacrylate does not seem very probable in the presence of Ziegler-Natta catalysts (cf. Section V C). Therefore, it is decisive in order to attain an unique mechanism in the copolymerization of α -olefins and acrylic monomers, that the nucleophilicity of the ester group is neutralized by complexing it with a Lewis acid to avoid the reaction of carbonyl group with metallorganic species or, more generally, the interference of acrylic monomers with coordination sites.

VII. INDUSTRIAL PROCESSES

EPDM manufacturing is done industrially in plants working with continuous processes. The superiority of continuous technique with respect to batch procedure has been already recognized in laboratory experiments (cf. Section II E) to minimize fluctuations in the concentration of system components and to reudce any cause of heterogeneity in terpolymer.

Actually, two different types of processes for EPDM manufacturing have been proposed: a solution process and a suspension process, which will be discussed in next sections. However, there are some common

features necessitated by the particular characteristics of the polymerization under examination and they will be dealt with preliminarily. On the other hand, it is obvious that many details of any process depend on the specific solutions adopted by each manufacturer, e.g., type of termonomer and of catalyst, degree of conversion, finishing step, etc. An accurate analysis of several engineering processes so far proposed and a thorough discussion of two main procedures (i.e., solution and suspension) have been reported (Magovern, 1970). From a general point of view the following statements can be pointed out.

1. A fundamental prerequisite of all the components of the terpolymerization system is that they have high purity, since many impurities are effective at levels of 10 ppm, in particular any molecule containing oxygen, sulfur, or active hydrogen atoms.

The ability of these molecules to modify the catalyst components and active centers (at higher concentrations they deactivate active sites), requires a continuous, rapid monitoring of their concentration.

2. Another critical operation is the control of feed and catalyst component flow rates which are the principal variables controlling the polymer homogeneity. The solution proposed to assure the most efficient control of the gaseous monomer composition is one element of diversification between the industrial processes so far studied (cf. Section VII B).

3. The high viscosity of EPDM solutions requires the adoption of particular reactors to minimize mass and heat transfer effects and any heterogeneity source (cf. Section II F).

In order to overcome a part of these difficulties, some engineering process developments have been made: a novel wiped-film reactor (U.S. Pat., 1967b); polymerization in a cascated reactor system with a premix zone (U.S. Pat., 1967, 1969); an evaporatively cooled reactor system (U.S. Pat., 1963) have been claimed (Section VII B).

4. In order to obtain the best efficiency from the catalyst used, a series of reactors can be adopted where appropriate levels of activators, modifiers, etc., can be introduced.

Also the termonomer utilization should be improved by such a system of reactors (see below) used either as a series or a parallel arrangement.

However, different kinds of terpolymer would be produced by every reactor, thus the resulting terpolymer might be a blend of macromolecules differing both in composition and MW.

5. Devices which can guarantee a very quick catalyst quenching should be introduced to avoid side reactions (formation of branching

and gel), in particular when the acidity of the catalyst or the nucleophilic character of termonomer is prominent (cf. Section II D).

6. Generally the heat of polymerization (ca. 600 kcal/kg of EPDM) is dissipated through refrigerating systems (solution process) or by utilizing the vaporization heat of liquefied monomer (suspension process).

7. Beside solvent, monomers are also subjected to recycling for economic reasons. While ethylene conversion is always high, large quantities of propylene (and solvent, when used) must be recovered, dried, separated, and reutilized.

8. The utilization of termonomer, i.e., its consumption to introduce unsaturation into EPDM chains, depends on several factors; for instance: (a) its intrinsic reactivity in entering into polymer; (b) tendency to side reactions; (c) polymerization conditions (e.g., residence time, presence of activators and MW regulators, overall concentration of monomers, etc.); (d) concentration of unsaturation, and also of olefins in EPDM produced.

Therefore, all these factors are to be carefully considered, in addition to the termonomer price and its vapor pressure (i.e., a determining factor in recycling), before adopting the more suitable plant solutions. For instance, when the utilization of termonomer is sufficiently high and low levels of unsaturation are enough to give good vulcanization properties to EPDM, it may be convenient to neglect recycling of the third monomer.

9. The removal of catalyst residues trapped in the polymer solution is an important step of EPDM manufacturing, since the level of ashes influence aging and also mechanical and electrical properties of the rubber, even when stabilizers are added to polymer.

10. While several industrial plants have been built recently for the synthesis of high density polyethylene (Forsman, 1972) and polypropylene (*Eur. Chem. News*, 1973) which operate with highly efficient catalyst systems, there are only patent indications so far for the production of EPM and EPDM with high yields (Belg. Pat., 1972 and U.S. Pat., 1971).

A. Solution Process

Several points discussed above have found possible solution in the flow sheet reported in Figure 49 which refers to a continuous process for an EPDM-based on DCP and produced in hexane (Brennan, 1965).

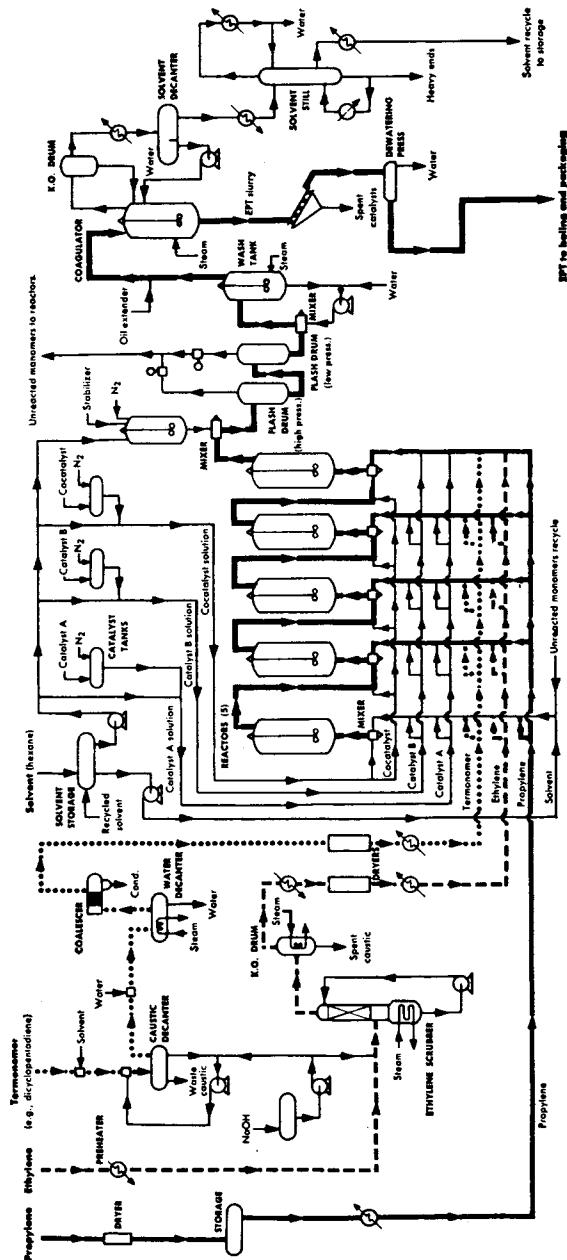


Fig. 49. Flow sheet for an industrial plant manufacturing EPDM through a solution process. Reproduced from Brennan, 1963 with permission of McGraw-Hill, Inc., New York.

All-electronic instruments are supplied to obtain instantaneous readouts of analysis and to quickly restabilize the preset equilibrium conditions in the system where sharp upsets would occur. The polymerization reaction is performed in a series of reactors, fed by in-line mixers which collect all streams. Polymerization is carried out at 15–18 kg/cm² and T = 38°C. A refrigeration system cools the reactors. The removal of unreacted monomers is obtained through two flashing steps operating one at 3 kg/cm² and the other at 0.1 kg/cm². The washing and steam-stripping procedures are performed by mixing the polymer stream with deaerated water and steam in order to bring the catalyst residues into solution and to recover the solvent and termonomers in the azeotrope formed. In this stage the polymer coagulates into crumbs of relatively small size which, finally, are sent to dewatering and drying in screw-type machines.

B. Suspension Process

This process has been developed (Crespi and Di Drusco, 1967) to carry out the terpolymerization (or copolymerization) reaction in the absence of solvent, the liquefied α -olefin being the principal component of the medium where the polymerization takes place. Since the terpolymer is insoluble in such a system, it separates after formation and the process occurs in two phases, i.e., in suspension.

Owing to the elevated concentration of monomers involved, the process allows a higher polymerization rate and higher specific production in comparison with solution process; furthermore, high conversion of monomers to polymer (30–35 wt %) can be obtained without complication because of the viscosity of the medium, since the polymer is insoluble.

Probably the most interesting feature of this process (cf. flow sheet in Fig. 50) is the removal of the reaction and stirring heats by vaporizing part of the liquefied monomers which are withdrawn, condensed, controlled for the composition, and recycled into reactor. In this way an easy and efficient control of temperature in all the parts of reactor is claimed.

The process utilizes a single reactor which works between –20 and +30°C, the pressure ranging between 3.5 and 10.5 kg/cm²; both the variables are not influenced by the presence of terpolymer which is insoluble. Therefore temperature, pressure, conversion and ratio of the third monomer to propylene in the feed, regulate the composition of

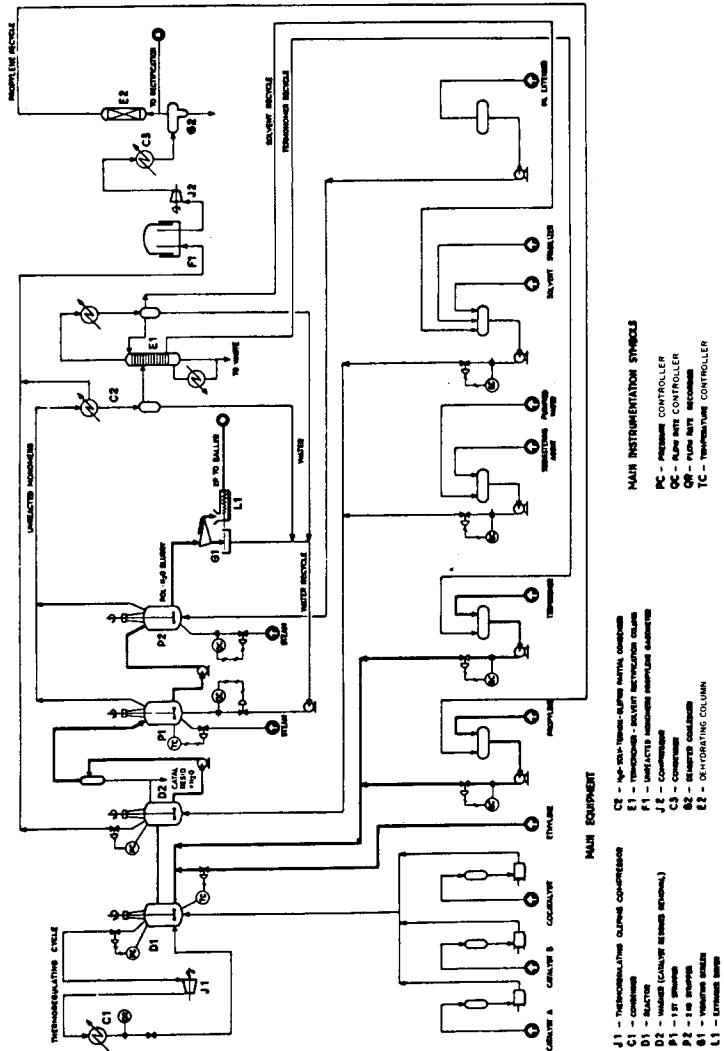


Fig. 30. Flow sheet of an industrial plant for the production of EPDM via a suspension process. Reproduced from Crespi and Di Drusco, 1967 with the permission of Editrice di Chimica, S.p.A., Milan.

EPDM. On the other hand pressure is regulated by the out flow of gaseous monomers (which is monitored) through the thermostating cycle, whereas temperature is controlled by the flow of ethylene into the reactor. The control of the monomer outflow and of catalyst flow regulate the degree of conversion.

The polymer recovered from the reaction suspension is then dissolved in a solvent in order to perform the washing step; successively the organic phase is steam stripped, and the polymer stabilized and dried.

The advantages of the suspension process have been mentioned in this section. However, some complication can be foreseen in the adoption of this process for EPDM manufacturing. For instance:

1. Although the process is carried out without a solvent, there is the need to introduce it in order to wash the polymer.
2. The elevated concentration of monomers (in particular termonomer) facilitates side reactions (e.g., branching and gel).
3. The polymerization, taking place partly in heterogeneous phase, may present some problems for monomer diffusion (e.g., composition and MW heterogeneity).
4. The separation of polymer can occlude particles of catalyst which facilitate the reaction of termonomer present in chains, in particular during the step of catalyst quenching.
5. Reactor fouling appears to be a common problem to copolymerization processes taking place in heterogeneous phase (Schroeder, 1971; U.S. Pat. 1958, 1961a).

However, in the case of EPM synthesis the drawbacks now stressed are greatly reduced; furthermore, substantial improvements can be realized by using highly active catalysts or introducing efficient procedures for deashing.

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