

PROGRESS IN POLYACETYLENE CHEMISTRY

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1. INTRODUCTION

Although studies referring to acetylene polymerization were reported in 1866 by Berthelot^{1,2} and linear polyacetylene was obtained in 1929 by Champetier and Job,^{3,4} the interest in acetylene monomers polymerization grew importantly only after Natta *et al.*⁵⁻⁸ described the synthesis of conjugated polymers with relatively high molar mass using Ziegler-Natta catalysts.

In a relatively short time, a new domain of macromolecular chemistry was created, dealing with synthesis and characterization methods of polymers containing long sequences of conjugated double bonds. These polymers are named polyconjugated systems.

The first 10 years of researches, although they cleared many aspects of the polyconjugated systems chemistry, were not fruitful with respect to the physical properties of the polyacetylenes obtained.

The researches were extended after the appearance of the Little's theory^{9,10} on the polyconjugated structure for a material presenting superconducting properties at high temperature. According to the theoretical calculation made by Wiley,^{11,12} polyarylacetylenes can be included into the class of polymers with possible superconducting properties. These theoretical results gave a strong impulse in acetylene polymer studies.

In the same time, some unclassical cases of acetylenic monomer polymerizations gave polymers with spectacular properties, and the interest of many research groups was directed toward them. Topochemical polymerization of diacetylenes elaborated by Wegner¹³⁻¹⁸ in 1969 and intensively developed by the research groups led by Baughman¹⁹ and Bloor,²⁰ copolycyclotrimerization of monoacetylenes with diacetylenes elaborated by Korshak^{21,22} in 1971 and oxidative coupling of diacetylenes, studied by Hay, Katlyarevskii²³ and more recently Hagiwara *et al.*²⁴ are the most important examples.

Finally, an increasing interest is given to the thermostable polymers obtained by thermally-induced reactions in heterocyclic oligomers containing acetylenic-type end groups.²⁵⁻²⁸ These thermostable polymers have the great advantage that do not eliminate volatile micromolecular compounds during crosslinking reactions, therefore permitting one to obtain non-porous films.

The researches concerning conventional polyacetylenes were dominated by this class of acetylenic polymers until 1977, when cis or trans polyacetylene films, prepared according to Ito, Shirakawa and Ikeda²⁹ in 1974, were transformed into conductive polymers by doping with electrono-donor or electrono-acceptor compounds. This work was performed by Heeger and Mac Diarmid's research group.^{30,31} These spectacular results definitively restarted the interest in conventional acetylene polymers.

A significant number of reviews of results obtained in this domain up to 1977 was published, the most recent being that of Cerkashin *et al.*³² and Davidov and Krentsel.³³ A more recent review published by Davidov and Krentsel deals only

with the results of the Soviet school,³⁴ whereas Misurkin and Ovchinnikov³⁵ examine in a review the modern concepts of the electronic structure of polymers with conjugated double bonds.

A great number of reviews, books and symposia proceedings present especially the electrical properties of different classes of semiconductive polymers, included the doped polyacetylenes and their applications.³⁶⁻⁴²

Beginning especially with 1977, researches in the polyacetylene field were undertaken by solid state physicists, not as a consequence of the resolving and understanding of all the chemical aspects, but due to the interest in the spectacular electrical properties of this polymer class.

Yet the progress obtained in structure-properties correlation or conduction mechanism understanding in this polymer class are insignificant, because the chemistry of polyacetylene synthesis (especially microstructure formation) was neglected, favouring electric properties studies in order to obtain practical applications.

In recent years, only two short papers reviewed polyarylacetylene microstructure^{43,44} and a very recent one deals with polyacetylene structure.⁴⁵

The aim of this paper is not to collect literature data referring to conventional polyacetylenes synthesis and properties, nor to correlate the structure and the properties of this polymer class, because such a correlation at this time is scarcely possible. Our aim is to select those aspects referring to *polyacetylenes synthesis* regarded from the point of view of polymer microstructure and of the synthesis efficacy, and to *polymer structure* regarded from the point of view of its consequence for polymer properties. This review is limited to acetylene and aryl-acetylene polymers only.

We omitted polyacetylenes applications treated in 1980 by Kryszewski⁴² in a book.

2. GENERAL CONSIDERATIONS ON ACETYLENIC MONOMER POLYMERIZATION

Acetylenic monomer reactivity is determined by the π -bond energy and by the triple bond electronic density. Acetylene has a 54 kcal/mole π -bond energy, whereas for ethylene it is of 65 kcal/mole. Moreover, due to the sp-type hybridization, the carbon atoms in acetylene are less distant from each other than in ethylene. This peculiarity, together with the cylindrical symmetry of π -electron distribution with respect to the molecular axis, lead to an increase of the triple bond π -electron density.

Consequently, the π -electron polarizability decreases; at the triple bond electrophilic attack is hindered and nucleophilic attack is favoured. These are reasons for the acetylene's facility to form π -complexes and metal acetylides. Therefore, acetylenes should be more easily polymerized by anionic or coordinative mechanisms.

Anionic and cationic polymerization behaviour of acetylenes was already confirmed by very detailed experimental results reviewed by Cerkashin *et al.*³² covering the literature data up to 1974. After 1974, no significant results appeared in the literature, and the configuration of polyacetylenes obtained by ionic mechanisms has not been reported, therefore the ionic polymerizations will not be the subject of our comments.

The most efficient catalytic systems for acetylene polymerization are the co-ordinative ones. Up to now, only these gave stereoregular structures.

The results obtained with the most representative coordinative catalytic systems will be discussed in this review and, on this basis, the structure of polymers prepared by other mechanisms also, will be interpreted.

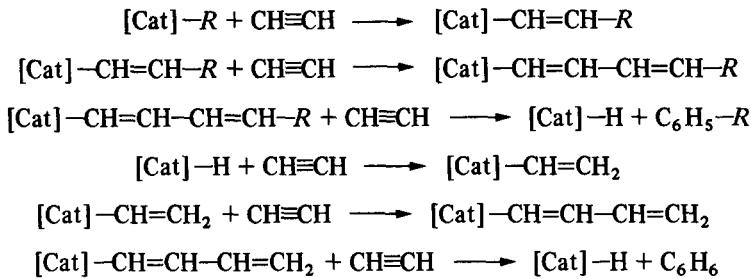
3. ACETYLENE POLYMERIZATION

3.1. Ziegler-Natta catalyst polymerization of acetylene

The first insoluble trans polyacetylene was synthesized by Natta *et al.*⁷ in 1958 by acetylene polymerization with the following catalytic systems: $\text{AlEt}_3/\text{Ti}(\text{OC}_3\text{H}_7)_4$, $\text{Al}(\text{C}_6\text{H}_{13})/\text{Ti}(\text{OC}_4\text{H}_9)_4$, $\text{AlEt}_3/\text{TiCl}_3$, $\text{Li}(\text{C}_3\text{H}_{11})/\text{Ti}(\text{OC}_3\text{H}_7)_4$, $\text{AlEt}_3/\text{TiCl}_4$, $\text{AlEt}_3/\text{VCl}_3$ and $\text{AlEt}_3/\text{Ti(OBu)}_4$. The polymer was crystalline only when obtained with $\text{AlEt}_3/\text{Ti(OBu)}_4$ ($\text{Al}/\text{Ti} = 1.4\text{--}25$) catalyst. Polymerizations were carried out in heptane at temperatures between 45 and 75°C. Watson *et al.*⁴⁶ were the first to point out that using Ziegler-Natta catalyst systems ($\text{Al(iBu)}_3/\text{TiCl}_4$) polyacetylenes having also cis structures can be obtained. However, only in 1966, was a polyacetylene having a high cis content obtained using the catalytic system $\text{AlEt}_3/\text{Ti(OBu)}_4$ ($\text{Al}/\text{Ti} = 4$) at low temperature,^{47,48} and in 1969 Kleist and Byrd⁴⁹ reported the synthesis of a polyacetylene having 60–70% cis sequences using the catalytic system $\text{AlEt}_3/\text{Fe(dmg)}_2\text{2Py}$ at 25°C.

Hatano *et al.*⁴⁸ studied for the first time the polymerization temperature influence on polyacetylene configuration, demonstrating that decreasing the polymerization temperature increases the cis content of the polymer.

The researches in linear polymerization of acetylene were accompanied by studies on cyclotrimerization of mono- or di-substituted acetylene derivatives with Ziegler-Natta catalysts like $\text{Al(iBu)}_3/\text{TiCl}_4$,⁵⁰ or $\text{AlEt}_3/\text{Cr}_2\text{O}_2\text{Cl}_2$.⁵¹ Using the system $\text{Al(iBu)}_3/\text{TiCl}_4$, changes in Al/Ti ratio give linear polymers or cyclic trimers, unlike the $\text{AlEt}_3/\text{TiCl}_3$ system which leads especially to linear polymers. The first acetylene cyclotrimerization was reported in 1961 by Lutz⁵² with $\text{AlEt}_3/\text{TiCl}_4$ catalyst in dilute solution in *n*-heptane. The total yield was 73.2%, benzene being 49.1%. The possibility to obtain cyclic trimers from acetylene or its derivatives implies the cis opening of the triple bond. Small quantities of toluene or ethylbenzene present in the benzene obtained by acetylene cyclotrimerization with $\text{AlMe}_3/\text{TiCl}_4$ or $\text{AlEt}_3/\text{TiCl}_4$ ($\text{Al}/\text{Ti} = 2:1$) catalytic systems led to the following mechanism proposed for cyclization reaction.⁵³ The mechanism is similar to that of anionic-coordinative polymerization of olefins:



Ikeda and Tamaki⁴⁷ performed a study to elucidate the catalyst components effect on cyclotrimerization or linear polymerization of acetylene, using several titanium derivatives and organometallic compounds. Their catalytic selectivity to benzene synthesis is presented in Table 1.

These results suggest that the active species for both linear polymerization and cyclotrimerization cannot be very different, but the selectivity is determined by the chlorine content of the active species. Thus, the active species having no chlorine give linear polymers ($\text{AlEt}_3/\text{Ti(OBu)}_4$, $\text{AlEt}_2(\text{OC}_2\text{H}_5)/\text{Ti(OBu)}_4$, $\text{AlEt}_3/\text{Ti(acac)}_2\text{O}$,

TABLE 1. Acetylene polymerization with various catalysts (reference 47)

Catalyst			Conversion %	Selectivity for benzene formation %
Ti-component	Al-component	Al/Ti		
TiCl_4	$\text{Al}(\text{CH}_3)_3$	1.0 <i>a,t</i>	75	70
TiCl_4	$\text{Al}(\text{C}_2\text{H}_5)_3$	2.0 <i>a,h</i>	83	75
TiCl_4	$\text{Al}(\text{C}_2\text{H}_5)_3$	2.0 <i>b,h</i>	66	93
TiCl_4	$\text{Al}(\text{C}_2\text{H}_5)_3$	2.0 <i>c,h</i>	95	45
TiCl_4	$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$	2.0 <i>a,h</i>	97	61
TiCl_4	$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$	100 <i>b,h</i>	100	74
TiCl_4	$\text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2$	400 <i>b,h</i>	86	43
TiCl_3	$\text{Al}(\text{C}_2\text{H}_5)_3$	30 <i>a,h</i>	10	13
TiCl_3	$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$	1 <i>b,h</i>	34	102
TiCl_3	$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}_2$	25 <i>a,h</i>	72	66
$(\text{C}_5\text{H}_5)_2\text{TiCl}_2$	$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$	4.0 <i>b,t</i>	43	34
$\text{Ti}(\text{OC}_4\text{H}_9)_4$	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.0 <i>b,t</i>	90	1
$\text{Ti}(\text{OC}_4\text{H}_9)_4$	$\text{Al}(\text{C}_2\text{H}_5)_2(\text{OC}_2\text{H}_5)$	4.0 <i>b,h</i>	62	6
$\text{Ti}(\text{OC}_4\text{H}_9)_4$	$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$	4.0 <i>b,h</i>	75	49
$[(\text{acac})_2\text{TiO}]_2$	$\text{Al}(\text{C}_2\text{H}_5)_3$	4.0 <i>b,t</i>	61	4
$(\text{acac})_2\text{TiCl}_2$	$\text{Al}(\text{C}_2\text{H}_5)_3$	2.0 <i>b,t</i>	62	52
$(\text{acac})_3\text{Ti}$	$\text{Al}(\text{C}_2\text{H}_5)_3$	30 <i>b,t</i>	35	1
$(\text{acac})_3\text{Ti}$	$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$	100 <i>b,t</i>	100	97
$(\text{acac})_3\text{Ti}$	$\text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2$	100 <i>b,t</i>	100	17

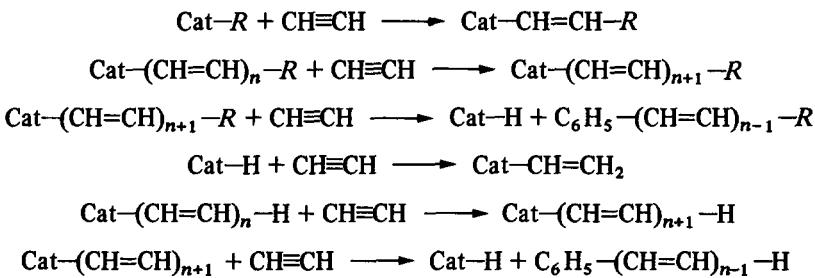
Catalyst systems were prepared by mixing 20 mmol of the Al- and Ti-components in the listed Al/Ti ratios. *a*, Heterogeneous mixed catalyst; *b*, soluble catalyst or liquid-phase catalyst freed from solid phase by centrifuging the mixed system; *c*, solid-phase catalyst separated from mixed system. *t*, toluene; *h*, hexane. Nearly 30 mmol of acetylene was polymerized at room temperature for about 10 hr in a vacuum line system at initial pressure of about 700 mm Hg.

$\text{AlEt}_3/\text{Ti}(\text{acac})_3$) whereas all catalytic systems having chlorine atoms give especially cyclization reactions. In order to verify if the linear polymerization mechanism is the same as the cyclization mechanism proposed by the same authors⁵³ the oxidation products of polyacetylene were studied and the alkyl end-groups presence was followed.⁴⁷ Methyl and ethyl end-groups obtained in AlMe_3 and AlEt_3 -catalysed polymerizations, respectively, were evidenced by separation of reaction products obtained from alkaline oxidation with permanganate of polyacetylene. The sources of the identified products are presented in Table 2.

TABLE 2. Possible sources of the carboxylic acids obtained as permanganate oxidation products of polyacetylene (reference 47)

Acids	Sources
CH_3COOH	$\text{CH}_3\text{CH}=\text{CH}-\cdots-\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}-\cdots-$
$\text{CH}_3\text{CH}_2\text{COOH}$	$\text{CH}_3\text{CH}_2\text{CH}=\text{CH}-\cdots-$
$\text{HOOC}-\text{COOH}$	$\cdots-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\cdots-$
$\text{HOOC}-(\text{CH}_2\text{CH}_2)_1 \text{ or }_2 \text{ COOH}$	$\cdots-\text{CH}=\text{CH}-(\text{CH}_2\text{CH}_2)_1 \text{ or }_2 \text{ CH}=\text{CH}-\cdots-$
$\text{C}_6\text{H}_5\text{COOH}$	$\text{C}_6\text{H}_5\text{CH}=\text{CH}-\cdots-$

Besides alkyl end-groups, arising from the organometallic component of the catalytic system, phenyl-type end-group were evidenced. They can result from the terminal cyclization of the growing chain. Consequently, a reaction mechanism similar to that of olefine polymerization was proposed including also the intramolecular cyclization termination reaction:



Olefine polymerization with Ziegler catalysts takes place by cis opening of the double bond,⁵⁵⁻⁵⁷ and sometimes a cis-trans isomerization can occur.^{58,59} Ikeda and Tamaki⁴⁷ used this idea proposing a mechanism for acetylene polymerization by cis addition of acetylene at metal-carbon bond, followed by metal substitution with the monomer maintaining the configuration. The cis-trans isomerization takes place before the entrance of the propagation chain into the polyacetylene crystallite.

The sole evidence for the triple bond cis opening was the appearance of cyclic oligomers.

In 1971, Shirakawa and Ikeda⁶⁰ definitively proved the polymerization temperature influence on polyacetylene cis or trans configuration for the system $\text{AlEt}_3/\text{Ti(OBu)}_4$ ($\text{Al}/\text{Ti} = 3/4$). Polyacetylene obtained at -78°C has a cis configuration and that obtained at 150°C a trans configuration. Deuterated acetylene polymerization in the same conditions permitted the evidence of ethyl end-groups from catalyst by IR spectroscopy. This was a further proof for an anionic-coordinative polymerization mechanism of both cyclotrimerization and polymerization reactions.⁶⁰ This mechanism is supported also by the results obtained by Shirakawa and Ikeda⁶¹ when reinvestigating acetylene cyclotrimerization with $\text{AlEt}_2\text{Cl}/\text{Ti(acac)}_3$ catalyst, known as one of the most efficient catalysts for acetylene cyclotrimerization. In this case, the selectivity toward benzene formation is independent on solvent nature and polymerization temperature, being above 75%. A small quantity of ethylbenzene (0.5% from the benzene) was evidence in the reaction products. Deuterated acetylene polymerization in the same conditions gave benzene-d₆ and ethylbenzene-d₅.

Of the ethylbenzene-d₅ molecule, only the benzene nucleus is deuterated, as demonstrated by mass spectroscopy and NMR. This indicates that the ethyl group in ethylbenzene arises from the catalytic system. Because the alkylation of benzene with the catalyst can be neglected, it is clear that the ethyl group derives from the active intermediate having a metal-ethyl bond.

Analysis of deuterium distribution in ethylbenzene molecule obtained from an equimolecular mixture of acetylene and acetylene-d₂, can be interpreted only by ω -hydrogen elimination and, consequently, the probable mechanism for ethylbenzene synthesis is as presented in Fig. 1.

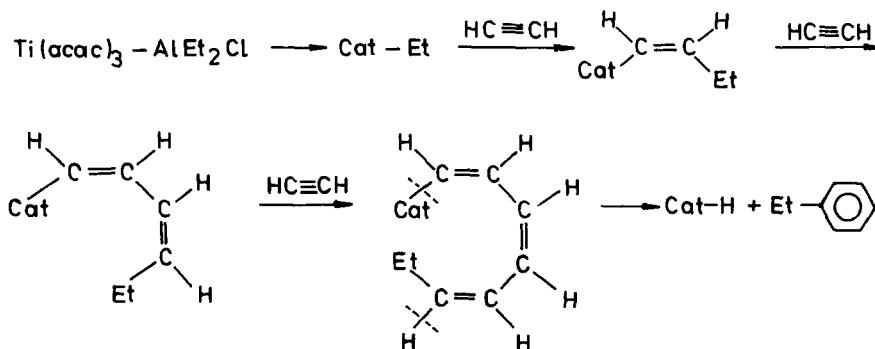


FIG. 1. Mechanism proposed for ethylbenzene formation during the polymerization of acetylene with Ziegler-Natta catalysts (reference 61).

The benzene formation mechanism is identical, excepting the initial insertion which takes place in the metal-hydrogen bond and not in metal-ethyl bond. The hydrogen atom of the intermediate metal hydride is noted as H* (Fig. 2).

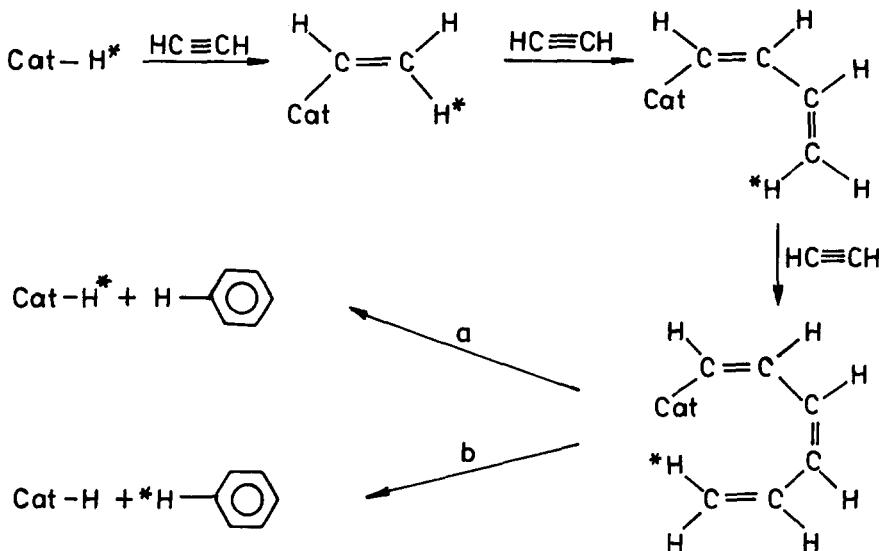


FIG. 2. Mechanism proposed for benzene formation during the polymerization of acetylene with Ziegler-Natta catalysts (reference 61).

In this case there are two different hydrogens in ω -position (one from hydride (H^*), the other from the first acetylene insertion), and three possible situations for ω -H elimination: case a) only H^* elimination, case b) only first acetylene elimination, case c) both H^* and H are eliminated with equal probability. Analysis of deuterium distribution in benzene proved that ω -H elimination takes place only in case a). Selective H^* elimination in benzene formation can be explained by supposing the cis opening of the triple bond and elimination of cis ω -H with respect to the chain. On the other hand, ethylbenzene formation implies a trans ω -H elimination, if it is supposed that acetylene insertion in the metal-ethyl bond takes place by cis opening of the triple bond. Because it is not convenient to explain ethylbenzene formation by a trans ω -H elimination if cyclization and hydrogen elimination takes place simultaneously, one can consider two paths for the reaction: either by ethyl containing double bond rotation followed by simultaneous cis ω -H elimination and cyclization, or trans ω -H elimination followed by cyclization.

All these are proofs for an anionic-coordinative mechanism of benzene formation and of linear polymerization of acetylene.

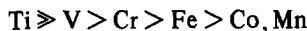
Additional proofs for an anionic-coordinative mechanism of linear polymerization of acetylene by soluble Ziegler-Natta catalysts such as: $\text{AlEt}_3/\text{Ti}(\text{OBu})_4$, $\text{AlEt}_3/\text{VO}(\text{C}_5\text{H}_7\text{O}_2)_2$, $\text{AlEt}_3/\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$, $\text{AlEt}_3/\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_3$ were obtained correlating the catalytic activity of these systems with the maximum ionization degree of the catalyst determined by electrical conductivity, absorption spectroscopy and ESR measurements.⁶²⁻⁶⁶ The optimum ratio for acetylene polymerization with

the following catalytic systems: $\text{AlEt}_3/\text{Ti}(\text{OBu})_4$ ($\text{Al}/\text{Ti} = 1$ in *n*-heptane), $\text{AlEt}_3/\text{VO}(\text{C}_5\text{H}_7\text{O}_2)_2$ ($\text{Al}/\text{V} = 2$ in toluene) $\text{AlEt}_3/\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3$ ($\text{Al}/\text{Cr} = 3$ in toluene) and $\text{AlEt}_3/\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_3$ ($\text{Al}/\text{Co} = 3$ in toluene) was found in this way.

The catalytic activity of different catalysts obtained from transition metal acetylacetones and AlEt_3 decreases, according to Kambara *et al.*,⁶⁷ as follows (for Ti and V oxobis(acetylacetone)Ti^{IV} and oxobis(acetylacetone)V^{IV} were used):



This order is similar to that found for tris(acetylacetone)Me^{III} and AlEt_3 :



3.1.1. Synthesis of polyacetylene films — Cis or trans polyacetylene is an insoluble polymer with an almost unknown structure, due to its insolubility. All syntheses performed up to 1974 gave a powdered polymer. The first polyacetylene film was synthesized by Ito, Shirakawa and Ikeda²⁹ in 1974 and until now no spectacular improvements of polymerization techniques have been reported.

The most important factors in obtaining polyacetylene films are: the catalyst dispersion degree, the catalytic activity of the system used in polymerization, and concentration of the catalytic system. Uniform films of polyacetylene were obtained only with soluble Ziegler-Natta catalysts such as: $\text{AlEt}_3/\text{Ti}(\text{OC}_4\text{H}_9)_4$, $\text{AlEt}_3/\text{Ti}(\text{acac})_3$ and $\text{AlEt}_3/\text{Cr}(\text{acac})_3$. Soluble catalytic systems, highly selective for linear polymerization, but rather inefficient for polymer formation, such as: $\text{AlEt}_3/\text{Co}(\text{acac})_3$ and $\text{AlEt}_3/\text{Mn}(\text{acac})_3$ do not give uniform films. The $\text{AlEt}_2\text{Cl}/\text{Ti}(\text{acac})_3$ system, a very efficient catalyst, but with low selectivity for linear acetylene polymerization, generates powders not films.

The most efficient catalytic system giving films with good physical properties is $\text{AlEt}_3/\text{Ti}(\text{OC}_4\text{H}_9)_4$ ($\text{Al}/\text{Ti} = 3-4$). The minimum concentration for obtaining film is ca 3 mmoles/1 $\text{Ti}(\text{OC}_4\text{H}_9)_4$ for $\text{Al}/\text{Ti} = 4$. Below this critical concentration, powdered polyacetylene is obtained.

The polymer state is determined especially by the diffusion of acetylene into the catalytic system. For high catalyst concentrations, the polymerization takes place on catalyst solution surface, generating a polyacetylene film which hinders subsequent polymerization due to the limited monomer diffusion through the film. At lower concentrations, subsequent diffusion is permitted, and a gelatinous mass is obtained by polymerization. At very low catalyst concentrations, one cannot produce a continuous mass and the polymer is obtained as a powder.

The best solvent used for polymerization temperatures under 80°C is toluene, and above 80°C is *n*-hexadecane.

Polymerization takes place by acetylene introduction on the catalyst surface. The film formation is observed immediately after. The thickness of polyacetylene films can be designed by the initial acetylene pressure and reaction time. Polymerization is stopped through system evacuation. Film purification is realized by

removing the catalyst solution laying under the film with a syringe, followed by repeated washing with toluene or hexane until the solution becomes colorless. Purification is conducted at polymerization temperature in order to avoid cis-trans isomerization. Destroying catalyst with a HCl-MeOH mixture produces not only cis-trans isomerization, but polymer decomposition, also.

The cis and trans contents of polyacetylene films obtained at different temperatures are given in Table 3.

TABLE 3. Cis and trans content of polyacetylenes prepared at various temperatures (references 29)

Polymerization temperature °C	Cis content %	Trans content %
150	0.0	100
100	7.5	92.5
50	32.4	67.6
18	59.3	40.7
0	78.6	21.4
-18	95.4	4.6
-78	98.1	1.9

Catalyst: $\text{Al}(\text{C}_2\text{H}_5)_3/\text{Ti}(\text{OC}_4\text{H}_9)_4$; Al/Ti = 4; 10 mmole/l

It is to be noted that with lower Al/Ti ratios (less than 3-4) a high-trans polyacetylene film is obtained, even at lower temperatures. This is a suggestion for the change of the mechanism of obtaining trans configuration, depending on Al/Ti ratio. Until now it is not clear if for $\text{Al}/\text{Ti} < 3-4$ the mechanism should imply trans opening of the triple bond or the triple bond should be opened in cis position and a cis-trans isomerization should be initiated non-thermally. Very recent results⁶⁸ show that in acetylene polymerization with $\text{AlEt}_3/\text{Ti}(\text{OBu})_4$ there are many types of active species. All of them initiate acetylene polymerization by cis opening of the triple bond. In our opinion, one cannot neglect the influence of the excess Lewis acid from the Ziegler-Natta catalyst, which can initiate a cationic isomerization of cis double bonds or an intramolecular cyclization.

Polyacetylene films having different densities can be obtained by pressing polyacetylene foams obtained in the gel state.⁹⁷⁻¹⁰⁰

Catalyst concentration influence on acetylene polymerization with $\text{AlEt}_3/\text{Ti}(\text{OBu})_4$ (Al/Ti = 4) is presented in Fig. 3.

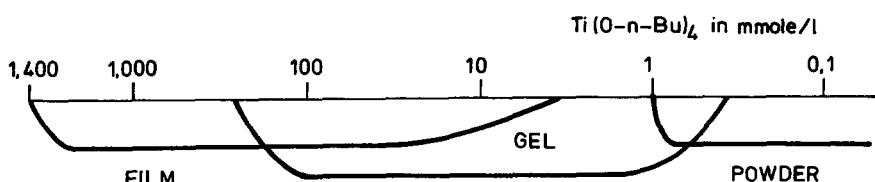
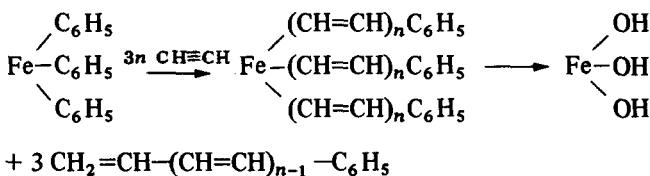


FIG. 3. Schematic illustration of macroscopic morphology of as-prepared polyacetylene as a function of Ziegler-Natta catalyst concentration (reference 99).

3.2. Acetylene polymerization with other coordinative catalysts

As was stated in the introduction, the first acetylene polymerization in the presence of organometal catalysts was reported in 1929 by Job and Champetier.³ In order to elucidate some aspects of the catalytic systems, Champetier and Martynhoff reinvestigated in 1961⁶⁹ acetylene polymerization with: $C_6H_5MgBr/FeCl_3$ ($Mg/Fe = 3/1$, ethylic ether solution), $C_2H_5MgBr/FeCl_3$ (ether, $Mg/Fe = 3/1$), $MgEt_2/FeCl_3$ (ether, $Mg/Fe = 1.5/1$) and $C_6H_5MgBr/TiCl_4$ (benzene, $Al/Ti = 4/1$).

A reaction mechanism was proposed, postulating as the real catalyst the unstable $Fe(C_6H_5)_3$ obtained in situ by $FeCl_3$ reaction with phenyl magnesium bromide:



The polymers have a trans configuration, being spectrally identical with the polyacetylene obtained by Natta *et al.*⁷

In 1960, Luttinger⁷⁰ proposed a new class of very active catalysts for acetylene polymerization. They consist of a salt or a complex of a VIII-th group metal (e.g. $NiCl_2$ or $(Bu_3P)_2NiCl_2$) and a reducing agent such as sodium or potassium borohydride, lithium aluminium hydride or a diborane. This class of catalyst is active in a broad range of solvents (e.g. water, ethanol, acetonitrile, diglyme, etc) and the presence of oxygen does not affect the catalytic activity. All Co, Ni, Ru, Os, Pt, Pd salts or complexes are very efficient in these catalytic systems. Fe compounds are completely inactive.

Green, Nehme and Wilkinson⁷¹ proposed, at the same time as Luttinger, a catalytic system for acetylene polymerization from a Ni or Co phosphinic complex (very active are: $(nBu_3P)_2.NiCl_2$, $(nPr_3P)_2.NiBr_2$, $(Ph_3P)_2.Ni(SCN)_2$ and $(Ph_3P)_2.CoCl_2$) with Na borohydride in tetrahydrofuran. The two catalytic systems are identical and permit a high crystalline trans polyacetylene to be obtained at room temperature.

The researches on this class were extended by Luttinger,^{72,73} who showed that the order of introduction of reactants and monomer in the reaction medium is essential for obtaining a high reactivity. Thus, mixing the two components of the catalytic system before introducing the monomer, results in loss of the catalytic activity. For this reason, the following order of addition is performed: solvent, monomer, reducing agent and transition metal compound. There is a very broad range of transition metal compounds active in these systems,⁷² however the polymerization mechanism has not been elucidated, although some assumptions have been made regarding the active species as a transition metal hydride.⁷³

In 1964, Daniels⁷⁴ demonstrated that phosphinic complexes of Ni halides are active in acetylene polymerization, especially in a solvent mixture consisting of 10% THF and 90% EtOH, without the reducing agent used by Luttinger and Wilkinson.⁷⁰⁻⁷³

The polymers obtained present mainly trans configuration but some cis sequences are also evidenced. Their degree of crystallinity is higher than of polyacetylene prepared with Luttinger's catalyst. Some important polymerization data are presented in Table 4.

TABLE 4. The polymerization of acetylene with phosphinic complexes of VIII-th group transitional metals

No.	Catalyst	Solvent	Temp. °C	Exotherm (hr)	Product g	Yield g of polymer vs. g of catalyst
1	NiCl ₂ (PPh ₃) ₂	THF	-15	none	2.1	0.63
2	NiBr ₂ (PPh ₃) ₂	THF	10-20	10-140(1)	23.6	6.37
3	NiBr ₂ (PPh ₃) ₂ (1/9,v/v)	THF/EtOH (1/9,v/v)	16-18	none	47.0	12.70
4	NiI ₂ (PPh ₃) ₂	THF	21-24	22-75(1)	20.0	4.75
5	NiBr ₂ (PnBu ₃) ₂	THF	19-22	none	22.0	6.67

Polymerization time, 24 hr.

The polymerization can proceed with the same yields in *n*-propanol, benzene, acetone and acetonitrile. Pd and Co phosphinic complexes are not active in these polymerizations.

A polymerization mechanism was proposed, based on the Cl- and Ni-containing end groups presented in polyacetylene⁷⁴ (Fig. 4). IV has a vacant coordination site and can thus add a new acetylene as in eq. (3) repeating the complexation and monomer addition cycle as in eq. (4) (Fig. 4).

In 1964, Tsumura and Hagihara⁷⁵ used dicyclopentadienyl vanadium for acetylene polymerization in toluene or benzene solutions under a pressure of 15-22 Kg/cm². A year later, Yokohawa and Azuma⁷⁶ showed that dicyclopentadienyl titanium is a much more active catalyst as compared with dicyclopentadienyl vanadium. Acetylene polymerized by simple bubbling through dicyclopentadienyl titanium solution in toluene at 30°C. In similar conditions, dicyclopentadienyl vanadium has no catalytic effect. Dicyclopentadienyl titanium is active for acetylene polymerization even at -70°C. The polymers obtained are highly crystalline, having trans configurations. Some results are presented in Table 5.

In 1966, Odaira, Hara and Tsutsumi^{77,78} obtained a trans polyacetylene using PdCl₂ or bis(benzonitrile)PdCl₂ as catalyst in acetic acid at 120°C. Bis(benzonitrile)PdCl₂ was 20 times more active than PdCl₂ (for acetylene polymerization). Changing the solvent from acetic acid to benzene leads to almost complete deactivation of the catalyst. A Ziegler-Natta mechanism was proposed, because at least one of the polymer end-groups is of the acetyl-type.

Acetylene polymerization in the presence of triphenylchromium, diphenylmanganese, diphenylcobalt and diphenylnickel in tetrahydrofuran solution⁷⁹ gives a polyacetylene having phenyl end-groups: Ph-(CH=CH)_n-Ph. Catalyst reactivity

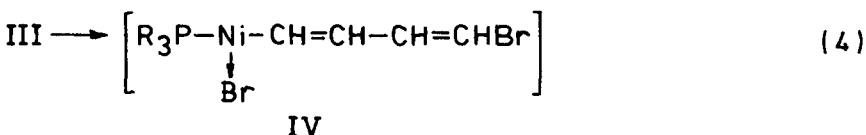
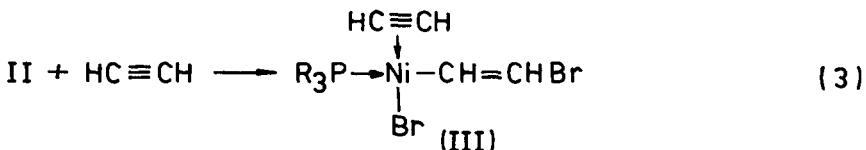
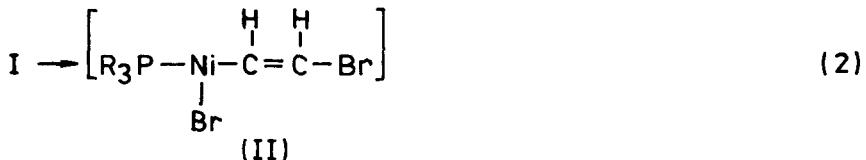
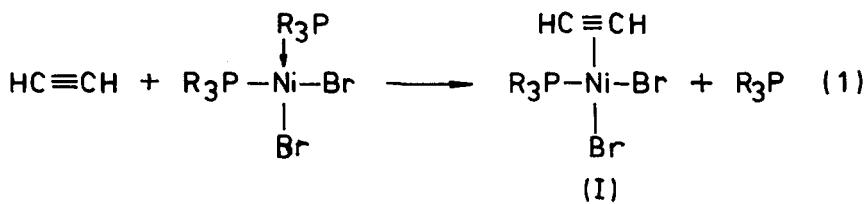


FIG. 4. Mechanism of acetylene polymerization by $(\text{R}_3\text{P})_2\cdot\text{NiX}_2$ catalysts (reference 74).

TABLE 5. The polymerization of acetylene by dicyclopentadienyl titanium (DCT) and dicyclopentadienyl vanadium (DCV) (reference 75)

No.	DCT mmole	DCT mmole/l	C_2H_2 mm Hg	T °C	Time min	Solid product g
1	1.0	25	760	80	60	1.04
2	1.0	25	760	30	60	0.84
3	1.0	25	760	-15	60	0.68
4	1.0	25	760	-50	60	0.45
5	1.0	25	760	-65	60	0.32
6	0.5	13	760	30	60	0.46
7	0.24	6	760	30	60	0.16
8	0.24	6	150	20	60	0.1
9	0.24	6	150	-70	60	0.1
10*	6.0	25	760	30	60	3.2
11*	1.0	25	760	27	60	0.0
12	1.0	25	760	75	180	0.0

*DVC instead of DCT

depends on the thermal stability of the metal–carbon bond. These results confirm Champetier's idea⁶⁹ about acetylene polymerization by $\text{Fe}(\text{C}_6\text{H}_5)_3$ as the active species. Polymer configuration is also trans. The authors followed the linear oligomer separation and not polymer synthesis.

Pori *et al.*⁸⁰ obtained a crystalline polyacetylene by acetylene polymerization in the presence of 1,5-cyclooctadiene nickel halide at 20°C without reporting the polymer configuration. In 1968 also, acetylene was polymerized in aqueous solution in the presence of potassium hexacyanoidnickelate ($\text{K}_4\text{Ni}(\text{CN})_6$).⁸¹

In 1978, Hsu *et al.*⁸² synthesized a cis or trans (according to the polymerization temperature: at -80°C , 86% cis; at room temperature, trans) polyacetylene using as catalyst $(\text{C}_5\text{H}_4)(\text{C}_5\text{H}_5)_3\text{Ti}_2$ (μ –(η^1 : η^5 –cyclopentadienyl)tris(η ncyclopentadienyl)ditungsten) in n-hexane solution. Acetylene was introduced on the catalyst surface and generated polyacetylene films.

Finally, in 1980, Voronkov *et al.*⁸³ performed acetylene polymerization in the presence of MoCl_5 , WCl_6 and MoCl_4 in 1,2-dichloroethane or benzene solutions, by bubbling acetylene through catalyst solution or under pressure. Unfortunately, the oxygen was not completely removed from the reaction medium or during polymer handling, so the polymer obtained contains up to 16.6% oxygen. Some representative results are presented in Table 6.

TABLE 6. Polymerization of acetylene in the presence of some molybdenum and tungsten derivatives (reference 89).

No.	Catalyst concentration (mmole)	Acetylene concentration mmole	Temperature of polymerization °C	Duration hr	Polymer yield %
1	MoCl_5 (5.0)	190	50	1	98
2	WCl_6 (0.1)	18	20	3	45
3	OMoCl_4 (1.2)	100	20	1	90

Solvent: 1,2-dichloroethane

In conclusion, there are many coordinative catalytic systems, other than of Ziegler–Natta type, which are very active in acetylene polymerization. They are efficient in such different solvents as: water, acetic acid, tetrahydrofuran, ethylic ether, ethanol, 1,2-dichloroethane, etc.

Although not much studied, some of them permit the design of the polyacetylene end-groups. The best example is the polymerization in the presence of $\text{Cr}(\text{Ph})_3$, $\text{Mn}(\text{Ph})_2$, $\text{Co}(\text{Ph})_2$ or $\text{Ni}(\text{Ph})_2$,⁷⁹ giving phenyl end-groups. The replacement of the phenyl group with other aromatic substituents can lead to a polyacetylene with functionalized ends.

Except for the work of Hsu *et al.*⁸² in all cases thermal cis–trans isomerization during propagation has not been avoided; this is the reason for the trans configuration of the polymers obtained.

Although the reaction mechanisms are not completely elucidated, we believe

that, in these cases also, the polymerization proceeds by cis-opening of the triple bond. Polymerization of monosubstituted acetylenes with aromatic substituents will support this hypothesis.

When one carefully eliminates thermal effects in a polymerization, these catalytic systems must give a cis polyacetylene, and the film or gel state of the polymers can be determined by the catalyst concentration. Anyway, the first polyacetylene in the gel state was obtained in 1961 by Champetier⁶⁹ with the catalyst PhMgBr/FeCl₃.

By changing the solvent, one can also control the film morphology.

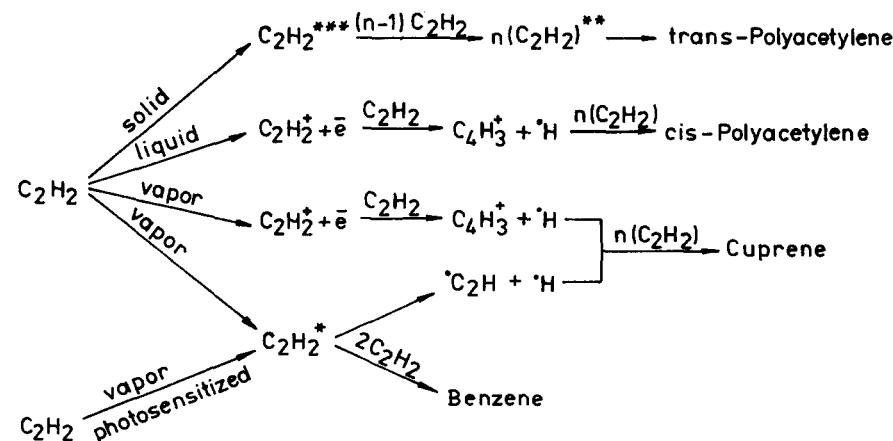
3.3. Acetylene polymerization by irradiation

Thin films of polyacetylene were obtained by acetylene polymerization in electric discharges.⁸⁴ The polymer configuration and crystallinity were not reported.

Linear acetylene polymers were obtained by liquid (at -78°C) or solid (at -196°C) acetylene polymerization with γ -radiation given by a Co⁶⁰ source.⁸⁵ The polymer obtained in the liquid state has a cis configuration, that obtained in the solid state has a trans configuration. The irradiation period determines the polymer solubility. In the liquid state, the polymerization proceeds by a cationic mechanism, and in the solid state by a mechanism named "electronic polymerization", different from the conventional radical or ionic ones.

UV⁸⁶ or electron⁸⁷ irradiation of acetylene in the gaseous state gives probably cuprene-type polymers, their structure being rather unknown.

Tabata⁸⁵ proposed a mechanism for acetylene polymerization induced by irradiation (Fig. 5).



*** superexcited state ; ** collective excited state ; * triplet state

FIG. 5. Mechanism proposed for radiation-induced acetylene polymerization (reference 85).

One of the most plausible mechanisms for obtaining cuprene is polyacetylene oxidation (see also Section 4.2.1.). Taking this into account, one can consider that gaseous state polymerization of acetylene under irradiation gives a linear polymer, but, due to the oxygen presence in the reaction medium, it is transformed into cuprene.

4. POLYACETYLENE STRUCTURE AND PROPERTIES

4.1. Polyacetylene structure

Cis or trans polyacetylene is an insoluble and infusible material, having the highest crystallinity degree 0.81 (as determined by the Ruland method) of all polymers synthesized by conventional methods.⁸⁸ These peculiarities determined the beginning of intensive structural researches only after the polymer was obtained as a film.²⁹

However, polyacetylene configuration was studied in 1971⁶⁰ analysing IR spectra of polyacetylene, polyacetylene-d₂, poly(acetylene-co-acetylene-d₂) and poly(acetylene-co-acetylene-d₁-co-acetylene-d₂) prepared with AlEt₃/Ti(OBu)₄ over a broad range of temperatures (-100 - + 180°C). Spectral assignments were made on the basis of structural models for different configurations. Spectral data were best interpreted on the basis of a cis-transoidal (or trans-cisoidal) configuration for the polymers prepared at temperatures lower than -78°C and of a trans-transoidal configuration for the polymers prepared above 150°C (Fig. 6).

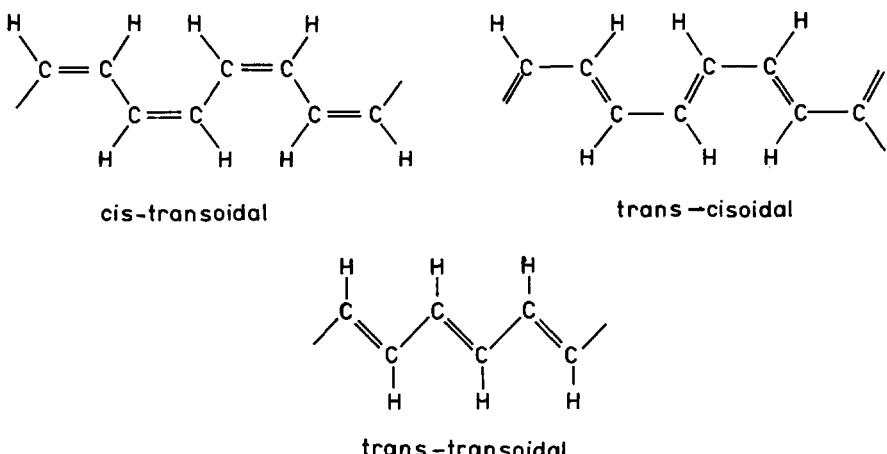


FIG. 6. Possible cis and trans configurations of polyacetylene obtained by Ziegler-Natta catalysts.

Using the absorption coefficient ratio of C–H trans deformation out of plane (1015 cm^{-1}) from a 100% trans polymer to C–H cis deformation out of plane band (740 cm^{-1}) from a 100% cis polymer (this ratio being 1.30 ± 0.01), the following equations were proposed to determine the cis and trans content in a polyacetylene²⁹:

$$\text{cis content (\%)} = 100 [1.30 A_{\text{cis}} / (1.30 A_{\text{cis}} + A_{\text{trans}})]$$

$$\text{trans content (\%)} = 100 [A_{\text{trans}} / (1.30 A_{\text{cis}} + A_{\text{trans}})]$$

where A_{cis} and A_{trans} represent the absorbances at 740 and 1015 cm^{-1} , respectively.

More information about polyacetylene vibration modes was obtained from laser Raman diffraction spectra.⁸⁹ Trans polyacetylene presents three characteristic bands: 1474 ($\nu_{\text{C}=\text{C}}$ vibration deformation), 1080 ($\nu_{\text{C}-\text{C}}$ vibration deformation) and 1016 cm^{-1} , whereas the cis polymer presents three bands at 1552 , 1262 and 920 cm^{-1} . An irreversible cis–trans isomerization was observed during spectra registration, initiated by the laser radiation thermal effect. Therefore one could not obtain a pure cis polyacetylene spectrum. $\nu_{\text{C}=\text{C}}$ trans frequencies in the Raman spectrum strongly depend on excitation wavelength, unlike cis frequencies which are independent of excitation wavelength.⁹⁰ One can then conclude that, during thermal cis–trans isomerization, trans polyenic sequences having different lengths are obtained. The $\nu_{\text{C}=\text{C}}$ (cm^{-1}) dependence on excitation wavelength suggests that trans polyenic sequences are polydisperse in length, being between 4 and 100 effectively conjugated double bonds. This demonstrates that trans sequences with different lengths are connected by structural defects, which can be i.e. polyenic cis sequences in the best case.⁹⁰ In cis–polyacetylene, the length of the conjugated sequences is constant.

Trans polyacetylene films have an intense black colour with a metallic lustre, whereas cis polyacetylene films have a copper-like lustre. Very thin cis or trans polyacetylene films are dark blue and red coloured, respectively. The electronic spectra obtained from polymer films prepared by direct polymerization on the quartz cell wall present strong absorptions arising from the lowest $\pi-\pi^*$ transitions in visible domain, with maxima at 594 nm for cis and 700 nm for trans polymers. Independent of polymer synthesis conditions, the maxima arise at the same wavelength. The lower wavelength of cis polyacetylene as compared with the trans one is explained by a smaller effective conjugation of the cis chain. This is a consequence of the partial rotation of the polymer chain around the simple bonds, caused by steric repulsion between neighbouring hydrogen atoms in cis sequences.

Although the absorption maximum of the trans polymer arises at a higher wavelength as compared with the cis polymer, the absorption spectrum is much broader.⁸⁹ This proves a higher polydispersity of the number of effectively conjugated double bonds in trans polymer with respect to the cis one.

Information on polyacetylene molar mass, molar mass distribution, crosslinking and branching can be obtained only after transforming the polyacetylene into a

soluble olefinic polymer. The simplest ways to obtain a polyolefine from polyacetylene are chlorination and hydrogenation.

Natta *et al.*⁷ were the first to chlorinate trans polyacetylene in suspension in CCl_4 and they obtained a white insoluble polymer containing 64% chlorine. 85% of the chlorine content was fixed by addition and 15% by substitution. The same reaction was performed by Champetier⁶⁹ but in the dark, in order to avoid the substitution. The polymer obtained was insoluble and had 42.46% chlorine. The theoretical chlorine content is 67.70%.

Tsumura and Hagihara were the first to obtain polymer soluble in dimethylformamide by polyacetylene chlorination.⁷⁵ This method of solubilization was completely neglected until 1980, when Wegner^{45,45a} showed that by cis polyacetylene (obtained by Luttinger catalyst) chlorination, a completely soluble polymer (e.g. in CH_2Cl_2) is obtained, whereas by chlorination of a cis or trans polymer obtained by the Shirakawa method only insoluble polymers are obtained. The molar mass of chlorinated polyacetylene is generally of the order of 20,000–50,000, if chlorinated immediately after the polymerization. If kept for some time even at -30°C (typically 3–4 days) the polymer can no longer be solubilized by polymer analogous reactions. In sharp contrast, cis-polyacetylene prepared according to Shirakawa, can be chlorinated as well, but gives never a soluble reaction product. Wegner *et al.* assume that the Shirakawa procedure leads to crosslinking even during the polymerization process.

Other information on polyacetylene molar mass was published by Shirakawa *et al.*^{91,92} They have been obtained on the polyethylene synthesized by polyacetylene hydrogenation. This was performed on polyacetylene films Na-doped under high hydrogen pressure at 200°C during 24 hours.⁹¹ The polymer obtained was partially soluble (between 5 and 80%), although the same polyacetylene was used. It is not clear whether crosslinking occurs during isomerization, doping or hydrogenation, due to some impurities present, e.g. oxygen or water. The number average molar mass measured by GPC was 6200 with a \bar{M}_w/\bar{M}_n value of 3.44.

Cis polyacetylene K-doped hydrogenation in a temperature range of 175–260°C and a hydrogen pressure of 30 Kg/cm² during 20 hours leads to polymers completely soluble in tetraline.⁹² The polymer molar mass is presented in Table 7.

TABLE 7. Influence of hydrogenation temperature on the hydrogenated polyacetylene molar mass distribution (reference 92)

No.	Sample	Hydrogenation temperature °C	\bar{M}_n ^{a)}	\bar{M}_w ^{a)}	$Q(\bar{M}_w/\bar{M}_n)$
1	(CHK _{0.03}) _x	175	7900	18700	2.3
2	(CHK _{0.10}) _x	195	6100	14900	2.4
3	(CHK _{0.03}) _x	235	5700	14100	2.5
4	(CHK _{0.07}) _x	260	6500	15500	2.4

^{a)} obtained in o-dichlorobenzene at 140°C

These results demonstrate that cis polyacetylene is not crosslinked. However, with increasing hydrogenation temperature, a decrease of molar mass occurs, indicating some scission reactions. These take place probably during thermal cis-trans isomerization and are concurrent with chain crosslinking. Due to the very high temperatures required for hydrogenation, polyacetylene structure and molar mass cannot be determined in this way. More convenient are the chlorination reactions. Wegner *et al.*^{45,45a} believe that the formation of low molecular weight linear poly(ethylene) by polyacetylene hydrogenation is the consequence of hydrogenolysis of the crosslinked polymer.

Molar mass determinations for trans polyacetylene were reported also by Higashiura and Masayoshi.⁹³ They considered the polyacetylene obtained by Ziegler-Natta catalyst to be $\text{Et}-(\text{CH}=\text{CH})_n-\text{H}$ and determined, from elemental analysis, polymerization degrees up to 100. Their results cannot be taken into account, because there is no quantitative determination of end-groups in polyacetylene.

Crystalline structure of polyacetylene was studied first by Natta, who proposed a pseudohexagonal-type elemental cell for trans polyacetylene⁵ and was intensively reinvestigated by Baughman *et al.*^{94,95} and Akaishi *et al.*⁸⁸ Recently, Baughman *et al.*⁴¹ reviewed these data together with the doubts existing about validity of the proposed model. Consequently, we will not repeat it in this review. It is noteworthy that X-ray diffraction studies at small angles do not evidence a lamellar structure for acetylene polymers.⁸⁸

In 1980 Wegner *et al.*^{45,45a,45b} reinvestigated the structure of cis and trans polyacetylenes obtained both by polymerization with the Ziegler-Natta catalyst ($\text{AlEt}_3/\text{Ti}(\text{OBu})_4$) and with the Luttinger catalyst ($\text{Co}(\text{NO}_3)_2/\text{NaBH}_4$). Cis-polyacetylene prepared by Shirakawa's and Luttinger's methods do not differ with regard to the overall morphology. Both samples seem to consist of irregularly shaped lamellar-like particles of typically a few hundred Å diameter and a thickness of 50–100 Å as the smallest discernible morphological subunit. The cis polymer presents an orthorombic unit cell with the following parameters: $a = 7.74 \pm 0.01 \text{ \AA}$; $b = 4.32 \pm 0.01 \text{ \AA}$; $c = 4.47 \pm 0.02 \text{ \AA}$; $Z = 2$; $\rho = 1.16 \pm 0.0 \text{ g.cm}^{-3}$.^{45a} The trans polymer can be obtained in two different structures, one having an orthorombic unit cell with $a = 5.62 \pm 0.05 \text{ \AA}$; $b = 4.92 \pm 0.02 \text{ \AA}$; $c = 2.592 \pm 0.05 \text{ \AA}$; $Z = 2$; $\rho = 1.20 \text{ g.cm}^{-3}$ and the other having a monoclinic unit cell with $a = 3.73 \pm 0.05 \text{ \AA}$; $b = 3.73 \pm 0.05 \text{ \AA}$; $c = 2.44 \pm 0.02 \text{ \AA}$; $\gamma = 98 \pm 2^\circ$; $Z = 1$ and $\rho = 1.27 \text{ g.cm}^{-3}$. Considering the cis-trans isomerization as a phase transition, the authors showed that the solid-solid transformation of the cis to either of the two trans modifications can be achieved by simultaneous shear and glide processes.^{45b}

Cis and trans polyacetylene film morphology was studied by transmission, electron diffraction, scanning and scanning transmission microscopy. The first studies are due to Ito, Shirakawa and Ikeda.²⁹ They showed that the films present a fibrillar morphology, being constructed by indefinite length fibrils with a thickness between 200 Å for the polymer prepared at -78°C and 300 Å for the material

obtained at 100°C. Polymer density is about 0.4 g/cm³ and in comparison with the density obtained by flotation method for films (1.2 g/cm³) indicates that polymer fibrils use only *ca.* a third of the film total volume,⁹⁶ the distance between cis polymer chains being approximately 3.6 Å.

Polyacetylene films having different densities were obtained by pressing polyacetylene foams obtained in the gel state.⁹⁷⁻¹⁰⁰ From initial foams having densities between 0.02–0.04 g/cm³ with a fibrillar fraction between 0.015 and 0.03, one obtains films having a density between 0.1 and 0.4 g/cm³. Typical diameter of fibrils from gel state material is 600–800 Å, as compared with 200 Å for the diameter of fibrils in films obtained directly by polymerization. Details on the fibrillar structure of polyacetylene films were obtained by microscopic analyses of films produced directly on a microscope grid.¹⁰¹ Fibril diameter is between 50 and 400 Å, most usually 200 Å.

4.2. Polyacetylene properties

4.2.1. *Thermal properties of polyacetylene* — Trans polyacetylene thermal behaviour was studied for the first time by Fredericks *et al.*¹⁰² in air and in vacuum. The polymer is thermally very stable in vacuum up to 420°C. Below this temperature, no changes in the polymer IR spectrum were observed. Keeping the polymer in vacuum for 72 hours produces only a slight decrease of the crystallinity. In air, heating polymer at 90°C for 72 hours leads to an amorphous brown solid with X-ray diffraction and IR spectra identical to a cuprene sample prepared according to Reppe. At 205°C, polyacetylene becomes cuprene in two hours. Acetylene polymerization to cuprene requires 72 hours at 90°C in tetrahydrofuran and with Ni(CN)₂ as catalyst. Cuprene can be considered to appear through polyacetylene oxidation with the oxygen from the reaction medium. Cis-trans isomerization, which takes place during propagation, leads to an increase of polymer reactivity toward oxygen in this reaction step.

Kleist and Byrd⁴⁹ were the first to study the thermal behaviour of the cis polymer. They showed that a 69% cis polyacetylene undergoes a cis-trans isomerization of 5.6% per day, even at room temperature. By DSC measurements performed under nitrogen, these authors evidenced an exothermic irreversible maximum for cis-polyacetylene between 320–500°K, which was assigned to the cis-trans isomerization. The calculated heat of isomerization was equal to 1.6 kcal/mole for the cis-rich polymer and 1.7 kcal/mole for trans-rich polymer. Another exothermic effect, existing in both cis- and trans-polyacetylene, was observed between 550 and 650 K. The maxima of this caloric effect are located at 630 K for cis polymer and 610 K for trans polymer. The heats corresponding to this transition for cis and trans polymers are equal to 24 and 5.3 cal/g, respectively, and were assigned to some crystallization phenomena. The cis polymer melts with rapid decomposition at 740 K, whereas the trans one decomposes without melting at 685°C. Thermo-gravimetric analysis in air of a cis-polymer sample kept four weeks at –30°C

reveals an increase in weight beginning at 350 K and a maximum of this increase of 13.5% at 505 K. Above this temperature a linear decrease in weight occurs when increasing the temperature. At 1000 K the polymer lost 72% from the initial weight. The maximum rate of weight increase lies between 455–475 K, whereas the maximum isomerization rate under nitrogen lies between 420 and 455 K. Therefore, the weight increase in this temperature range can be explained by the maximum reactivity toward oxygen of the double bonds during cis-trans isomerization. Thermogravimetric analysis of a trans sample kept four weeks at –30°C shows an explosive weight loss at 335 K due to the peroxides obtained from oxidation with atmospheric oxygen.

The thermal behaviour of cis and trans polyacetylene films was investigated in detail by Ito, Shirakawa and Ikeda¹⁰³ in 1975. There are no weight losses up to 420°C for either cis or trans polymers. The cis polymer presents an exothermal maximum at 145°C assigned to cis-trans isomerization. The enthalpic change for the exothermal phenomenon at 145°C is equal to 1.85 kcal/mol (calibrated for 100% cis polyacetylene) and corresponds to the values obtained by Kleist and Byrd,⁴⁹ but, because in the solid state the isomerization is not an independent phenomenon, the exothermal effect at 145°C must include the cis-trans isomerization (exothermic), in-plane disordering of molecular chains (endothermic) and the rearrangement to a new crystalline structure (exothermic).

IR and Raman spectroscopy indicate that the cis double bond stretching arises at a higher frequency (1552 cm^{-1}) than the trans one (1474 cm^{-1}) and, consequently, the force constants of cis and trans bond stretching are 4.8 and 4.7 mdyne/ \AA , respectively. According to these results, breaking a cis double bond requires more energy than for a trans one. However, because the trans polyacetylene is more coplanar, having no steric hindrances and a maximum in resonance stabilization energy, the steric repulsion between neighbouring hydrogens in cis polyacetylene generates a slight rotation around the cis double bond. Due to these steric effects, cis polyacetylene is thermodynamically less stable than trans.

Both cis and trans polymers present a second exothermal maximum at 325°C which is assigned now, in disagreement with Kleist and Byrd,⁴⁹ to hydrogen chain scission and crosslinking. The polymer obtained by 5 minutes treatment in vacuum at 325°C is amorphous, brown-coloured and presents IR bands characteristic of $-\text{CH}_2-$, $-\text{CH}_3$, $-\text{C}\equiv\text{C}-$ and $-\text{C}_6\text{H}_5$ groups. No volatile products have been evidenced during this reaction. Only at 420°C an endothermal peak arises, characteristic of elimination of volatile products due to thermal degradation. At this temperature, the polymer loses 63% of its weight. The remaining product is a brown oil having the same structure as the brown polymer obtained at 325°C.

Thermal cis-trans isomerization kinetics do not follow a simple reaction order. The dependence of isomerization activation energy on the trans content of the polymer is presented in Fig. 7. One can observe an increase of the activation energy when decreasing the cis content of polyacetylene. Because the isomerization activation energy depends on the electronic density of the double bond, it must

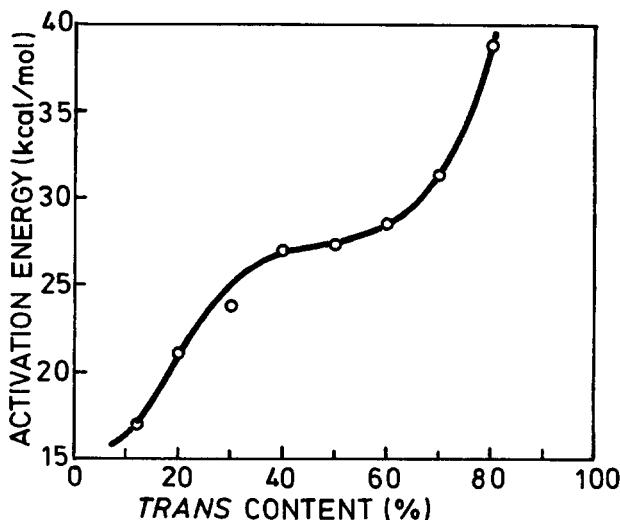


FIG. 7. Activation energy-trans content relation for the thermal cis-trans isomerization of polyacetylene (reference 103).

decrease with increasing polymer chain conjugation. As was already discussed, trans polyacetylene presents a higher effective conjugation as compared with cis polyacetylene.^{89,90} Therefore, the increase of the cis-trans isomerization activation energy when increasing the trans content of the polymer cannot be explained. Because the reaction is performed in solid state, the steric hindrances caused by a statistical isomerization can affect consequently the remaining cis double bond isomerization. The cis-CH out of plane deformation band (747 cm^{-1}) in the IR spectrum does not disappear completely even after a long thermal treatment at 200°C . The maximum trans content which could be obtained in such a way is 98%. On the other hand, there are no absorptions due to the cis configuration in the spectrum of the polymer obtained by polymerization at temperatures higher than 150°C .

The fact that the 100% trans polymer was obtained directly by high temperature polymerization, proves that, at the same time as polymerization with cis-opening of the triple bond, a thermal cis-trans isomerization takes place during propagation, followed by crystallization. This difference between the trans polymer obtained by isomerization during propagation and the trans polymer obtained by isomerization after polymerization, although very small (2% cis sequences), can be assigned to some crosslinking reactions appearing during isomerization, especially in solid state. Until now, one has not been able to find other reasons than a crosslinked structure or intramolecular cyclization to explain the irreversibility of cis-trans isomerization and the curious dependence between the isomerization activation energy and the trans content of polymer.

The polymer thermal history strongly affects polymer structure and, therefore, its properties. This effect was studied by the synthesis of a polyacetylene having different cis-trans compositions by three different methods:¹⁰⁴

Type 1 — controlling the acetylene polymerization temperature (between -78 and 150°C) with the catalytic system AlEt₃/Ti(OBu)₄ (Al/Ti = 4)

Type 2 — controlling the ratio Al/Ti = 1-3 of the same catalytic system at a polymerization temperature of 0°C

Type 3 — by cis-trans thermal isomerization of type-1 polymer prepared at -78°C.

The comparison between the three types of polymers was made by X-ray diffraction and density measurements. Polyacetylenes having the same cis-trans composition belonging to a different type presented different crystalline structures and densities. Type-2 polymers seem to be obtained through different catalytic species, a fact recently confirmed by Chien *et al.*⁶⁸ whereas type-1 and type-3 polymers are obtained by thermal isomerization. Trans sequences of type-1 polyacetylenes are obtained by cis-trans isomerization during propagation reaction, whereas type-3 polyacetylenes are obtained by solid state isomerization of the polymer.

4.2.2. Mechanical properties of polyacetylene — Mechanical properties of polyacetylene films were recently studied by Shirakawa and Ikeda⁹⁹ and Dray *et al.*¹⁰⁵

Figure 8 presents the tensile strength and the elongation to break against cis/trans content of polyacetylene film.⁹⁹ The experiments are carried out in an inert atmosphere.

The tensile strength decreases with the polymer cis content from 3.8 kg/mm² for a 98% cis polymer to 2.4 kg/mm² for a 96% trans polymer. At the same time, the elongation to break dramatically decreases when decreasing the cis content of the polymer, its value becoming near zero for trans-rich films. The brittleness of trans-rich films can be explained only by the increase of polymer crosslinking during cis-trans thermal isomerization.¹⁰⁵ For 85% cis polymer, the extension ratio $1/l_0$ (where l = maximum stretched length and l_0 = initial length) is equal to *ca* 3.3, but for a 90% trans polymer this value does not surpass 1.05-1.1.¹⁰⁵

Cis polymer film-stretching performed at the same time as cis-trans thermal isomerization gives an extra elongation of the polymer around 130-160°C. This is the maximum cis-trans isomerization rate temperature interval; here the ratio $1/l_0$ can reach the value of 4. Taking into account the bond lengths and angles along the carbon-carbon chain, one can conclude that trans isomer is longer than the cis one by *ca* 18%. When cis isomers were stretched during isomerization, the trans isomers became 20% longer than cis isomers. One can thus deduce that the extra elongation arises from the increase of the polymer length as a consequence of cis-trans isomerization.¹⁰⁵

A decrease of pore size and volume in the polyacetylene film takes place simultaneously with the elongation, which indicates an increase in polyacetylene fibril packing. Initially, the fibrils occupy only 36% of the total volume. After the elongation they represent 71% of the film volume.⁹⁹ The increase in fibril packing

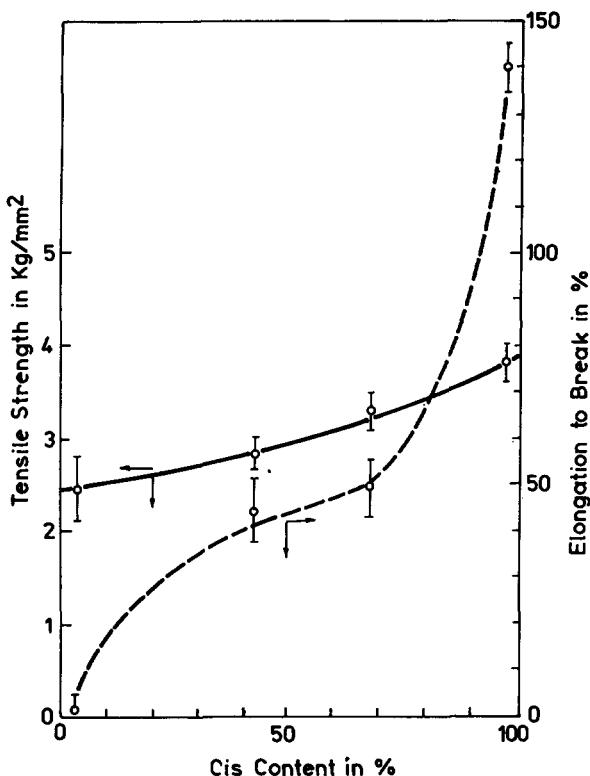


FIG. 8. Mechanical properties of polyacetylene film as a function of polymer cis content (reference 99).

is a consequence of orientation and is easily observable by electronic or scanning microscopy.^{99,105} The oriented films present optical and electrical anisotropy.⁹⁹

It is noted that the extension ratio $1/1_0 = 3.3$ value was obtained for a polyacetylene film which had no contact with air. Contact with air (oxygen) causes a decrease in the polymer maximum extension ratio, proportional to the contract time. It seems that the process determining the decrease of the extension ratio during air exposure is crosslinking. As evidence one can consider the fact that for a given extension ratio $1/1_0$, the polyacetylene resistance is higher when exposed at a higher oxygen percent. Therefore, if the polymer is crosslinked, it requires a higher stress to be elongated to a given length and at the same time the maximum elongation decreases.¹⁰⁵

As is clear from the results presented, the crosslinked structure of the trans polymer is again proved, and also the action of oxygen on polyacetylene is evidenced. Experimental proofs for polyacetylene crosslinking in the presence of the oxygen support the proposed mechanism of obtaining cuprene by polyacetylene oxidation.¹⁰²

4.2.2. Polyacetylene paramagnetism — Although the first paper on polyacetylene paramagnetism was published by Hatano *et al.*¹⁰⁶ in 1961, and the researches have been continued by Berets and Smith¹⁰⁷ and Shirakawa *et al.*¹⁰⁸ the first significant results on origin of the ESR signal in polyacetylene appeared in 1979 and 1980.^{68,109,110}

Thus, Snow *et al.*¹⁰⁹ studied the influence of temperature and oxygen, nitrogen oxide, halogens, nitrogen, ammonia and water vapour on a cis (98.1%) polyacetylene film directly prepared in the ESR sample tube. The first contact with oxygen causes a three-fold increase of the spin density, the ESR spectrum shape becoming symmetric and Lorenzian. At the same time, broadening occurs. The increase of the paramagnetic centres caused by oxygen is irreversible, but the change of ESR spectrum shape against oxygen pressure in the sample tube is reversible. The concentration of paramagnetic centres caused by the first polymer–oxygen contact is maintained. Therefore, after the first contact with oxygen, the oxygen pressure has no further influence on the ESR spectrum area, but only on ESR signal geometry. A similar effect is given also by nitrogen oxide.

The analysis of paramagnetic centre concentration dependence on temperature for two samples having different cis content (98.1% and 60%) shows an increase of the paramagnetic centre concentration up to a maximum. On cooling, the paramagnetic centres obey the Curie law up to -162°C . The increase of paramagnetic centre concentration is proportional to the initial cis content of the analysed sample. Thus, for the sample having 60% cis content, the increase is two-fold, whereas for the sample having 98.1% cis content a ten times increase is noted.

Recently, Chien *et al.*⁶⁸ reinvestigated oxygen and temperature influence on the ESR signal of polyacetylene prepared under vacuum directly in the sample tube. Experiments carried out in very rigorous conditions showed that cis polyacetylene prepared at -78°C does not present an ESR signal, which proves that cis polymer is diamagnetic. Heating this sample up to 25°C generates a weak ESR signal which can be assigned only to the unpaired electrons from double bond breaking during cis–trans isomerization. Such unpaired spins are presented in Fig. 9 and are considered as neutral defects, because they do not have electric charge.

Such a defect can be considered a phase kink as it can be observed by point line representation of the wavefunction. One can estimate that this unpaired electron is delocalized on approximately 15 lattice units at 25°C . Such an electron is named soliton.^{68,100,100a,110}

Introducing oxygen in this sample at 25°C produces an increase of 3–5 orders of magnitude in the ESR signal intensity. On the other hand, oxygen introduction *in situ* into the polymerization mixture at -78°C leads to an ESR signal having the same intensity as that obtained by temperature increase of the anaerobic sample from -78°C to 25°C . When evacuating the oxygen introduced into the sample, no change of the ESR signal can be observed. It is to be noted that IR analysis of polymers which had oxygen contact does not reveal carboxylic bands. In these conditions Chien *et al.*⁶⁸ consider that the oxygen acts as a dopant on polyacetylene,

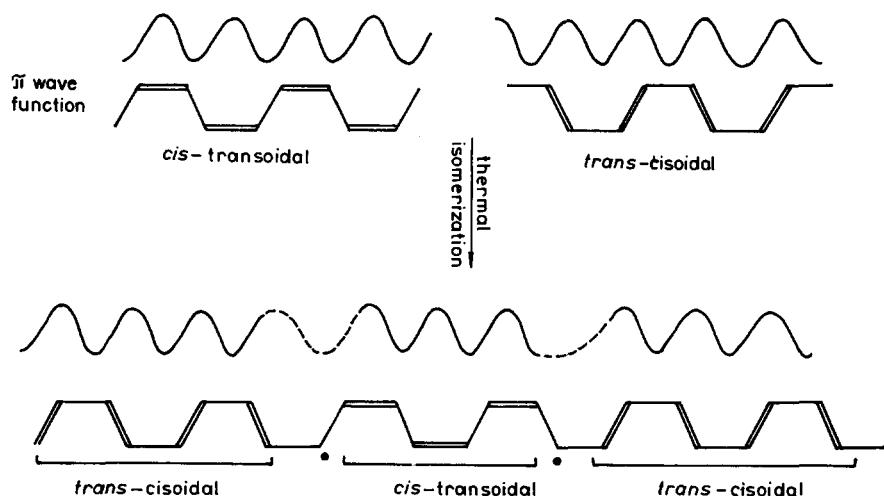


FIG. 9. Introduction of soliton-type structural defects by thermal cis-trans isomerization of polyacetylene (reference 100).

creating a charge transfer complex (CTC). Another alternative, proposed by the same authors, is that oxygen, being a triplet molecule, can catalyse the cis-trans isomerization introducing therefore structural defects which give the ESR signal.

The theories referring to the ESR signal origin in conjugated polyenes can be divided in two classes which were reviewed and applied to particular cases by Nechtschein,^{111,112} Misurkin and Ovchinnikov,³⁵ Berlin¹¹³ and more recently by Bloor *et al.*¹¹⁵⁻¹¹⁸ They are based on alternating defects in the conjugated double bonds on the chain¹¹⁹⁻¹²³ and on CTC.¹²⁴ For polydiacetylenes, the paramagnetism was assigned to conformational defects in the polymer chain.¹¹⁴⁻¹¹⁸

Taking into account the results presented by Snow *et al.*,¹⁰⁹ Goldberg *et al.*,¹¹⁰ and Chien *et al.*,⁶⁸ one can consider that the origin of polyacetylene paramagnetic centres is mixed. The fact that pure cis polymer noncontaminated with oxygen is diamagnetic proves that a part of polyacetylene paramagnetism is the consequence of structural defects arising from cis-trans isomerization. On the other hand, due to the very long conjugated chain of polyacetylene, the polymer ionization potential must be very low.^{110b} Consequently, oxygen acts as an electron-acceptor, creating cation-radical structures in the polyacetylene chain. Such a structure was recently proposed also for paramagnetic centres of poly(p-phenylene)s.¹²⁵ Oxygen evacuation after the first contact does not affect the paramagnetic centre concentration, because the ion-radical structure of polyacetylene can be stabilized through a new CTC between the neutral polyacetylene and the cation-radical one⁴⁵ (Fig. 10).

This type of complex can explain the irreversible nature of the paramagnetism introduced in polyacetylene by oxygen.

One can conclude that the paramagnetism of a polyacetylene which suffered air

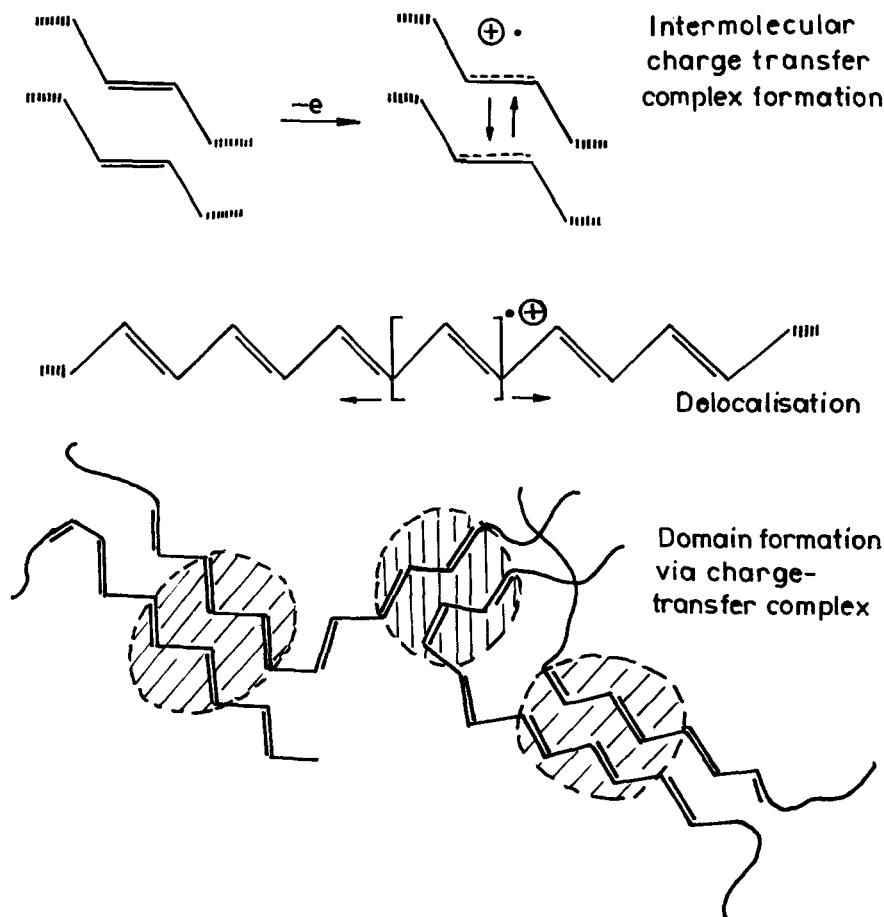


FIG. 10. Intermolecular charge transfer complex and domain with delocalised charge and spin formation in doped PA via charge-transfer interaction (reference 45).

contact is due to both solitons which appear from structural defects as a consequence of isomerization, and to cation-radicals which appear from the oxygen-polymer CTC.

4.2.4. Electrical properties of polyacetylene – According to the aromaticity intermolecular migration theory,^{126,127} the principal characteristic for efficient charge transport in an organic system is the presence of equally distanced atoms or of equally distanced molecules being in different oxidation states. The simplest example is a cyanine molecule (Fig. 11), the resonant structures indicating the positive charge migration between the two molecule ends. The molecule presented

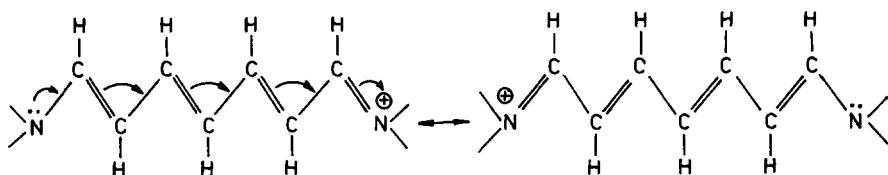


FIG. 11. Resonance structures of a cyanine (reference 126).

contains 10 electrons on 9 atoms, which represents approximately 1.1 electrons/atom. This inadequate ratio arises from the formally different oxidation states of the two nitrogen atoms. Such a molecule must theoretically behave like a metal if it is infinitely long and electric conductors could be attached to its ends. For a polyacetylene, as presented in Fig. 12, the resonance structure is energetically unfavourable. In this case there are no interactions between mixed valences. All

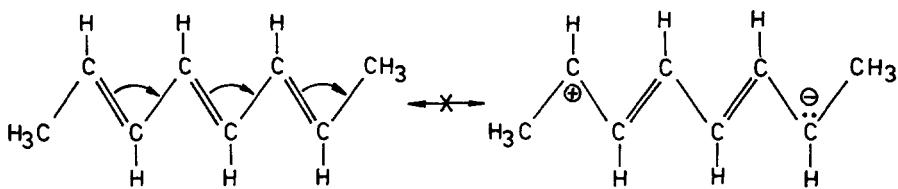


FIG. 12. Resonance structures of a polyacetylene (reference 126).

π -electrons are located on atoms in the same oxidation state, exactly one electron/atom. In this situation, the bond lengths will be between that of a pure simple bond and that of a pure double bond. Consequently, for the cyanine molecule (Fig. 11), the π -electrons can be delocalized on the chain, which is not possible for a simple polyacetylene molecule (Fig. 12).

Having in mind the polymerization mechanisms presented in Section 3 and the structural aspects from Section 4, one can conclude that the polyacetylene synthesized by all catalytic systems can reach the structural conditions for only a polymer of the type presented in Fig. 12. Consequently, from the theoretical point of view pure, polyacetylene must be a good insulator.

To transform polyacetylene into a conductor, one must functionalize the chain-ends with groups having different oxidation states. This is possible only when controlling the initiation and termination reactions during polymerization. The second possibility is to oxidise or to reduce the polymer chain creating a CTC with a micromolecular donor or acceptor. The first way seems to be more difficult and the second cannot be avoided, due to the inherent contact between the polymer and oxygen.

Although there are many studies referring to polyacetylene electrical properties,^{49,97-99,106-108,128} we shall present only some opinion regarding this polymer

conductivity by reporting some results published in 1980.^{129,130,130a} Pochan, Gibson and Bailey^{129,130} and Kiess *et al.*^{130a} were the first to measure electrical conductivity on a polyacetylene which had air contact for only 30 seconds to 3 minutes. Oxygen exposure for such a sample causes an increase of cis or trans polymer conductivity of more than one order of magnitude. Washing the sample with an argon flow causes a partial regeneration of the initial electrical conductivity, which proves that the oxygen influence is only partially reversible, as in the case of the paramagnetic properties of the polymer. Oxygen exposure for more than 50 minutes causes a strong decrease of the polymer electrical conductivity as a consequence of the oxidation and crosslinking reactions already mentioned.

These reactions destroy the conjugated double bond system, and both electrical conductivity and mechanical properties are worsened. The high slope of the electrical conductivity decrease against oxygen-exposure time leads to the conclusion that cis polymer which had no oxygen contact is in fact a good insulator.^{129,131,45} This proves that oxygen acts as an electron-acceptor, creating a CTC which induces cation-radical formation on the polymer chain. The acceptor part played by the oxygen is supported also by the fact that majority of charge carriers are the holes for polyacetylene.¹⁰⁷

The cis content influence on polyacetylene electrical resistivity (for samples which had air contact) was studied by Shirakawa *et al.*¹⁰⁸ They showed that the resistivity value decreases when increasing the trans content, from 1.66×10^8 ohm.cm for 85% cis polymer to $\sim 10^4$ ohm.cm for a 20% cis polymer.

The polymer having more than 80% trans content presents an increase of the resistivity which reaches 2.07×10^5 ohm.cm for a 100% trans polymer. These data cannot be correctly interpreted, although they have been correlated with X-ray diffraction and ESR data, because the oxygen-polymer contact has not been taken into account.

On the other hand, the real microstructure of the trans polymer is yet unknown. It is probable that the polymer having more than 80% trans sequences presents a high crosslinking degree which increases the effective conjugation polydispersity and decreases the electrical conductivity.

The synthesis of CTC using acceptors with higher affinity than oxygen, leads to organic conductors having very promising properties and utilization perspectives. As acceptors the following were used: Cl_2 , Br_2 , I_2 ,³⁰ AsF_5 ,^{31,132,133} ICl , IBr , HBr ,¹³⁴ AgBF_4 , AgClO_4 ,^{135,136} $(\text{FSO}_2\text{O}^-)_2$.¹³⁷ In the case of AsF_5 and $(\text{FSO}_2\text{O}^-)_2$ conductivities up to 10^3 ohm $^{-1}$.cm $^{-1}$ were obtained, and even higher. The majority of charge carriers are the holes.¹³² For the polymers complexed with sodium,¹³⁴ *n*-type conductors are obtained. Polyacetylene film orientation prior to complexation creates polymers with anisotropic conductivity^{96,98,99} with values surpassing 2×10^3 ohm $^{-1}$.cm $^{-1}$. There are proofs of the ion-radical structure of these CTC.^{100,138,139,139a}

It is not the purpose of this review to comment on the electrical properties of these CTC, intensively reviewed by other authors,^{36,38,39,41} although data inter-

pretation was based on a trans polymer whose structure requires further elucidation. This is the reason for the impossibility to correlate the electrical properties of polyacetylene CTC with the polymer structure.

However, very promising results can be expected for solar energy conversion into electric energy through photovoltaic effects.^{100,141-145} Until now, only 1% efficiencies were obtained for the direct conversion, but the low cost of polyacetylene and the low energy required for polyacetylene synthesis in the film state having great surfaces are factors which influence the constantly increasing interest in this polymer.

5. PHENYLACETYLENE POLYMERIZATION

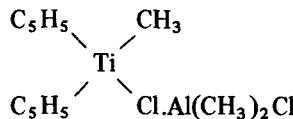
5.1. *Phenylacetylene polymerization with Ziegler-Natta catalysts*

The first phenylacetylene (PA) polymerization in the presence of Ziegler-Natta type catalysts was reported by Natta *et al.*⁵ in 1955. They used the same soluble and insoluble catalysts as for acetylene polymerization ($\text{AlEt}_3/\text{TiCl}_3$, $\text{ZnEt}_2/\text{TiCl}_3$, $\text{AlEt}_3/\text{Ti}(\text{OC}_3\text{H}_7)_4$) obtaining an orange soluble polymer. Then, all soluble and insoluble Ziegler-Natta catalysts used to polymerize acetylene were used also for phenylacetylene polymerization. These were detailed reviewed in two papers^{32,146} which present the literature up to 1974. For this reason, we shall select only the most typical results from before 1974, especially those referring to the polymerization mechanisms, polymer configuration and catalyst efficacy, and we shall emphasise more recent literature data.

The presence of chlorine in the Ziegler-Natta catalytic system gives the possibility, as for acetylene polymerization,⁴⁷ of obtaining of linear polymers or cyclic trimers, through variation of the Al/Ti ratio. Furlani *et al.*¹⁴⁷ extensively studied the Al/Ti ratio influence for the catalyst $\text{AlEt}_3/\text{TiCl}_4$ on the reaction products obtained when polymerizing PA in benzene at 10°C. The Al/Ti ratio is important not only for the reaction products, but also for the yield. At the ratios $\text{Al/Ti} < 1$, the monomer is very stable, no cyclic trimer or linear polymer is formed. For higher Al/Ti ratios, 1,3,5-triphenylbenzene and 1,2,4-triphenylbenzene are obtained, the maximum yield of cyclic compounds (~75%) being at $\text{Al/Ti} = 2-3$. Then, the cyclization reaction decreases (for $\text{Al/Ti} > 7$ no cyclic compounds are obtained) accompanied by polyphenylacetylene (PPA) appearance. Above $\text{Al/Ti}=7.5$ only a soluble PPA is obtained. These authors showed that the replacement of the aromatic solvent with an aliphatic one decreases the tendency to form cyclic compounds.

The increase in chlorine content of the Ziegler-Natta catalyst, realized using the catalyst $\text{AlEt}_2\text{Cl}/\text{TiCl}_4$, leads to only cyclic trimers synthesis, independent of the Al/Ti ratio in the range $\text{Al/Ti}=1-25$.¹⁴⁸ In this case, even the timerization yield is very little affected by the Al/Ti ratio. Thus, in the range $\text{Al/Ti}=1-7$, the yield is approximately 80% and decreases very slow to only 60% at ratios $\text{Al/Ti} > 5$. This

reaction was speculated on simultaneously by Korshak *et al.*,^{21,22,149} Bracke,¹⁵⁰ Chalk and Gilbert¹⁵¹ who published in 1971 and 1972, respectively, a method for soluble branched polyphenylenes synthesis by phenylacetylene and p-diethynylbenzene copolymerization. Berlin *et al.*¹⁵² proposed an anionic-coordinative mechanism for PA polymerization and cyclotrimerization in the presence of $\text{AlEt}_3/\text{TiCl}_3$, similar to that proposed by Ikeda *et al.*^{47,58,61} for acetylene polymerization. This mechanism is supported also by the direct proof of phenylacetylene insertion into the $\text{Ti}-\text{CH}_3$ bond for polymerization in the presence of $\text{Al}(\text{CH}_3)_2\text{Cl}/(\text{C}_5\text{H}_5)_2\text{-TiCl}_2$ and $\text{Al}(\text{CH}_3)_3/(\text{C}_5\text{H}_5)_2\text{TiCl}_2$. Performing the polymerization in the NMR sample tube, Dyachkowski *et al.*¹⁵³ showed that during 3 minutes from PA introduction into the catalytic system, the TiCH_3 bond from the compound:



disappears and a $\text{Ti}-\text{CH}=\text{C}(\text{CH}_3)_2$ bond appears.

Kambara and Noguchi¹⁵⁴ were the first to use PA polymerization soluble catalytic systems of the type: $\text{AlEt}_3/\text{Fe}(\text{acac})_3$, $\text{AlEt}_3/\text{V}(\text{acac})_3$ and $\text{AlEt}_3/\text{VO}(\text{acac})_2$. The same authors proposed in 1963 some very efficient Ziegler-Natta catalysts for linear PA polymerization:¹⁵⁵ $\text{AlEt}_3/\text{Ni}(\text{dmg})_2$, $\text{AlEt}_3/\text{Co}(\text{dmg})_2$, $\text{AlEt}_3/\text{Fe}(\text{dmg})_2 \cdot 2\text{Py}$, $\text{AlEt}_3/\text{Fe}(\text{dmg})_2 \cdot 2\text{NH}_3$, and $\text{AlEt}_3/\text{Fe}(\text{dmg})_2$. The maximum efficacy is obtained at $\text{Al}/\text{Fe}=10$ ratio and decreases in the following order: $\text{Fe}(\text{dmg})_2 \gg \text{Fe}(\text{dmg})_2 \cdot 2\text{Py} > \text{Fe}(\text{dmg})_2 \cdot 2\text{NH}_3$. Conversions higher than 90% are obtained in a maximum of one hour, and the maximum molar mass reaches 8900, being the highest obtained with a Ziegler catalyst.

In 1968, Kern^{156,157} synthesised for the first time a cis PPA using the catalysts: $(i\text{Bu})_2\text{AlH}/\text{Fe}(\text{acac})_3$ and $\text{NaBH}_4/\text{RhCl}_3$. Using the same type of catalysts: $\text{AlEt}_3/\text{VO}(\text{acac})_2 (\text{Al}/\text{V}=2)$, $\text{AlEt}_3/\text{Cr}(\text{acac})_3 (\text{Al}/\text{Cr}=3)$, $\text{AlEt}_3/\text{Co}(\text{acac})_3 (\text{Al}/\text{Co}=3)$, $\text{AlEt}_3/\text{Ti}(\text{OC}_4\text{H}_9)_4 (\text{Al}/\text{Ti}=4)$ and $\text{AlEt}_3/\text{TiCl}_2(\text{C}_5\text{H}_5)_2 (\text{Al}/\text{Ti}=2)$, Simionescu and Dumitrescu¹⁵⁸⁻¹⁶⁰ reported a trans PPA synthesis, proposing an anionic-coordinative mechanism. The IR spectra previously published^{158,160} were reinvestigated and the conclusion was that a cis-rich polymer was obtained by PA polymerization in the presence of $\text{AlEt}_3/\text{VO}(\text{acac})_2$ (Fig. 5c from lit.¹⁶⁰).

A cis PPA was obtained also by Berlin and Cerkashin¹⁶¹ in 1971 using the catalyst $\text{AlEt}_3/\text{TiCl}_3$.

Polymers with high cis content were obtained by Simionescu *et al.*¹⁶² by PA polymerization with the catalyst $\text{AlEt}_3/\text{Fe}(\text{dmg})_2 \cdot 2\text{Py}$. Taking into account that both trans and cis polymers can be obtained by PA polymerization with different or the same Ziegler-Natta catalysts and at similar temperatures, Simionescu *et al.*^{43,44,163,164} investigated the factors which affect configuration. Studying PA polymerization in the presence of catalysts like $\text{AlEt}_3/\text{Fe}(\text{dmg})_2 \cdot 2\text{Py}$, $\text{AlEt}_3/\text{Fe}(\text{acac})_3$, $\text{AlEt}_3/\text{VO}(\text{acac})_2$, $\text{AlEt}_3/\text{Co}(\text{acac})_3$, $\text{AlEt}_3/\text{TiCl}_4$, Simionescu *et al.* demonstrated that PA polymerization takes place by cis opening of the triple

bond. Trans sequences appear, as for acetylene polymerization, by thermal isomerization of cis sequences. Thermal isomerization can be initiated by the thermal effect arising from: a) the heat of polymerization, b) the temperature of polymerization, c) the destruction of the catalytic system. The first two heat sources initiate thermal isomerization especially during propagation, whereas the last effect determines thermal isomerization of the polymer. Taking into account the fact that cis-trans thermal isomerization takes place more easily during propagation, one must have in mind that efficient heat transfer during initiation is decisive for obtaining a cis-rich polymer.^{43,44,163,164} Indeed, when the monomer is introduced into the catalytic system cooled at -78°C (in order to eliminate the polymerization initiation heat) and the catalytic system is destroyed in order to avoid an increase in temperature above the polymerization temperature (i.e. by introducing HCl/MeOH into the reaction mixture at -78°C) even if the polymerization is performed at room temperature (~25°C), PPA with very high cis content are obtained (near 100%). When the monomer is introduced into the catalytic system and the catalyst is destroyed at room temperature, polymers with very low cis content are obtained. A decrease of the cis content (but much lower) is obtained also when the monomer is introduced into the catalytic system at -78°C, polymerization performed at room temperature and the catalyst destroyed at 0°C. In these conditions, polymers with ca. 80% cis sequences are obtained.¹⁶⁴

Famili and Farona¹⁶⁵ studied in 1980 PA polymerization with the catalytic system $\text{EtAlCl}_2/(\text{C}_5\text{H}_5)_2\text{TiCl}_2$ and showed that polymerization proceeds through a mechanism of successive 2 + 2 cycloadditions. The proof for this mechanism was the separation of a ladder compound formed of fused cyclobutane rings. This ladder compound, considered as an intermediate in the reaction, is easily converted into the conjugated polymer which appears as the final reaction product. This mechanism will be presented in detail in the Section 5.3. and is completely different from the anionic-coordinative mechanism of successive insertion proposed for acetylene and phenylacetylene polymerization. Moreover, these authors consider that the 2 + 2 successive cycloaddition mechanism is valid for all catalytic systems containing metals of IVB and VIB groups. The insertion polymerization mechanism would be valid, in this case, only for catalytic systems based on VIIIB and VIII-th groups metals. According to the 2 + 2 successive cycloaddition mechanism, such cyclic derivatives as 1,2,4 and 1,3,5-triphenylbenzene are obtained through the intermediate formation of Dewar triphenylbenzene. The experimental proofs for this mechanism make questionable the validity of the anionic-coordinative mechanism through acetylene insertion into the metal-carbon bond for the catalytic systems based on IVB and VIB groups metals.

5.2. Structure of polyphenylacetylene obtained by Ziegler-Natta catalysis

Theoretically, a monosubstituted polyacetylene can exist in the following four configurations: trans-transoidal, trans-cisoidal, cis-transoidal and cis-cisoidal (Fig. 13).

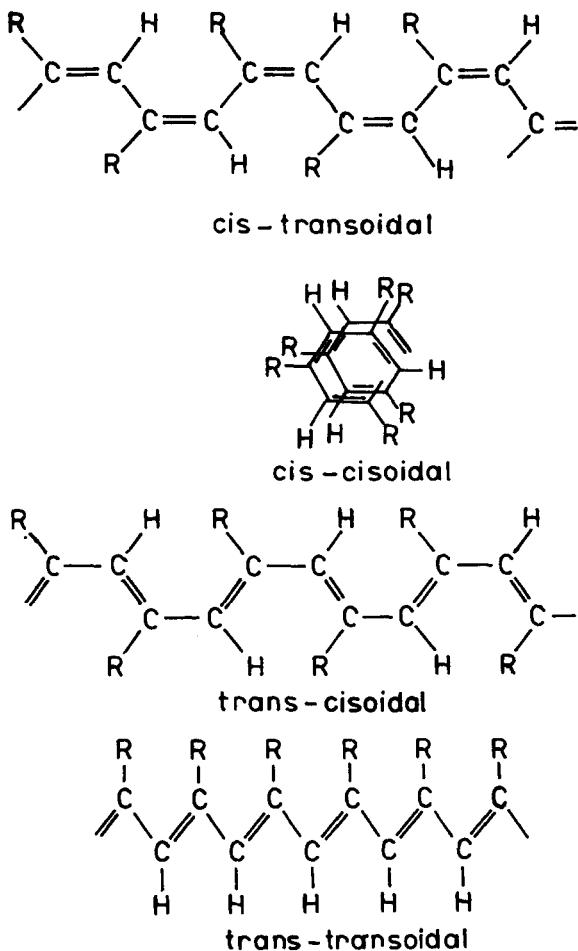


FIG. 13. Possible configurations of polyacetylenes (reference 43).

Analysing the chain conformation on atomic models (W. Büchi, Glassapparate Fabrik, Flawil Switzerland) and taking into account the distance between the phenyl ring centre and the chain hydrogen atoms and the distance between aromatic ring planes, the chemical shifts in the NMR spectra were calculated for these four structures.

Thus, for trans-transoidal structure (12/1), two aromatic protons must be shifted to higher fields, for cis-cisoidal structure (3/1) an aromatic proton must be more shielded, whereas for cis-transoidal structure (3/1) two protons (one aromatic and one polyenic) are shifted to higher fields. Only for the trans-transoidal (3/1) structure, all protons resonate in the same spectral domain.^{43,44,161,163,164}

With catalysts which favour linear polymerization (especially those soluble), two polymer fractions are obtained. One is soluble in aromatic and halogenated solvents, yellow-orange coloured, possessing a crystallinity lower than 10–15% and the other is insoluble with crystallinities higher than 60%,¹⁴⁶ intensely red coloured. During polymerization, a transformation of the soluble polymer into the insoluble one is observed. When the thermal effects which initiate cis-trans isomerization are eliminated, both polymers present IR spectra characteristic for cis polymers (740 cm^{-1} cis-CH out of plane and 895 cm^{-1}). A typical NMR spectrum of the soluble fraction, cis-rich (95%) is presented in Fig. 14 and corresponds to a cis-transoidal structure, having three proton resonances centered at 5.82 ppm (one olefinic proton), 6.70 ppm (one aromatic proton) and 6.85 ppm (four aromatic protons). The best spectral resolution is obtained at 70°C .^{43,44,163,164}

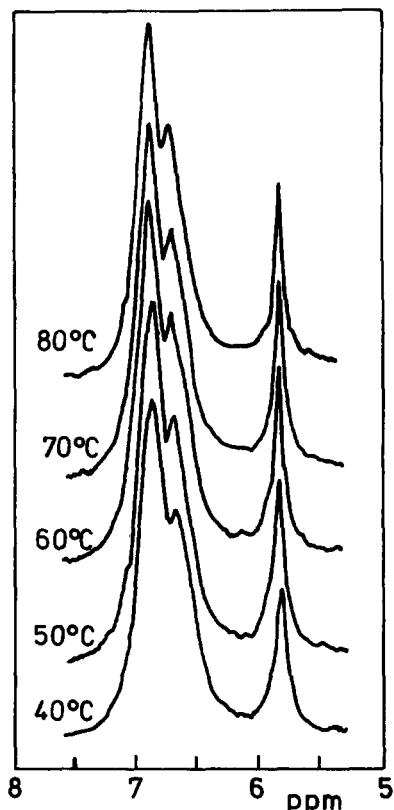


FIG. 14. H-NMR spectrum of cis-transoidal polyphenylacetylene as a function of registration temperature (solvent CCl_4 , reference TMS, 95% cis content) (reference 164).

The insoluble polymer obtained with Ziegler-Natta catalyst has a cis-cisoidal structure, highly crystalline and can be regarded as the homologue of the isotactic α -vinylic polymers.^{164a}

The cis-content of the cis-transoidal PPA can be determined from the NMR spectrum using the equation:¹⁶⁴

$$\% \text{ cis} = A_{5.82} [10^4 / A_t \times 16.66]$$

where

$A_{5.82}$ = area of the 5.82 ppm signal

A_t = total area of the NMR spectrum.

Lower cis-contents than 70% cannot be determined from the NMR spectrum, due to the overlapping of 5.82 ppm and aromatic protons signals. In these situations, the calibration in Fig. 15 can be used, correlating A_{760}/A_{740} of the IR spectra with the cis content determinated by NMR. The A_{760}/A_{740} ratio calculation permits the determination of cis-contents between 100 and 40% for both cis-transoidal (soluble) and cis-cisoidal (insoluble) polymer.

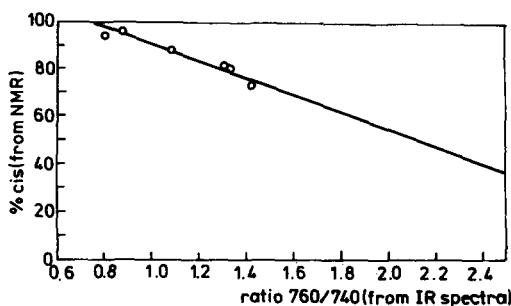


FIG. 15. Dependence of polyphenylacetylene cis-content determined by $^1\text{H-NMR}$ vs. $760 \text{ cm}^{-1}/740 \text{ cm}^{-1}$ ratio (reference 164).

Figure 16 presents the $^1\text{H-NMR}$ spectrum of a cis-transoidal PPA registered at different temperatures in hexachlorobutadiene.¹⁶⁴ The spectrum resolution increases up to 80°C . At higher temperatures, the cis-polyenic proton signal area (5.82 ppm) begins to decrease, and above 100°C , a new signal at 7.6 ppm appears. This signal was assigned to the 2,4,6 protons of 1,3,5-triphenylbenzene.

The NMR spectrum of the product eliminated from the sample tube at 190°C and purified by reprecipitation in petroleum ether from hexachlorobutadiene solution has no signal at 7.6 ppm and becomes identical with that of the so-called trans polymer obtained with Ziegler-Natta catalysts without elimination of thermal effects. This is a proof for the existence of concurrent cyclization and chain scission reactions during cis-trans isomerization.

$^1\text{H-NMR}$ spectrum of the polymer purified after isomerization is presented in Fig. 17b together with the $^1\text{H-NMR}$ spectra of cis-transoidal PPA (a), trans-cisoidal

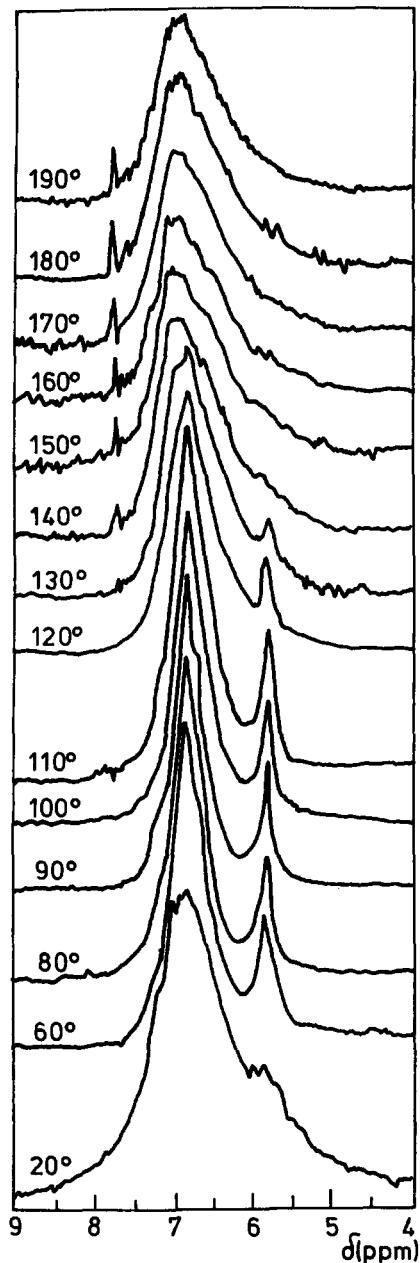


FIG. 16. ^1H -NMR spectrum of cis-transoidal polyphenylacetylene (95 % cis content) as a function of registration temperature (solvent hexachlorobutadiene, reference HMDS) (reference 44).

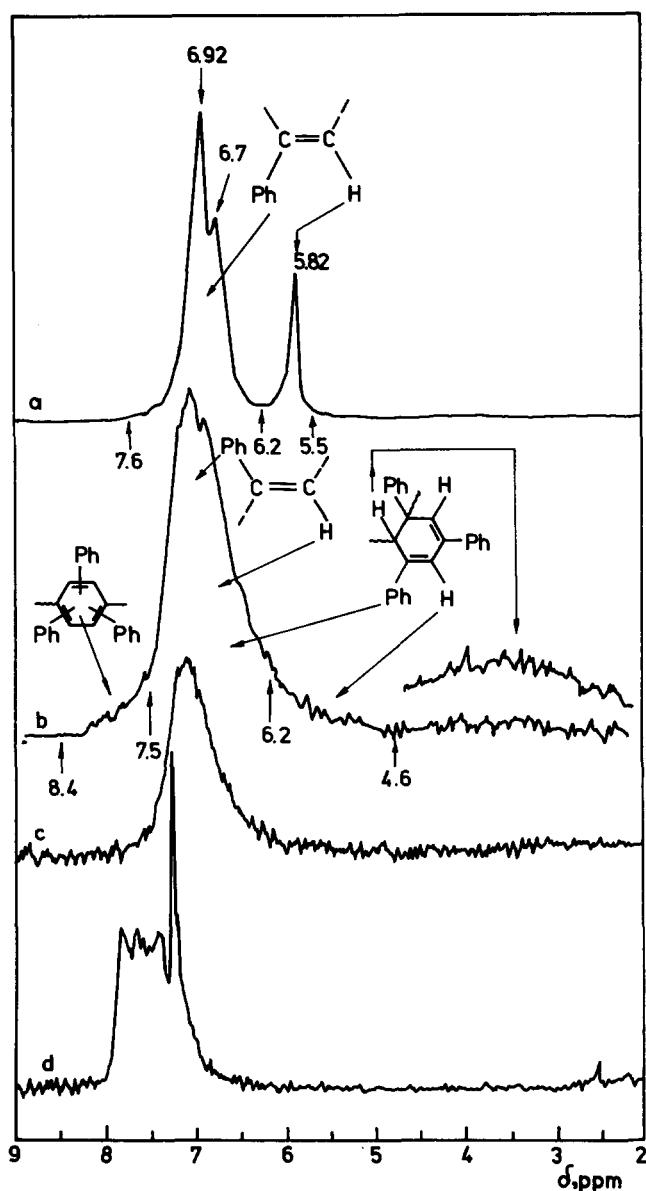


FIG. 17. ¹H-NMR spectra of (a) cis-transoidal PPA (CCl_4 , TMS); (b) trans-cisoidal PPA obtained by thermal isomerization of cis-transoidal PPA (CCl_4 , TMS); (c) trans-cisoidal PPA obtained by cationic polymerization of phenylacetylene (CCl_4 , TMS); and (d) polyphenylene obtained by copolycyclotrimerization of p-diethynylbenzene and phenylacetylene in the presence of $\text{AlEt}_2\text{Cl}/\text{TiCl}_4$ catalytic system (CDCl_3 , TMS) (reference 167).

PPA obtained by cationic polymerization (having 5 aromatic protons and the trans-polyenic proton at 6.20–7.20 ppm) (c) and a polyphenylene (having the aromatic proton signal at 6.6–8.1 ppm) obtained by phenylacetylene and p-diethynylbenzene copolycyclotrimerization (d).

The comparative study of spectra presented in figure 17 permitted the following assignments:¹⁶⁷ trans-cisoidal PPA obtained by thermal isomerization presents the methinic proton resonance at 2.5–4.5 ppm, arising from 1,3 and/or 1,4 cyclohexadiene structures, between 4.6 and 6.2 ppm the cyclohexadiene olefinic protons resonate, at 6.2–7.6 ppm monosubstituted benzene protons and trans-polyenic proton resonate and at 7.6–8.2 ppm one sees the polyphenylenic structures. Consequently, PPA thermal isomerization reaction is supposed to be accompanied by cyclization, aromatization and chain scission reactions, at least above 120°C (Fig. 18). The cis-PPA chain scission reactions at higher temperatures than 130°C in solid state were recently confirmed by GPC measurements.^{167a}

THERMAL INDUCED REACTIONS IN CIS POLYPHENYLACETYLENES

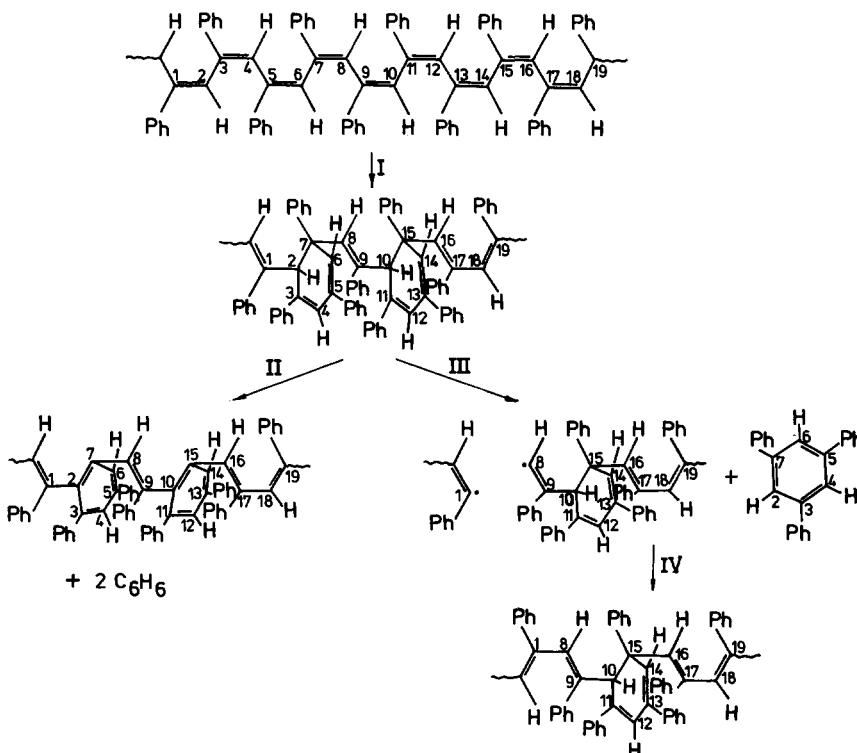


FIG. 18. Possible reactions occurring during cis-trans thermal isomerization of cis-transoidal polyphenylacetylene (reference 167).

The structure of the polymer obtained by thermal isomerization in the solid state of a cis-transoidal or cis-cisoidal PPA is identical with that of a trans polymer obtained by solution isomerization of cis-transoidal PPA. The heating of cis-cisoidal PPA at temperatures higher than 100°C is accompanied by colour-change from red to yellow-brown and by polymer transformation from crystalline into amorphous.

The study of the apparent cis-trans thermal isomerization, performed by Simionescu and Percec in solution and in solid state¹⁶⁶ on cis-transoidal PPA, led to the following conclusions. (It is to be noted that the kinetics follows only the decrease in the cis content not the variation in trans-content or cycles, due to the complexity of this analysis by NMR or IR. Also, it is performed at temperatures lower than 120°C in order to avoid chain scission reactions).

Both in solution and in the solid state, the reaction order is not a simple one, which can be explained by the coexistence of isomerization and cyclization reactions. The apparent activation energy for solution isomerization was 13.1 kcal/mol for 95% cis polymer and increased up to ca. 20 kcal/mol for 70% cis polymer, remaining then approximately constant. These relatively low activation energy values cannot reflect an isomerization based on thermal excitation of the double bonds mechanism without the interference of other reactions. Such a mechanism would require ca. 59.5 kcal for π -bond breaking and in addition 3.6 kcal for the resulting biradical rotation, which makes a total of 63.1 kcal/mol.

Cis-sequences disappear in solution at 20°C at a rate of 14.5% per day for 85% cis PPA and decreases to 3.9% per day for a polymer containing only 34% cis. Even at 70°C, 96% cis PPA loses only 40% of its cis content during 1.5 hours. On the other hand, when the heat of polymerization is not eliminated, the so-called trans PPA is obtained by room temperature PA polymerization with a reaction time of an hour. From these data, the conclusion is that trans PPA sequences arise by isomerization especially during chain propagation reactions.

On the other hand it was demonstrated that for PPA, polyenic structures are obtained only for near 100% cis-transoidal or cis-cisoidal polymers. Thermal isomerization of cis configurations leads not only to trans configurations, but also to cyclohexadienic sequences, even for an isomerization performed below 20°C. The thermal history of trans-polymer synthesis governs the microstructure for all the polymers.

Due to the low ratio of the methinic protons to olefinic and aromatic protons in cyclohexadiene structures (1/17), ¹H-NMR analysis could not offer quantitative results on the microstructure of these polymers. This was the reason for the analysis of pentadeuterophenylacetylene polymer microstructure.¹⁶⁸ Figure 19 presents the ¹H-NMR spectrum of an 81% cis polypentadeuterophenylacetylene (PDPA) with cis-transoidal structure registered as a function of temperature. The cis polymer has the cis polyenic proton signal at 5.82 ppm and at 6.85 ppm the trans polyenic proton signal. This last signal coincides with the sole signal present in a trans-cisoidal PDPA obtained by chemical isomerization by a method which will be described later.

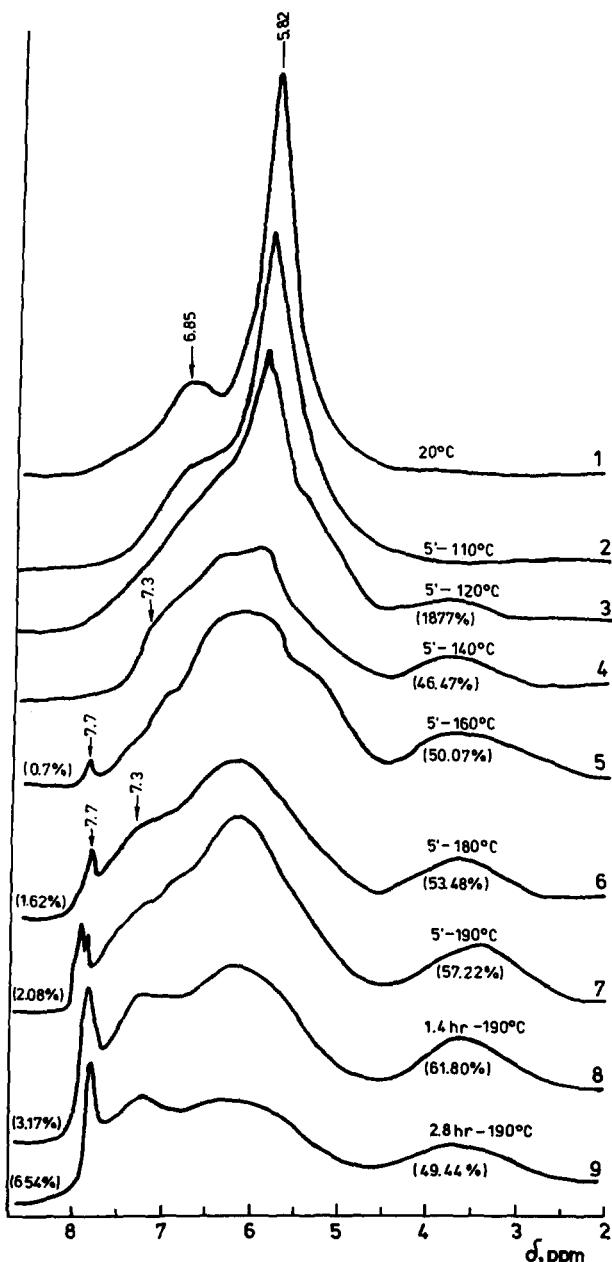


FIG. 19. ^1H -NMR spectrum of cis-transoidal polypentadeuterophenylacetylene (81% cis content) as a function of registration temperature (hexachlorobutadiene, HMDS). On the right-hand side the proton distribution in cyclohexadiene structure is given, on the left-hand side the proton distribution in 1,3,5-tris(penta-deuterophenyl)benzene is given (reference 168).

When increasing the temperature, an increase in the trans content is noted, together with the appearance of the methynic proton resonance from cyclohexadiene sequences (3–4 ppm), of the resonance from polyphenylenic sequences (7.3 ppm) and, finally, of the 2,4,6 aromatic proton resonance from 1,3,5-triphenylbenzene (7.7 ppm). At higher temperatures, or longer heating times, the cyclic trimer resonance and the polyphenylenic one increase, at the same time with decrease of the methynic proton resonance from cyclohexadiene units.

The NMR spectrum of the same polymer, registered at 68°C shows an increase of the trans-polyenic proton resonance accompanied by the appearance and increase of the methynic proton resonance from cyclohexadiene structures (Fig. 20). Maintaining the sample for 26 hours at 68°C, polymer composition becomes 48.43% cyclohexadiene structures and 51.57% trans-polyenic structures (Fig. 21). In these reaction conditions, no aromatization of cyclohexadiene sequences and chain scission reactions occur.

IR spectra of pentadeuterated and undeuterated polymers prove that 739 cm⁻¹ and 890 cm⁻¹ bands are specific for cis (C–H out of plane and, respectively, C–H in plane) configuration. At the same time, if the isomerization reaction is performed in air, polymer oxidation occurs much more easily than at room temperature. Thermal isomerization of cis-cisoidal PDPA gives a polymer with the same structure as obtained by thermal isomerization of cis-transoidal polymer.

The results obtained with PDPA confirm the scheme proposed in Fig. 18 for thermal-induced reactions of cis-transoidal and cis-cisoidal PPA. In the first step (I), thermal cyclization reactions give polymer chains containing 1,3-cyclohexadiene sequences. At the same time, the chain ends give by intramolecular cyclization end-groups of the 1,4-cyclohexadiene type. The occurrence of this reaction during polymerization causes chain termination by a first order reaction.

The cyclization reaction causes the migration of at least one cis double bond, which changes the configuration of this bond from cis to trans without breaking the π-bond.

The cis-trans isomerization mechanism can explain the low values of activation energies previously presented.

Thermal cis-trans isomerization is possible, also, but, as presented in Fig. 21, in very low proportion. Next, two reactions are most probable: cyclohexadiene structure aromatization (II) and chain scission with trisubstituted benzene elimination (III). All these reactions can explain the different shape and the exothermal effect of the DSC curves obtained for both PPA¹⁶⁹ and PDPA¹⁶⁸ with different cis contents (Fig. 22). The curve 1 is specific for both PPA and PDPA with cis-transoidal structure having more than 80% cis content, the rest being trans sequences. Exothermal peaks from 143, 156 and 181°C are, probably, the consequence of isomerization cyclization (or cyclization, isomerization) and aromatization, respectively. The fact that the corresponding thermal effects of these reactions are not cumulative (see curves, 1, 2, 2', 3, 3' the thermal effect values are given on the DSC curves) demonstrates that these exothermal reactions are successive and, consequently,

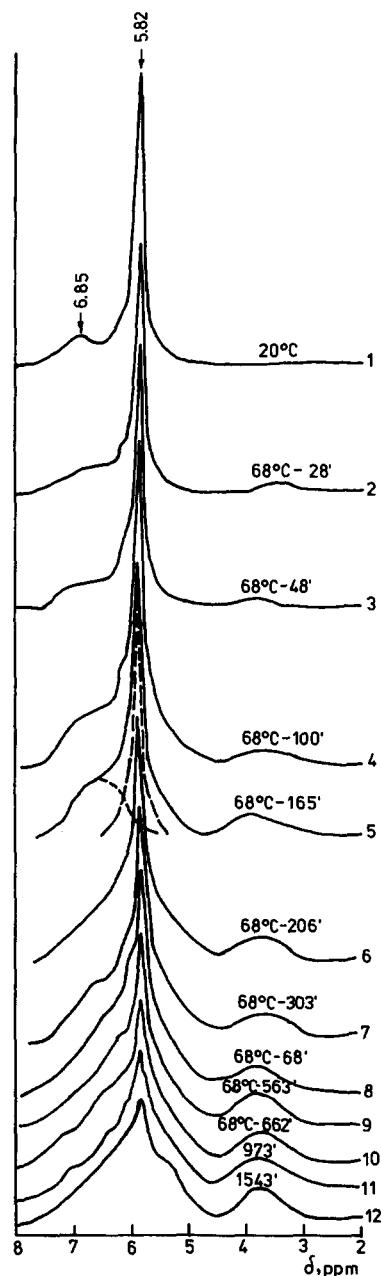


FIG. 20. ¹H-NMR spectrum of cis-transoidal polypentadeuterophenylacetylene (81 % cis content) at 68°C as a function of time (CCl₄, HMDS) (reference 168).

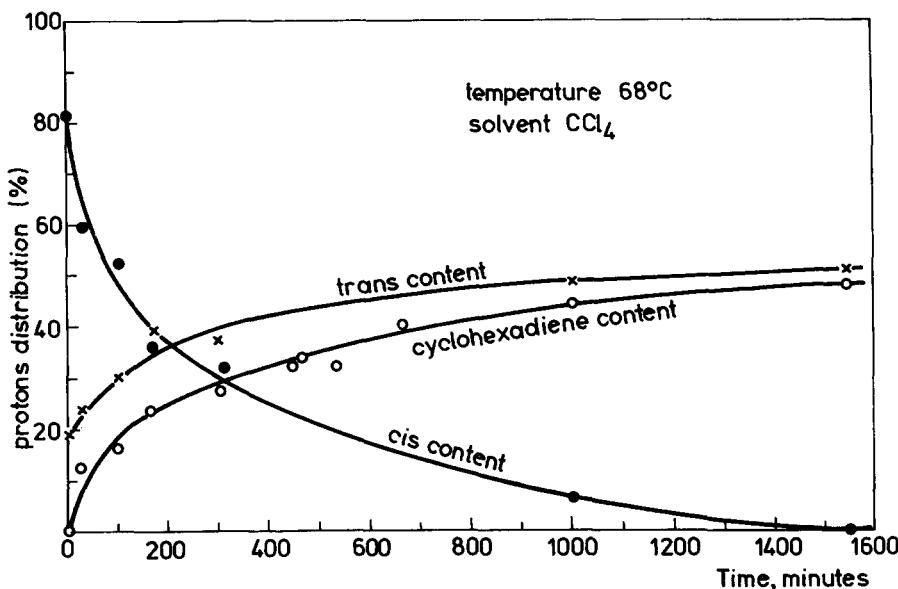


FIG. 21. Distribution of cis, trans and cyclohexadiene sequences in polypenta-deuterophenylacetylene from FIG. 20 (reference 168).

depend on the polymer's initial thermal history. At the same time, with decrease in polymer cis content (curves 4 and 5) and increase in cyclohexadiene sequences, the first two effects disappear and the main effect becomes that due to the aromatization reaction, which requires a higher temperature in these conditions and has a higher heat of reaction due to the higher initial content in cyclohexadiene sequences.

Ehrlich¹⁶⁶ showed for the first time that the insoluble polymer prepared with Ziegler-Natta or Luttinger catalysts has a higher crystallinity (80%). He considered that the polymer has a trans structure and showed that X-ray diffraction data can be indexed in the hexagonal system with an elemental cell not too different from that of isotactic polystyrene.

Berlin *et al.*¹⁷⁰ restudied the X-ray diffraction spectrum of cis-cisoidal PPA. They observed that the PPA projection into the ab plane is identical with that of the 1,3,5-triphenylbenzene structure. In these conditions, they considered that the *a* and *b* directions of the crystalline polymer must be identical with those of 1,3,5-triphenylbenzene and perpendicular to the polymer chain. The *c* value was adopted as 3.6 Å by analogy with the distance between planes containing aromatic molecules (benzene, naphtalene, etc). Consequently, PPA was assigned to an orthorombic symmetry, like 1,3,5-triphenylbenzene, and *a* and *b* axis determination led to an elemental orthorombic cell with the parameters: *a* = 10.8 Å, *b* = 19.3 Å, *c* = 3.6 Å.

Simionescu and Percec^{163,171} reinvestigated X-ray diffraction data for a cis-cisoidal PPA with a crystallinity of 60%. Using the same approach as Berlin *et al.*¹⁷⁰

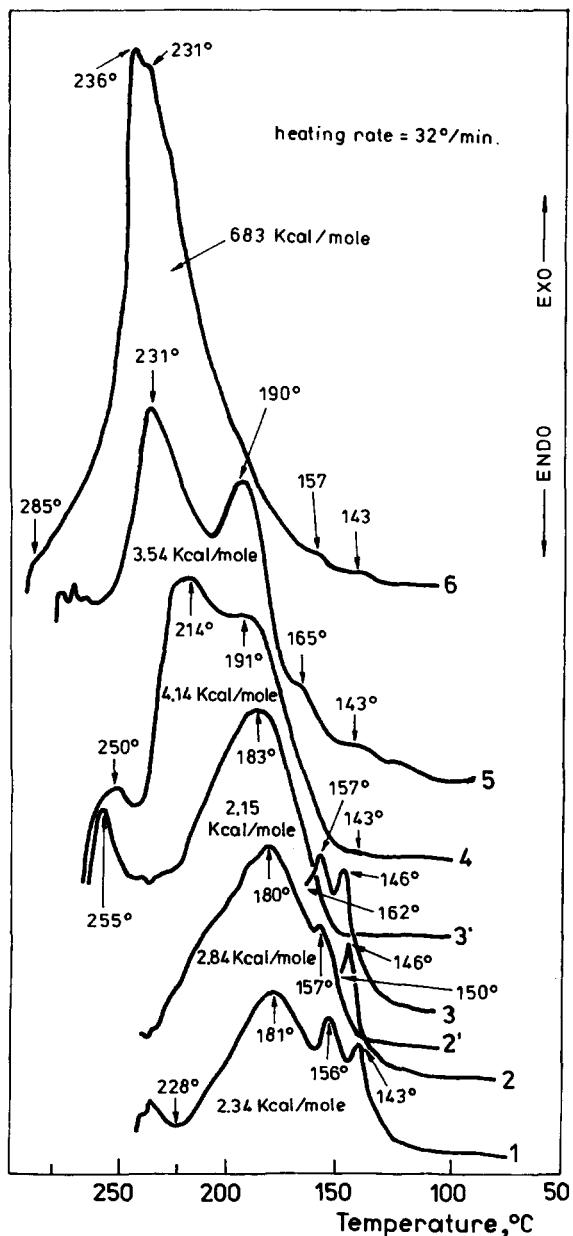


FIG. 22. DSC curves of (1) cis-transoidal polypentad deutero phenyl acetylene (81% cis content), (2) sample 1, registered up to 150°C only, (2') cooled sample 2, (3) sample 1 registered up to 162°C only, (3') cooled sample 3, (4) cis-transoidal PDPA (75% cis content), (5) cis-cisoidal PDPA (75% cis content), (6) PDPA obtained by polymerization with MoCl_5 at 60°C (reference 168).

an orthorombic elemental cell was obtained with the parameters: $a = 11.11 \text{ \AA}$, $b = 20.20 \text{ \AA}$ and $c = 3.6 \text{ \AA}$. The projection of molecular models for cis-cisoidal structure gives an image similar to that of opened 1,3,5-triphenylbenzene cycles. The attempt to index these data into a hexagonal cell failed.

Electronic absorption spectra of PPA of cis-transoidal structure with cis contents higher than 90% display an absorption maximum at 265 nm followed by a continuous absorption up to the visible domain with a second maximum at 400 nm.¹⁶³ The 265 nm maximum is present in the polystyrene spectrum also, and was assigned to the phenyl chromophore. The continuous absorption and the 400 nm maximum are due to chain conjugation. A decrease in cis-content to below 90% causes the disappearance of the 400 nm maximum and the appearance of a maximum at 332 nm accompanied by the same continuous absorption up to the visible domain. These data confirm the very homogeneous distribution of the effective conjugation for the polymer with high cis contents and the decrease of the homogeneity at lower cis contents.

Analysis of luminescence spectra of the cis-transoidal PPA¹⁶¹ shows that the conjugated sequences correspond to conjugated blocks formed from 4–7 structural units, whereas in the case of trans polymers, they do not exceed 3–5 structural units.

Bloor¹⁷² registered the diffuse reflection spectrum of a cis-cisoidal PPA prepared by Ehrlich without knowing the cis content, and obtained a strong absorption up to 550 nm which sharply decreases up to 650 nm. This absorption is very close to that obtained for cis polyacetylene,⁸⁹ which proves that the crystalline PPA chain is almost completely conjugated. The laser Raman spectra registered by the same authors¹⁷² prove that the side phenyl groups are also conjugated with the polyenic chain.

Ehrlich *et al.*^{173–175} studied the influence of PA polymerization conditions in the presence of $\text{AlEt}_3/\text{Fe}(\text{acac})_3$ on the molar mass and polydispersity of the polymer obtained by dissolving the cis-cisoidal PPA fraction in o-dichlorobenzene at 140°C. The Mark–Houwink equation parameters $[\eta] = k\bar{M}_v^a$ obtained for \bar{M}_v between 4800 and 6800 are $k = 1.03 \times 10^{-10}$ and $a = 2.42$. The high value of the a parameter can be explained only by rodlike polymer behaviour. At the same time, $\bar{M}_w/\bar{M}_n = 1.05$ indicates a completely different chain termination as compared with the vinylic monomers, if a living mechanism of polymerization is excluded. This value excludes chain transfer reactions and moreover is not compatible with a termination reaction by propagating centre desactivation, due to π -electron delocalization on the chain.^{176,177} Such a mechanism is valid only for oligomers.

Both the molar mass value and its distribution are independent of polymerization temperature in the range -30 – $+70^\circ\text{C}$, on polymerization solvent (quantity or nature) and on catalyst concentration.

Ehrlich *et al.*¹⁷⁵ supposed that the growing chain presents a π -delocalized radical character, in other words the character of a species with no differences between simple and double bonds length. At a critical polymer chain length, an

asymmetric chain configuration is obtained, presenting an unpaired electron at the chain end, breaking, consequently, the transition metal–carbon bond. The critical length depends on the relative energies of the ground states in the two electronic configurations and must be independent of temperature. This model can explain both the independence of temperature of the molar mass and the very low polymer polydispersity.

Using an idea published by Woon and Farona,¹⁷⁸ who showed that chlorine and bromine addition at PPA is arrested at stable cyclic halonium ions, Simionescu *et al.*^{168,179} developed a chemical method for PPA cis–trans isomerization (Fig. 23).

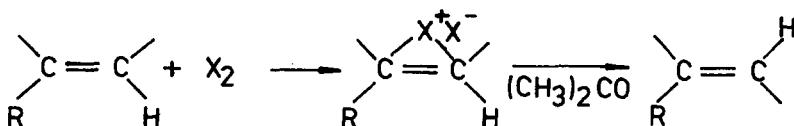


FIG. 23. Chemical cis–trans isomerization of polyarylacetylenes (reference 44).

Due to steric hindrances, PPA cyclic halonium ions are stable and can be isolated. Halogen elimination from halonium halides of the cis polymers gives the polymer in its thermodynamically stable state, i.e. trans. This is the sole method until now to synthesize pure trans polyarylacetylenes.

5.3. Phenylacetylene polymerization with other coordinative catalysts

All catalytic systems used for acetylene polymerization were tried also for PA polymerization. Generally, they are less active for mono or disubstituted acetylene polymerizations. Of them, the most attractive for a period of time were those proposed by Luttinger^{70,72,73} and Daniels.⁷⁴ Thus, Kern^{156,157} used a Luttinger-type catalyst ($\text{RhCl}_3/\text{LiBH}_4$) for PA polymerization in ethanol at room temperature. A cis–transoidal structure was obtained. One solvent mixture ethanol/tetralin gave cis–transoidal and cis–cisoidal structures. The same authors used for bulk PA polymerization a Daniels-type catalyst, namely $\text{RhCl}(\text{Ph}_3\text{P})_3$.^{156,157,180} In these conditions, PA behaves as a bifunctional monomer, the triple bond being one of the functions and the C–H bond the other. However, this catalyst is active above 50°C, and cannot give polymers with controlled microstructure. Other phosphinic complexes of the transition metals were used for PA polymerization (trans and cis $(\text{PPh}_3)_2\text{PtCl}_2$, trans and cis $(\text{PPh}_3)_2\text{Pt}(\text{C}\equiv\text{CPh})_2$, $(\text{Ph}_3\text{P})_2\text{PdCl}_2$, etc.^{163,164,181,182} but they are efficient above 100°C in bulk and lead to polymer having molar masses under 2000 and with structures impossible to control due to thermally induced isomerization, cyclization, aromatization and chain scission reactions. Polymerization mechanisms catalysed by these systems were discussed in relation to acetylene polymerization. They are similar to those proposed for Ziegler–Natta catalysts, in other words polymerization proceeds by monomer insertion into the metal–carbon bond.

Beginning with 1974, a research group led by Farona from Akron University,¹⁸³ and another led by Higashimura and Masuda from Kyoto University¹⁸⁴ became very active in working with very efficient catalytic systems for obtaining PA with molar masses higher than that obtained with Ziegler-Natta catalysts presented in Chapter 5.1. These systems are known as olefin metathesis catalysts.

The first group of very efficient catalysts for PA and other monosubstituted acetylene polymerization is of the type $\text{ArM}(\text{CO})_3$ where Ar is toluene or mesitylene and M can be a VIB group metal, i.e. Cr, Mo, W.^{183,185} PA polymerization takes place in bulk at room temperature or in benzene at reflux temperature, giving only linear polymers with $\bar{M}_w = 12000$.

Farona started from the idea that the type of cyclic product obtained in a catalytic reaction partially depends on the number of coordination vacancies existing on the metal. Therefore, cyclobutadiene derivatives are produced by two acetylene molecules coordinated in the cis position, benzene derivatives are formed by three acetylene coordinated in the cis position, whereas coordination in four vacant places produces a cyclooctatetraene. For the catalyst already presented, a maximum of two acetylenes can be coordinated at the same time, which suggests that no aromatic trimers could be formed. This was confirmed by the experimental results. Moreover, if the catalyst (tol) $\text{Mo}(\text{CO})_3$ (tol = toluene) gives a rapid quantitative PA polymerization, with the catalyst (mes)M(CO)₃ (mes = mesitylene, M = Cr or W) the reaction is much slower and in the first step a ladder compound formed from fused cyclobutane rings was separated also. Its structure is presented in Fig. 24.

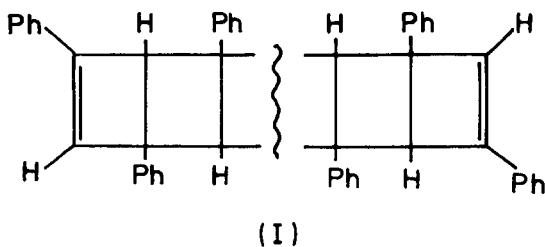


FIG. 24. Ladder compound type-I obtained during metathesis polymerization of phenylacetylene (reference 185).

This product is stable in the absence of the catalyst both in the solid state and in hexane at reflux temperature, but in the presence of the catalyst it quantitatively transforms into PPA. The ladder product molar mass is 2030 and its m.p. = 68–70°C.

These catalysts are also very efficient in transformation of Dewar benzene derivatives into the corresponding benzene derivatives, e.g. Dewar hexamethylbenzene into hexamethylbenzene. On the other hand, Dewar hexamethylbenzene was formed among the reaction products of 2-butyne polymerization in the presence of (tol) $\text{Mo}(\text{CO})_3$. Having these experimental proofs, Farona *et al.*^{183,184}

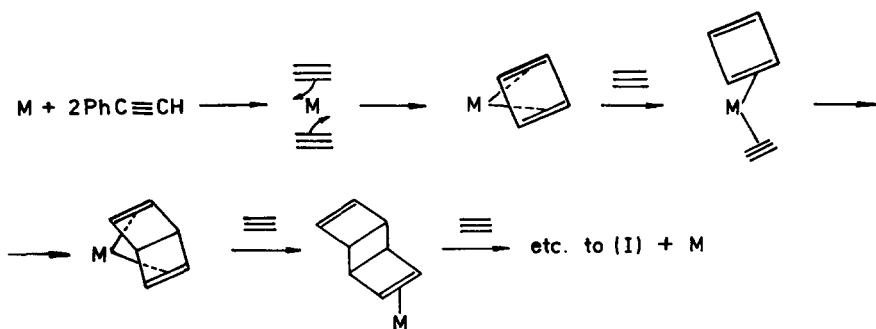


FIG. 25. Proposed mechanism of formation of ladder compounds of type-I
phenyl substituents are not shown for the sake of clarity (reference 185).

proposed the following mechanism for PA polymerization: the ladder compound of Fig. 24 is obtained by a series of $2 + 2$ cycloadditions producing cyclobutadiene as the first derivative, then the Dewar benzene, etc. (Fig. 25). Product I transforms into a PPA with a molar mass of 1200 as can be explained by fusion of many I-type products through a metathesis mechanism similar to that for olefins. This is presented in Fig. 26.

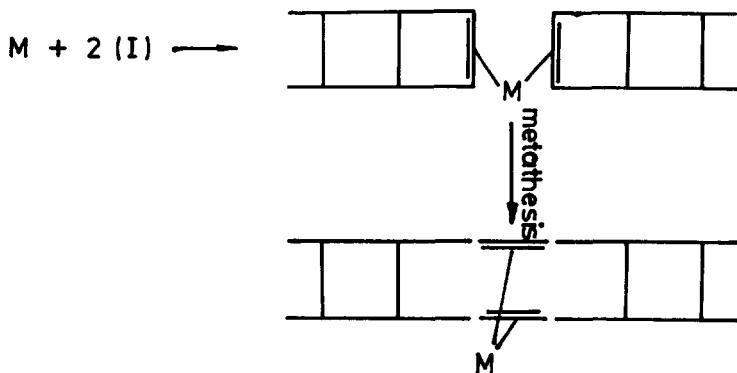


FIG. 26. Proposed mechanism of molar mass increase by olefin metathesis of end-groups of ladder compounds (reference 185).

During this metathesis reaction, the metal can form 5-membered rings with the olefinic bonds, which can have fluxional activity generating the intermediate 5-membered metalocyclic products presented in Fig. 27a and 27b. This leads to an electronic structure change by a step radical mechanism. The result of these reactions is linear or cyclic PPA. The proof of the radical scission mechanism is the fact that PA polymerization in the presence of free radical traps stops at the I intermediate.

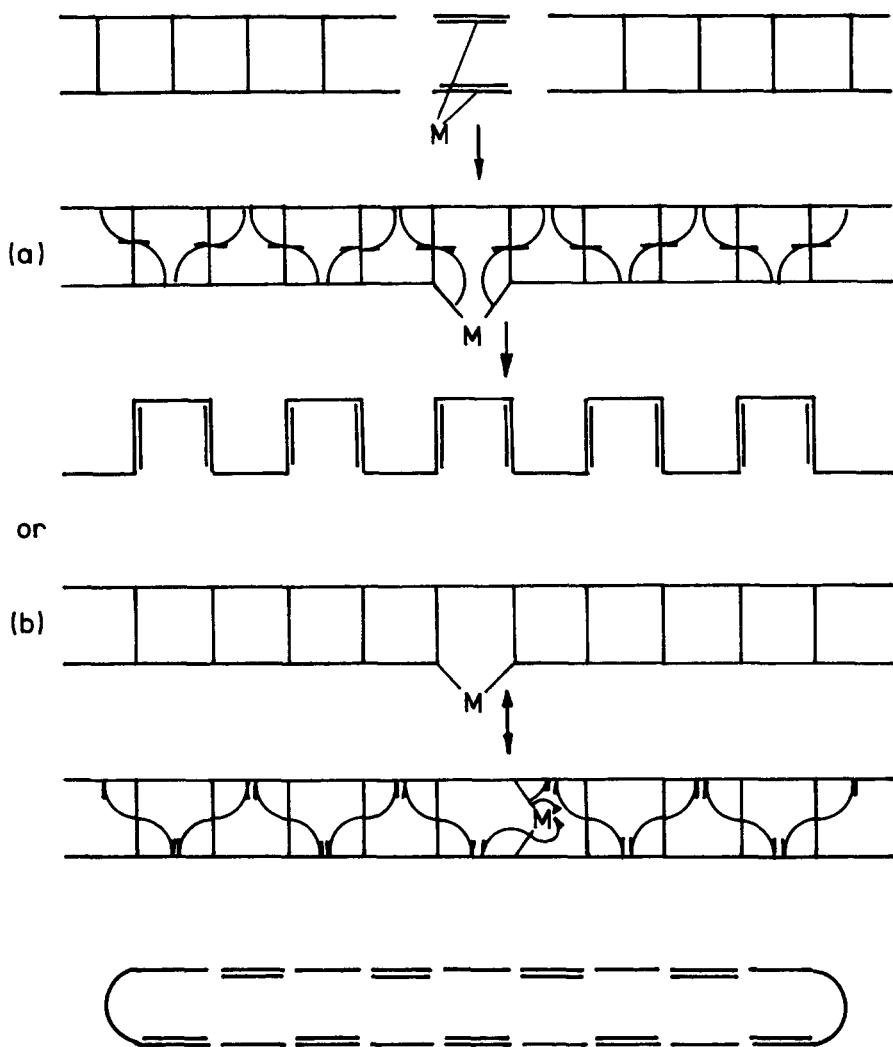


FIG. 27. Radical scission of the metathesized ladder compound giving (a) linear and (b) giant cyclic PPA (reference 185).

End-groups of the chains obtained by *a* and *b* reactions (Fig. 27) given an alylic radical shown in Fig. 28. Each alylic bond can participate in a new propagation reaction through metathesis.

Although the configuration of PPA so obtained was not analysed, the NMR spectrum presented by these authors suggests that a trans configuration is present.

The I-type ladder compound is formed by cis opening of the triple bond, but the PPA obtained has a trans configuration, probably due to thermal cis-trans isomerization reactions taking place during transformation of I into PPA.

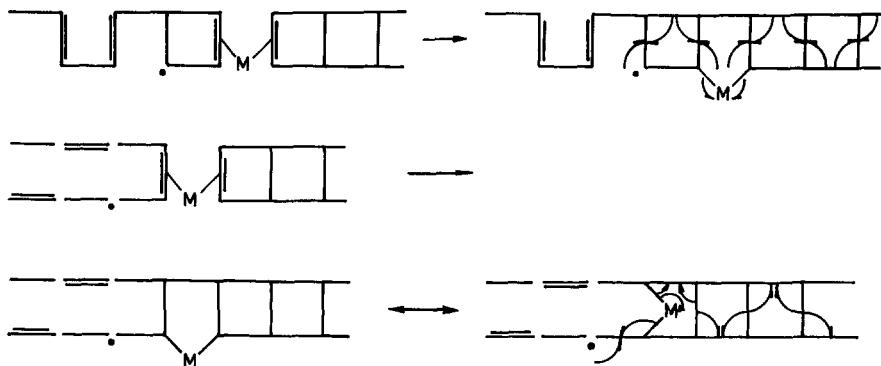


FIG. 28. End-group reactions giving metathesis and PPA (reference 185).

Navaro and Farona¹⁸⁶ proposed the same PA polymerization mechanism in the presence of catalytic systems: $\text{WCl}_6-\text{C}_2\text{H}_5\text{OH}$ and $\text{WCl}_6-\text{C}_2\text{H}_5\text{OH}-\text{AlEtCl}_2$. The first system is more efficient than the second, affording a 98% conversion of PA into PPA during 10 minutes. The sole difference from the $\text{ArM}(\text{CO})_3$ catalytic systems is that the ladder compound I (Fig. 24) is transformed into PPA by an ionic not radical, mechanism. No results on polymer configuration and molar mass were given.

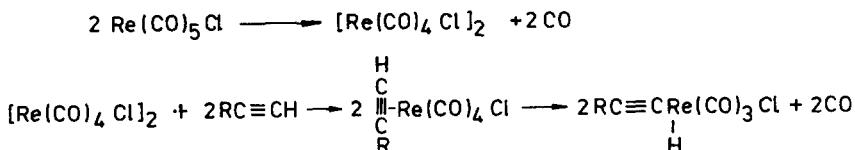
In 1979 Tsonis and Farona¹⁸⁷ investigated PA polymerization mechanism in the presence of VIIIB group catalysts as $\text{Re}(\text{CO})_5X$ where $X = \text{Cl}, \text{Br}$. They proposed a coordinative polymerization mechanism, the first step being a metal–acetylene active species formation, which acts as an initiator. Propagation proceeds through coordinated acetylene insertion into the metal–carbon bond of the growing chain. This mechanism is similar to that proposed by Meriweter *et al.*,^{188,189} Furlani *et al.*^{181,182} and Simionescu *et al.*^{163,190,191} for monosubstituted acetylene polymerization in the presence of phosphinic, arsenic and stibinic complexes of transitional metals of VIII-th groups.

$\text{Mn}(\text{CO})_5X$ is not active in acetylene polymerization, Tsonis and Farona¹⁸⁷ proposed the mechanism presented in Fig. 29. At high temperatures (*ca.* 90°C) the termination reaction through hydrogen transfer (*ec.* 3 Fig. 29) is balanced by propagation (*ec.* 2 Fig. 29), thus low molecular weight polymers are obtained (for PPA, e.g. less than 2200). As expected, the trans configuration predominates in such polymerization temperature conditions.¹⁸⁷

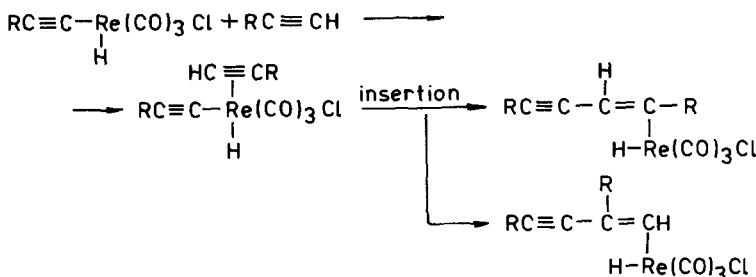
Recently, Davydov *et al.*¹⁹² performed PA polymerization in the presence of a catalyst proposed by Farona *et al.*^{183,185} (*mes*) $\text{Mo}(\text{CO})_3$ under UV radiations, and Garkova *et al.*¹⁹³ used the catalysts $\text{NiCl}_2/\text{NaBH}_4$ and $(\text{C}_5\text{H}_5)_2\text{TiCl}_2/\text{NaBH}_4$ in different alcohols. No results regarding the obtained polymers configuration were presented.

Masuda *et al.*¹⁸⁴ are the first to use WCl_6 and MoCl_5 for PA polymerization, which are efficient in benzene and in dichloroethane, but not in nitrobenzene. The

1) Activation of catalyst



2) Initiation and propagation



3) Termination

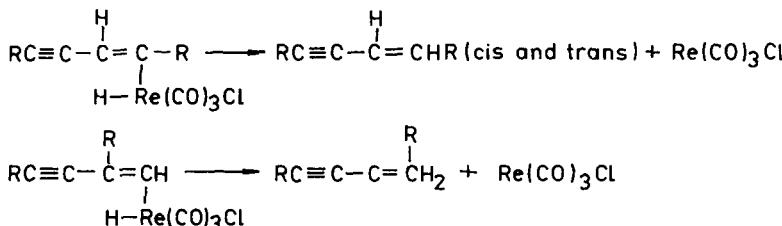


FIG. 29. Mechanism proposed for phenylacetylene polymerization in the presence of $\text{Re}(\text{CO})_5\text{Cl}$ catalyst (reference 187).

polymerization rate, the yield and the polymer molar mass increase when introducing into the reaction medium small quantities of water. At the same time, trichloroacetic acid reduces the polymerization rate and causes a decrease in polymer molar mass. With these catalytic systems, polymers having a maximum molar mass of 15000 were obtained. No cyclic trimers were obtained from PA. Studying styrene and PA copolymerization in the presence of these two catalytic systems, and the para-substituent polarity influence of the PA on the reaction rate, the same authors¹⁹⁴ showed that, unlike styrene, PA does not polymerize in the presence of WCl_6 and MoCl_5 by a cationic mechanism.

Further researches gave the conclusion that PA polymerization proceeds by a metathesis mechanism similar to olefin polymerization with metathesis catalysts,¹⁹⁵⁻¹⁹⁹ but different from the mechanism proposed by Farona *et al.*^{183, 185, 186}

According to the mechanism proposed by Hasegawa,¹⁹⁹ PA polymerization proceeds by successive 2 + 2 cycloadditions, producing in the first step a PPA cycle. The author excludes the possibility of fusion of sucy cycles according to the reaction

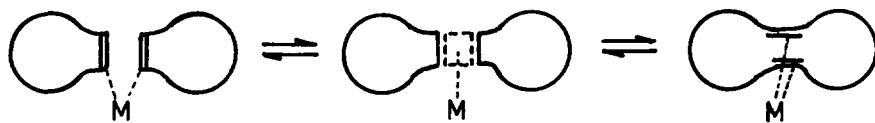


FIG. 30. Excluded mechanism of molar mass increase during metathesis polymerization (reference 199).

presented in Fig. 30, because the molar mass does not grow very much with conversion.

After scission of PPA giant rings, PA addition at the PPA chain-end becomes possible. The polymerization mechanism is presented in Fig. 31.

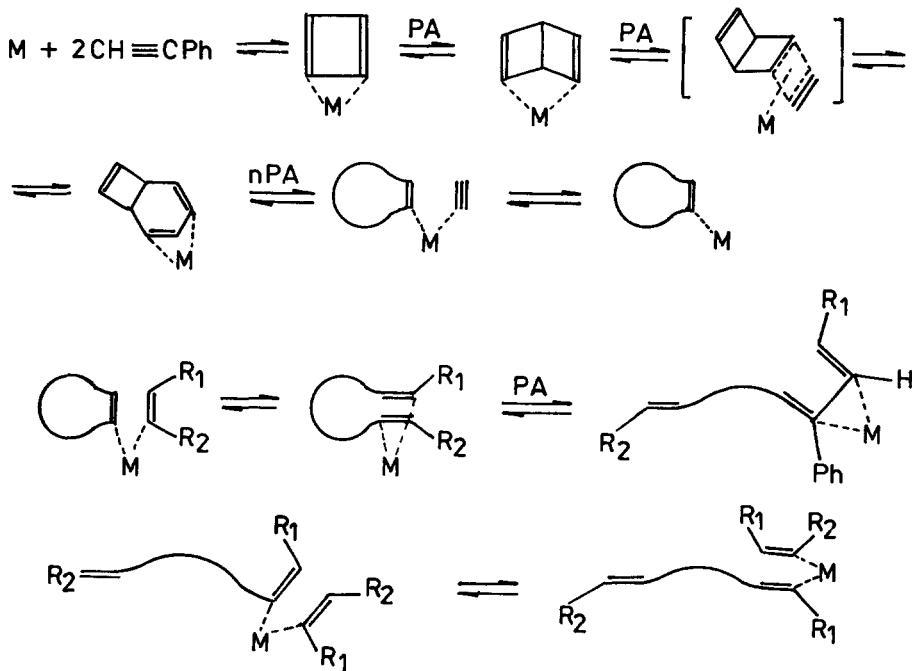


FIG. 31. Metathesis polymerization mechanism proposed by Hasegawa (reference 199).

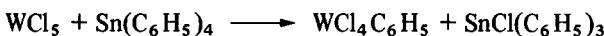
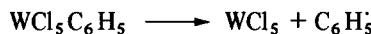
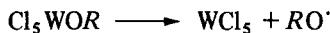
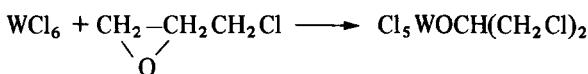
Solvent and catalyst influence on polymer configuration was studied by Masuda *et al.*¹⁹⁵ and Hasegawa.¹⁹⁹ The decrease of solvent polarity leads to an increase of polymer cis content. In the same time, for the same solvent, MoCl_5 gives polymers with higher cis contents than WCl_6 . The attempt to polymerize phenylpropane only in the presence of MoCl_5 or WCl_6 failed.^{197,198} Phenylpropane easily polymerizes in the presence of $\text{WCl}_6/\text{SnPh}_4$. This catalyst is much more efficient than

WCl_6 for PA polymerization.¹⁹⁶ The increase of WCl_6 activity in the presence of SnPh_4 is explained by the reducing activity of SnPh_4 . For PA polymerization with WCl_4 or MoCl_5 only, the reducing agent for the catalytic system is the acid hydrogen of PA. The absence of an acid hydrogen in phenylpropane requires the presence of another reducing agent.

In these conditions, one can consider that PA polymerization in the presence of $\text{WCl}_6/\text{SnPh}_4$ proceeds through two active species, one being WCl_6 and PA as reducing agent, and the other WCl_6 and SnPh_4 as reducing agent.¹⁹⁶

More proofs for the coordinative mechanism of PA polymerization in the presence of WCl_6 were advanced by Hasegawa *et al.*²⁰⁰ who studied the influence of chain transfer agents, characteristic for anionic and cationic polymerization, on the PPA molar mass. In styrene polymerization with WCl_6 , cationic chain transfer agents are very efficient, whereas in PA polymerization neither anionic nor cationic chain transfer agents influence the polymer molar mass. This clearly proves that PA polymerizes through a coordinative mechanism in the presence of WCl_6 , whereas styrene polymerizes through a cationic mechanism.

Hasegawa¹⁹⁹ studied the influence of additives (e.g. epichlorohydrin, ethylene chlorhydrin and SnPh_4) on PA polymerization in the presence of WCl_6 and MoCl_5 . In all cases, an increase of the catalyst efficacy was observed when increasing additive concentration up to the ratio additive/ $\text{WCl}_6 = 1$. After that, a decrease occurs. This increase is explained by reducing of W^{VI} and Mo^{V} valences, according to the following reactions:



or

Masuda *et al.*²⁰¹ confirmed that W^{VI} is reduced even by PA at W^{V} and then to W^{IV} , which is in fact the active species in polymerization of PA and other acetylenic monomers. Moreover, these authors studied the influence of some additives containing oxygen on PA polymerization in the presence of WCl_6 . As can be seen in Table 8. the PA polymerization efficacy is very much increased.

TABLE 8. Polymerization of phenylacetylene initiated by $\text{WCl}_6 \cdot \text{PhA.O.1Z}^a, b, c$ (reference 201)

Z^a	Conversion %	\bar{M}_n
1,4-Dioxan	95.5	10300
Tetrahydropyran	90.5	13000
1,2-Dimethoxyethane	92.5	11300
Dibutyl ether	92.0	10800
Anisole	90.5	—
Phenetole	94.0	—
Acetone	96.0	11300
2-Butanone	94.0	—
Ethanol	94.0	—
Water	92.0	—
WCl_6 (as catalyst)	61.0	11600
$\text{WCl}_6 \cdot \text{PhA}$ (as catalyst)	66.0	13900

^a Polymerized in benzene at 30°C for 1 hr under nitrogen; $[\text{M}_0] = 1.0 \text{ M}$, $[\text{WCl}_6 \cdot \text{PhA.O.1Z}] = 5.0 \text{ mM}$.

^b PhA, phenylacetylene as a catalyst component.

^c Z, oxygen – or nitrogen – containing compound as a third catalyst component.

The compounds used can be divided in two classes: some of them can eliminate protons (e.g. water) the other are completely inert (e.g. 1,4-dioxane). Consequently, they cannot directly react with WCl_6 , but only coordinate the W derivative through the oxygen. The fact that the presence of these compounds does not influence the molar mass value or polyenic configuration, suggests that they do not produce other more active, catalytic species but cause an increase in the number of propagating species. If one considers W^{IV} as the active species in polymerization, and takes into account that WCl_4 is insoluble in most solvents, one can conclude that by W^{IV} coordination with these modifiers, soluble active species are obtained, which determine an increase of the reaction rate.

Additional proofs for the coordinative PA polymerization mechanism in the presence of WCl_6 were evidenced by the fact that PA does not copolymerize with styrene in these conditions,²⁰² but gives a homopolymer mixture. This fact can be explained by the different polymerization mechanisms of the two comonomers in the presence of WCl_6 . On the contrary, an initiator like $\text{SnCl}_4 \cdot \text{CCl}_3\text{COOH}$, which polymerizes both PA and styrene by a cationic mechanism, generates a copolymer.²⁰²

Dyachkovskii *et al.*²⁰³ studied PA polymerization using Mo(V), Mo(IV) and W(VI) compounds immobilized on polymer supports as catalysts. Polymers used as supports were PE-g-polyallylic alcohol, PP-g-poly(4-vinylpyridine), PE-g-polyacrylonitrile and PE-g-polypropargyl alcohol, obtaining immobilized catalysts with the structures: $-\text{O}-\text{MoCl}_4$, $-(\text{C}=\text{N})_2\text{MoCl}_4$, $-(=\text{N})_2\text{MoCl}_4$ and respectively $-\text{O}-\text{MoCl}_4$ (where PE = polyethylene, PP = polypropylene).

PA polymerization in benzene at 70°C in heterogeneous phases (with immobilized catalysts) and homogeneous phase (with unimmobilized catalysts) showed that both molar mass and conversion are higher for the heterogeneous phase. Cis and trans polymers were obtained. In all cases, three polymer fractions were separated: soluble in benzene, soluble in the mixture THF-MeOH (1/1, V/V) and soluble in methanol. The authors proposed that the first fraction is obtained through a coordinative polymerization mechanism (by 2 + 2 cycloadditions), the second through an insertion mechanism into the Mo-C bond of coordinative polymerization and the last fraction through cationic polymerization.

Vatanatham and Farona^{203a,204b} showed in 1980 that phenylacetylene and diphenylacetylene are polymerized by polystyrene-supported molybdenum, also through a 2 + 2 cycloaddition mechanism.

Recently, Katz and Lee²⁰⁴ showed that mono- and disubstituted acetylene polymerization initiation (PA included) takes place with metallic derivatives of carbenes such as (phenylmethoxycarbene)pentacarbonyltungsten and (diphenylcarbene)-pentacarbonyltungsten. These data support the idea that metathesis polymerization proceeds through metallic carbenes,^{195,204} following the mechanism presented in Fig. 32.

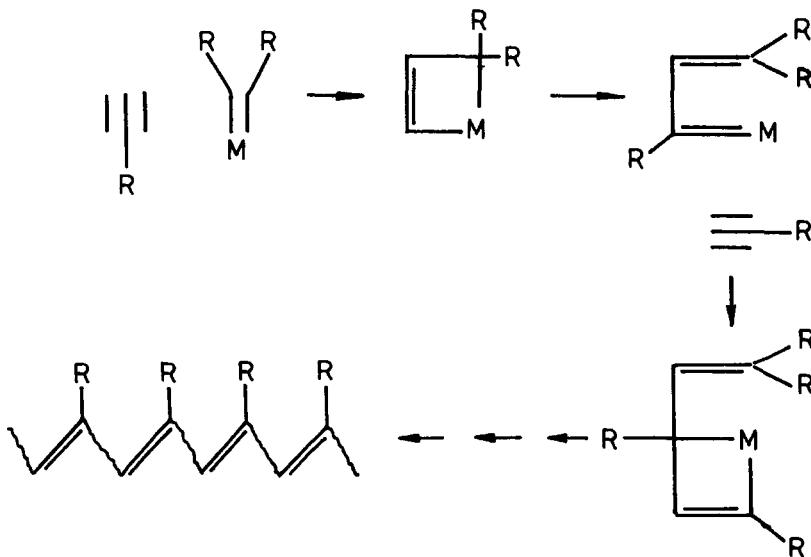


FIG. 32. Proposed metathesis polymerization mechanism through metallic-carbene derivatives (literature 204).

Also in 1980, Voronkov *et al.*⁸³ showed that PA can give high conversions and molar masses not only in the presence of Mo and W halides (MoCl_5 and WCl_6) but also in the presence of oxohalides of the type OMoCl_4 .

Very recently, Masuda *et al.*²⁰⁵ used the carbonyls of the metals W, Mo and Co, known to be efficient olefin metathesis catalysts, and showed that in the presence of UV irradiation and of halogen-containing solvents (e.g. CCl₄), W(CO)₆ generates a PPA with a molar mass of 80000. This is the highest molar mass obtained until now for PPA. Mo(CO)₆ is less effective for PA polymerization. Acetylene monomers having a halogen in their molecule do not require a halogenated solvent presence in the reaction medium. For example, 2-chloro-1-phenylacetylene gives a $M_n = 400000$ polymer in toluene under UV irradiation and Mo(CO)₆.

It is to be noted that V-group metal halides (NbX₅, TaX₅ where X = Cl, Br, I), unlike those of VI-th group, produce only PA cyclic trimers, also through a coordinative mechanism. Of them, only NbF₅ and TaF₅ generate small quantities of linear polymers, but through a cationic mechanism.²⁰⁶

5.4. *Electroinitiated polymerization of phenylacetylene*

In 1977, Simionescu *et al.*²⁰⁷ performed electrochemical PA polymerization using DMSO as solvent. Efficient electrolytes were proved to be only NaNO₃ and especially, NiBr₂. The polymerization proceeds through an anionic mechanism and give polymers with molar masses lower than 1000 and yields under 30%. Using DMF as solvent and NaNO₃ as electrolyte, Subramanian *et al.*²⁰⁸⁻²¹⁰ confirmed the anionic mechanism and obtained polymers with maximum molar mass of 3349 and maximum yields of 52%. The PPA ¹H-NMR spectrum published by Subramanian *et al.*²⁰⁸⁻²¹⁰ evidences cyclohexadiene sequences in the chain, which means that the polymerization takes place by cis-opening of the triple bond and that cyclization and cis-trans isomerization reactions occur during propagation.

5.5. *Radical polymerization of phenylacetylene*

Radical polymerization of PA, thermally initiated or with radicals initiators was intensively studied and the results reviewed by Cerkashin *et al.*³² The most significant results referring to the polymer structure and polymerization mechanism were published only in recent years.

Thus, in 1977, Cerkashin *et al.*,²¹¹ studying the structure of PPA and polypenta-fluorophenylacetylene obtained by radical mechanism evidenced the high proportion of cyclohexadiene and polyphenylene structures. PDPA obtained by thermal polymerization contains also cyclohexadiene and polyphenylene sequences,⁴⁴ and the mechanism proposed by Simionescu and Percec is based on cis opening of the triple bond followed by cyclization, aromatization and chain scission reactions during propagation. These reactions explain cyclic trimer occurrence during thermal polymerization, as a consequence of chain scissions. In these conditions, the termination reaction is a consequence of intramolecular cyclization of the growing chain end. PA polymerization radical mechanism with cis-opening of the triple bond was confirmed also by the microstructural analysis of PA copolymers with methyl

acrylate and methacrylate.²¹²⁻²¹⁴ PA structural units have both cis and trans configurations. A part of the polyphenylacetylene sequences longer than three structural units contain cyclohexadiene structures.

Ehrlich *et al.*²¹⁵ studied in detail the kinetics of PA radical polymerization in the presence of AIBN at 50°C in bulk and in toluene or benzene solutions. The conclusions are as follows: the polymerization rate is approximately of the first order with respect to initiator concentration. The average molar mass of the polymer is independent of initiator concentration when polymerization is carried out in bulk and nearly proportional to initiator concentration in solution. The polymer molar mass does not depend on solvent nature. The kinetic study showed that in radical polymerization, as in the coordinative one, there is no transfer to monomer. Also, as in coordinative polymerization, the molar mass distribution is very narrow ($\bar{M}_w/\bar{M}_n \sim 1.2$) and independent of reaction conditions. Another peculiarity of this reaction, valid also for coordinative polymerization, is that chain termination reaction is of the first order. Therefore it can be considered as a consequence of an electronic or structural rearrangement of the growing polymer chain which produces in this way an inactive growing centre. According to the kinetic data obtained by Ehrlich *et al.*,²¹⁵ the deactivation termination reaction and the propagation reaction control the radical PA polymerization both kinetically and from the point of view of the molecular chain length. Because the termination reaction controls the polymerization rate in a polymerization when only short chains are obtained, an electronic rearrangement from a σ -localized radical to a π -delocalized radical is excluded, because these changes take place on the time scale of a molecular vibration. In these conditions, it is most probably that there is an isomerization mechanism which generates an inactive radical.

Ehrlich *et al.*²¹⁵ proposed for the first order termination reaction as the first step extraction of the initiator residue giving an α -styryl radical more inactive than the β -styryl radical (Fig. 33).

Another possibility proposed by the same authors is an intramolecular cyclization

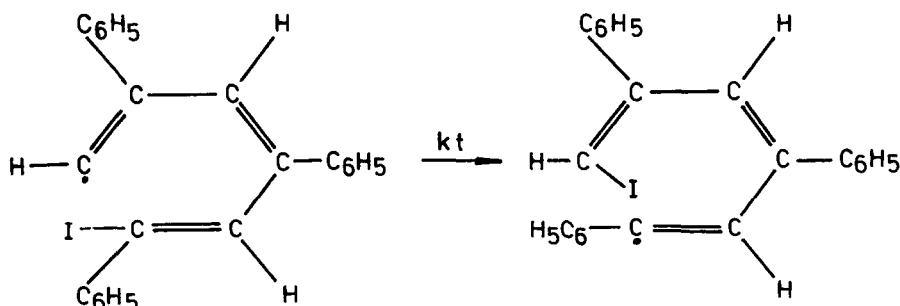


FIG. 33. Intramolecular chain termination mechanism through α -styryl radical (reference 215).

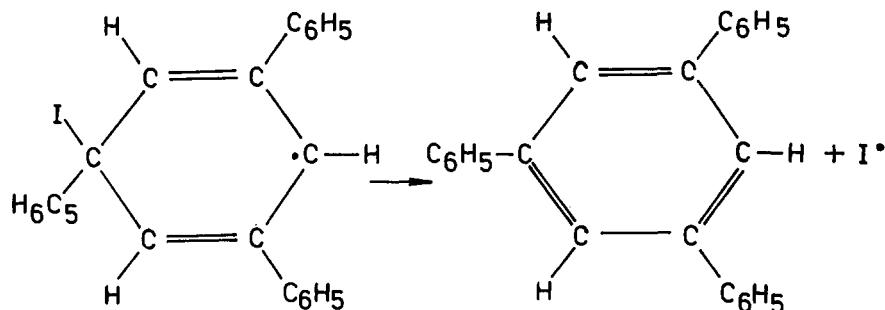


FIG. 34. Intramolecular chain termination mechanism occurring through cyclohexadienyl radical (reference 215).

giving in the first step an inactive cyclohexadienyl radical, which after initiator elimination can generate cyclic trimers as secondary reaction products (Fig. 34). This termination mechanism by intramolecular cyclization is similar to that proposed by Simionescu and Percec.⁴⁴

6. SYNTHESIS AND STRUCTURE OF POLY(α -ETHYNYLNAPHTHALENE) AND POLY(β -ETHYNYLNAPHTHALENE)

6.1. *Synthesis and structure of poly(α -ethynylnaphthalene)*

Kambara *et al.*²¹⁶ performed the first α -ethynylnaphthalene polymerization in the presence of soluble Ziegler-Natta catalysts. They used the catalytic systems: AlEt₃/Ti(OC₄H₉)₄, AlEt₃/VO(acac)₂, AlEt₃/Cr(acac)₃, AlEt₃/Fe(acac)₃ and AlEt₃/Co(acac)₃ (Al/M = 2.9) in toluene at 25°C. The system AlEt₃/Co(acac)₃ gave the highest molar mass and conversion. These authors did not study polymer configuration.

Simionescu *et al.*^{162, 163, 190} showed that α -ethynylnaphthalene polymerization in the presence of AlEt₃/Fe(dmg)₂.2Py gives three polymer fractions. The first two, one insoluble in benzene and the other soluble in benzene and insoluble in methanol, are highly crystalline (80%), red-violet coloured and possess a cis-cisoidal configuration.¹⁶³ The third fraction is insoluble in the mixture methanol/water = 3/1, has an amorphous structure, a yellow colour and a trans-cisoidal configuration. This fraction, having a very small molar mass (below 500) is probably obtained by cationic polymerization in the presence of AlEt₃, and not by a coordinative mechanism.

Cationic α -ethynylnaphthalene polymerization gives a yellow, amorphous polymer with trans-cisoidal structure.¹⁶³ The use of phosphinic complexes of VIII-th group transition metals of the type (PPh₃)_a.MX_b (where a = 2, 3; M = Ni, Pd, Co, Pt, Rh; X = Cl, Br, I, SCN and b = 2, 1) for bulk polymerization of α -ethynyl naphthalene at 140°C, and thermal polymerization give only trans-cisoidal

structures.^{163,190} The $^1\text{H-NMR}$ spectrum of the soluble cis-cisoidal structure displays the aromatic protons resonance at 7.0 ppm and the cis-polyenic proton resonance at 6.4 ppm. The $^1\text{H-NMR}$ spectrum registered as a function of temperature (in solution in hexachlorobutadiene) presents no modifications up to 200°C. Then, the 6.4 ppm signal disappears, and a sole signal including aromatic and polyenic protons remains. This signal is centered at 7.4 ppm and corresponds to the spectrum of trans-cisoidal polymer obtained directly from synthesis.¹⁶³ Recently, Rohde and Wegner²¹⁷ reinvestigated by Raman spectroscopy the structure of poly(α -ethynylnaphthalene) synthesized in the presence of $\text{AlEt}_3/\text{Fe}(\text{dmg})_2 \cdot 2\text{Py}$ and confirmed the presence of cis sequences in the polymer chain.

The X-ray diffraction spectrum indexation of the cis-cisoidal polymer gave an orthorombic structure with the parameters: $a = 12.159 \text{ \AA}$, $b = 22.38 \text{ \AA}$, $c = 3.6 \text{ \AA}$.¹⁶³

The electronic absorption spectra of cis-cisoidal and trans-cisoidal structures are completely different. Thus, the cis-cisoidal polymer presents two maxima in the UV domain, at 262 nm and 286 nm and a maximum in the visible domain at 467 nm, then the absorption decreases up to 650 nm.^{163,217} The trans-cisoidal polymer presents the maxima at 262 nm, 286 nm and a third maximum at 345 nm, followed by a continuous decreasing absorption up to ca. 600 nm. The 262 and 286 nm maxima are due to the α -substituted naphthalene chromophore, and the absorption in the visible domain to conjugated polyenic system.²¹⁸ The continuous absorption obtained for the trans-cisoidal polymer can be explained by a high polydispersity of the conjugated chain sequence lengths, as compared with the cis-cisoidal polymer.

6.2. Synthesis and structure of poly(β -ethynylnaphthalene)

Poly(β -ethynylnaphthalene) was synthesized for the first time by Wiley and Lee²¹⁹ through β -ethynylnaphthalene polymerization in the presence of $\text{Al}(\text{iBu})_3/\text{TiCl}_4$. The authors performed three polymerizations, with the results presented in Table 9.

TABLE 9. Polymerization of β -Ethynylnaphthalene with $\text{Al}(\text{iBu})_3-\text{TiCl}_4$ catalyst (reference 219)

Monomer mole/l	TiCl_4 mole/l	$\text{Al}(\text{iBu})_3$ mole/l	Molar Ratio Al/Ti	Polymerization yield %	M_n	M_p capillary °C
0.125	2.4×10^{-2}	6.1×10^{-2}	2.8	44.1	2091	190–200
0.125	2.4×10^{-2}	2.1×10^{-2}	0.9	4.9	495	220–230
0.125	2.4×10^{-2}	10.1×10^{-2}	4.9	31.0	1050	220–210

Surprisingly, the softening point of the polymer increases with the decrease of the molar mass. Probably, the $M_n = 495$ fraction contains mainly cyclic trimers, if one regards the $\text{Al}/\text{Ti} = 0.9$ ratio used in this polymerization.

Simionescu *et al.*^{163,191,220} investigated in detail the polymerization of this monomer and the structure of the polymers obtained.

Polymerization with soluble Ziegler-Natta catalysts such as: $\text{AlEt}_3/\text{VO}(\text{acac})_2$, $\text{AlEt}_3/\text{Cr}(\text{acac})_3$, $\text{AlEt}_3/\text{Co}(\text{acac})_3$, $\text{AlEt}_3/\text{Fe}(\text{acac})_3$ and $\text{AlEt}_3/\text{Fe}(\text{dmg})_2.2\text{Py}$ gave in all cases three polymer fractions. The first fraction, insoluble in benzene, is red coloured and has a crystallinity above 60% and a cis-cisoidal structure. The second polymer fraction is soluble in benzene and insoluble in methanol, and the third fraction is soluble in methanol and insoluble in the mixture methanol/water = 3/1. These last two fractions are yellow-coloured and amorphous. Their structure is identical with that of the pure thermal or cationic polymer, being trans-cisoidal. One can consider that crystalline cis-cisoidal structure is formed by isomerization of the cis-transoidal growing chain. This isomerization takes place during propagation. At the same time, the heat of polymerization can induce cis-trans isomerization giving trans-cisoidal structures. On the other hand, trans-cisoidal structures can arise also from a cationic polymerization initiated by AlEt_3 in the presence of traces of humidity in the reaction medium.

β -ethynylnaphthalene polymerization in the presence of $\text{AlEt}_3/\text{TiCl}_4$ gives, depending on the Al/Ti ratio, a linear polymer ($\text{Al}/\text{Ti} = 8$) with small quantities of 1,3,5-tri(β -naphthyl)benzene, or especially cyclic trimers ($\text{Al}/\text{Ti} = 2.3$).¹⁹¹ It is to be noted that the catalytic system $\text{AlEt}_3/\text{TiCl}_3$ does not give cis-cisoidal structures. The use of Luttinger-type catalysts ($\text{NaBH}_4/\text{Co}(\text{NO}_3)_3$) in ethanol at room temperature generated only trans-cisoidal structures.

Another class of catalysts used for β -ethynylnaphthalene polymerization contained phosphinic, arsinic and stibinic complexes of VIII-th group metals of type: $(ZY_3)_a.MX_b$ (where $M = \text{Rh}, \text{Pd}, \text{Pt}, \text{Ni}, \text{Co}; X = \text{Cl}, \text{Br}, \text{I}, \text{NO}_3, \text{SCN}; Z = \text{As}, \text{P}, \text{Sb}; Y = \text{butyl or phenyl}; a = 2, 3; b = 2, 1$). Polymerizations were carried out in bulk at 140°C. The efficacy of these catlytic systems decreases as follows: for M , $\text{Rh} > \text{Pt} > \text{Pd} > \text{Ni} > \text{Co}$; for X , $\text{I} > \text{Br} > \text{Cl} > \text{NO}_3 > \text{SCN}$; for Z , $\text{As} > \text{P} > \text{Sb}$ and for Y , $\text{Bu} > \text{Ph}$. The analysis of the reaction mixture of β -ethynylnaphthalene polymerization in the presence of cis and trans- $(\text{PPh}_3)_2.\text{PtCl}_2$ evidenced the occurrence of the product trans- $(\text{PPh}_3)_2.\text{Pt}(\beta\text{C} = \text{CC}_{10}\text{H}_7)_2$. With this product as catalyst, a higher yield of polymerization was obtained, as compared with cis or trans- $(\text{PPh}_3)_2.\text{PtCl}_2$. These results prove the validity of the insertion polymerization mechanism proposed by Simionescu *et al.*¹⁹⁰ for acetylene polymerization with these catalysts.

Thermal isomerization of cis-cisoidal polymer¹⁹¹ occurs only above 220°C. The polymer obtained by thermal isomerization is soluble, yellow-coloured and has a trans-cisoidal structure. An attempt to detect intramolecular cyclization reactions in thermal isomerization of both poly(α - and β -ethynylnaphthalene) by $^1\text{H-NMR}$ spectroscopy failed. It seems that, due to the bulky substituent, cis-trans isomerization is not accompanied by side reactions, due to steric hindrances. X-ray diffraction data of the cis-cisoidal polymer indexing gave an orthorombic elemental cell with the parameters: $a = 16.129 \text{ \AA}$, $b = 20.40 \text{ \AA}$, $c = 3.6 \text{ \AA}$.¹⁶³

Electronic absorption spectra of the cis-cisoidal polymers (obtained from KBr pellets) show an absorption maximum at 500 nm and an absorption decrease up to 650 nm. The trans-cisoidal structures present only a continuous absorption from UV to visible domains.^{163, 191}

Recently, Masuda *et al.*^{221, 222} studied β -ethynylnaphthalene polymerization in the presence of catalytic systems based on WCl_6 and $MoCl_5$. WCl_6 generated molar masses up to 9200. The polymers are soluble, amorphous and possess a trans-rich configuration. The polymers obtained in the presence of catalytic systems based on $MoCl_5$ are crystalline, insoluble and present a cis-cisoidal structure.

In PA polymerization with catalysts based on $MoCl_5$ and WCl_6 , no cis-cisoidal fraction was obtained. As previously supposed, the cis-cisoidal structure is obtained by cis-transoidal growing chain isomerization. For PA, both cis-trans isomerization and intramolecular cyclization are initiated by the heat of polymerization. In the case of β -ethynylnaphthalene, the thermal cis-trans isomerization requires, probably, a higher thermal effect than the polymerization heat. Consequently, when the growing chain contains mainly cis sequences, as is the case for $MoCl_5$ -based catalysts, there is the possibility of cis-transoidal-cis-cisoidal isomerization.

Experimental results presented by Masuda *et al.*²²¹⁻²²³ for β -ethynylnaphthalene polymerization show the possibility of obtaining cis-cisoidal structures for other acetylene monomers with bulky substituents, also, using catalysts based on $MoCl_5$.

7. SYNTHESIS AND STRUCTURE OF POLYETHYNYLFERROCENE

Ethynylferrocene was first polymerized by Simionescu *et al.*²²⁴ in bulk in the presence of benzoyl peroxyde. Polymerization takes place only above 140°C, giving low molar masses (less than 1417) and trans structures.

The same authors^{225, 226} performed ethynylferrocene polymerization in the presence of lauroyl peroxyde and of triisopropylboron, but did not succeed in obtaining a polymer in the presence of the Ziegler-Natta catalyst $Al(iBu)_3/VO(acac)_2$. Ethynylferrocene readily polymerizes in the presence of $(PPh_3)_2NiCl_2$ and $(PPh_3)_2NiBr_2$ in a mixture of EtOH/THF (9/1 v/v) at reflux temperature.²²⁵ By radical polymerization, both soluble and insoluble polymers are obtained. The insoluble polymers are crosslinked through the cyclopentadienyl rings.²²⁵

Nakashima *et al.*²²⁷ investigated in detail ethynylferrocene polymerization in the presence of Ziegler-Natta catalysts. They showed that $AlR_3/TiCl_4$ catalyst gives mainly cyclic trimers. Catalysts such as $AlR_3/Ti(OBu)_4$ give linear polymers with maximum molar masses of 3500. As for acetylene or PA polymerizations, the chlorine content of the Ziegler-Natta catalyst is decisive in obtaining cyclic trimers or linear polymers. Thus, $AlEt_3/Ti(OBu)_4$ gives only linear polymers in a broad Al/Ti ratio range (Al/Ti = 3-20), whereas $AlEt_2Cl/Ti(OBu)_4$ and $AlEtCl_2/Ti(OBu)_4$ give only cyclic trimers.²²⁷ Because the thermal effects which initiate cis-trans isomerization were not eliminated in these systems, all polymers obtained have a trans structure.

Pittman *et al.*²²⁸ reinvestigated ethynylferrocene polymerization and confirmed that by radical mechanisms initiated by AIBN or benzoyl peroxyde, the polymer is obtained only in the temperature interval 180–200°C. The structure of polymer obtained by either the radical mechanism, or the coordinative one (in the presence of RhCl₂ in ethanol) is linear. The linear polymer is stable in air in solid state, but in solution is easily oxidised.

By ethynylferrocene polymerization in the presence of AlEt₃/Fe(dmg)₂.2Py or MoCl₅ catalytic systems, Simionescu *et al.*²²⁹ obtained cis-cisoidal (insoluble) and cis-transoidal (soluble) polymers. Thermal cis-trans isomerization generates an insoluble polymer, probably due to crosslinking reactions.

Simionescu *et al.*^{230,231} performed also 1-chloro-1'-ethynylferrocene and p-ferrocenyl-phenylacetylene polymerizations in the presence of benzoyl and lauroyl peroxides above 140°C. The first monomer generates two polymer fractions: one crosslinked, insoluble and one linear, soluble. The second monomer gives only crosslinked, insoluble polymer.

8. SYNTHESIS AND STRUCTURE OF POLY(N-ETHYNYLCARBAZOLE)

Poly(N-ethynylcarbazole) was first synthesized by Okamoto and Kundu²³² through thermal polymerization of N-ethynylcarbazole. Simionescu *et al.*^{163,233,234} investigated the structure of the polymer obtained by thermal and cationic polymerizations and also in the presence of Ziegler–Natta catalysts and in the presence of phosphinic complexes of VIII-th group transitional metals.

For Ziegler–Natta polymerization, the following catalysts were used: AlEt₃/VO(acac)₂, AlEt₃/Co(acac)₃, AlEt₃/Fe(acac)₃, AlEt₃/Fe(dmg)₂.2Py, AlEt₃/TiCl₄, AlEt₃/Ti(OBu)₄. In all cases, two polymer fractions were obtained: one insoluble in benzene, the other insoluble in methanol. Both fractions have the same structure, presenting identical IR and X-ray diffraction spectra. The polymers are dark-red coloured and crystalline. IR spectra show bands characteristic of the cis configurations at 880, 1010, 1142, 1280 and 1400 cm⁻¹. ¹H-NMR spectra of soluble fractions showed that the polymers are formed from cis-transoidal and cis-cisoidal stereoblocks. Electronic absorption spectra display, besides the absorptions characteristic of the carbazole chromophore in the UV domain (340, 327, 294, 285 and 263 nm in CCl₄), also an absorption maximum in the cis-cisoidal/cis-transoidal stereoblocks ratio; this maximum is located between 535 and 510 nm, and followed by a continuous absorption up to 700 nm.

Cis-trans thermal isomerization occurs at a temperature which depends on polymer configuration (the ratio cis-cisoidal/cis-transoidal) and is ranged between 200 and 305°C. In all cases, due to the very high chain rigidity accorded by the substituent size, cis-trans thermal isomerization is accompanied by thermal degradation of the polymer.²³⁴

On the other hand, when the heat of polymerization is not eliminated, trans-

cisoidal polymers are obtained. This definitively proves that cis-trans isomerization proceeds easily during propagation.²³⁴

The X-ray diffraction spectrum presents only a crystalline maximum, which proves that poly(N-ethynylcarbazole) molecules with stereoblock structure are rigid and rodlike, and are packed approximately parallel in a pseudohexagonal array. The lateral spacing of 11.62 Å, calculated from the diffraction pattern, can be interpreted as the (1010) diffraction of the pseudohexagonal lattice. In these conditions, the nearest chain-to-chain distance or the macromolecular diameter is equal to 13.42 Å.²³⁴

Polymers obtained by cationic mechanism at 25°C, thermal polymerization or with phosphinic complexes at 140°C are amorphous, soluble and present a trans-cisoidal structure. Their colour is light brown, and the absorption spectrum consists in only UV absorptions of carbazole chromophore and a continuous absorption from UV to the visible domain, which decreases up to 700 nm. Only the cationic polymer presents a maximum at 580 n. This was assigned to a CTC formed between polymer and TiCl₄.²³⁴

9. SYNTHESIS AND STRUCTURE OF POLY(9-ETHYNYLANTHRACENE)

9.1. Some peculiarities of 9-ethynylanthracene polymerization

Although 9-ethynylanthracene (9EA) polymerization was performed in 1967 by Michel²³⁵ in the presence of AlEt₃/TiCl₄ catalyst, structural details on the polymers obtained with different catalytic system were published only in the last few years.^{162, 236-239}

9EA can be considered as a bifunctional monomer, the functions being anthryl and ethynyl groups. Both groups can participate in polymerization, and this can give a very complex polymer structure. By analogy with 9-vinylanthracene polymerization,²⁴⁰ also for 9EA many enchainment possibilities can be considered, giving different structures.^{236, 239} Thus, by triple bond opening and 1,2 head-to-tail addition, a linear polymer with conjugated double bonds and the anthryl group as side-chain is obtained (Fig. 35). In this way, the cyclic trimer and tetramer can be obtained also. This polymerization type is common to polymerization of all acetylene monomers and implies only the ethynyl group. The a-type structure from Fig. 35 was obtained by coordinative polymerization in the presence of Ziegler-Natta catalysts and of phosphinic, arsenic and stibinic complexes of VIII-th group metals.²³⁶⁻²³⁹

Another method of polymerization is based on the tendency of anthracene and its derivatives to give Diels-Alder reactions. Successive cycloaddition of the ethynyl group (dienophile) of a 9EA molecule at 9,10 positions of anthracene ring (diene) from another monomer molecule gives a structure of b-type (Fig. 35). This structure was not evidence in 9EA polymerization, but in (9-anthryl)methyl propiolate polymerization (with the triple bond activated by the electrophilic group-CCO-).^{236, 241}

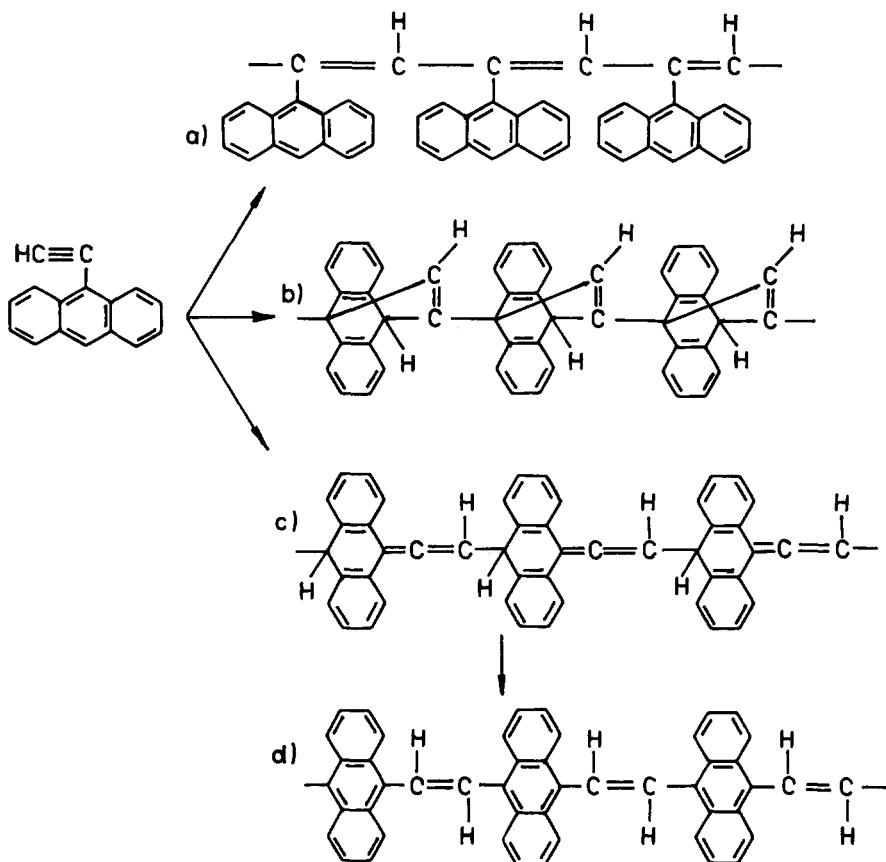


FIG. 35. Possible structures of 9-ethynylanthracene polymers (reference 239).

A last structural possibility can be obtained by isomerization polymerization of 1,6-type, giving structure *c*. Then, this structure can be thermally aromatized as *d*-structure (Fig. 35). The last two polymerization possibilities imply participation of both functional group. Structures *c* and *d*, together with the predominant *a* structure were evidenced in radical and ionic polymerization of 9EA.²³⁶ Besides these enchainment possibilities, the anthryl group can give during polymerization side-reactions of addition or substitution at meso-anthracene free carbon. All these generate a polymer with complex structure, especially when ionic or radical mechanisms are used.

9.2. Structure of radical poly(9-ethynylanthracene)

9EA easily polymerizes through a radical mechanism even without initiators. The air oxygen initiates the reaction in the presence of light.^{236,242} In 9EA molecule,

the ethynyl group is conjugated with the anthracene nucleus. Consequently, 9EA can go into the singlet excitation state S^* even in the presence of $\lambda > 400$ nm radiations. The consumption of this excitation state can take place by interaction with a normal state monomer molecule (*A*) or with air oxygen (*B*) (Fig. 36).

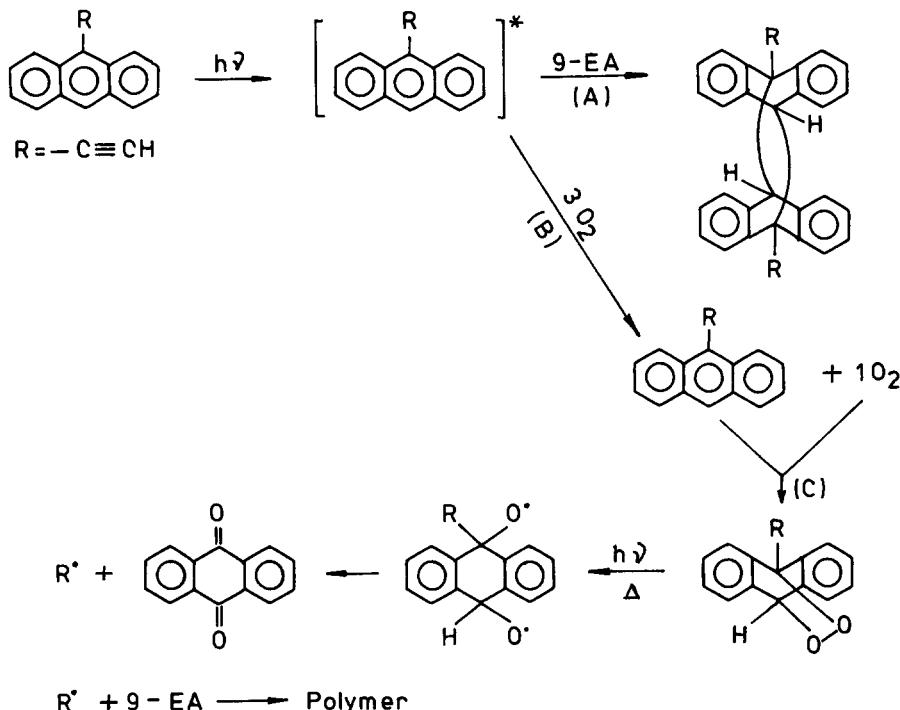


FIG. 36. Mechanism of initiation of spontaneous radical polymerization of 9-ethynylanthracene (reference 236).

The *A* way is reversible in the absence of radiations or thermally. In the presence of oxygen, the *A* way is less probable, because the *B* way deactivates the monomer molecule and forms singlet oxygen. The formed endo-peroxide is unstable and thermally decomposes under radiation to anthraquinone and free radicals, capable of initiating radical polymerization of 9EA.

In the absence of light and oxygen, 9EA polymerization proceeds very easily at 90°C in a purely thermal way or in the presence of AIBN or benzoyl peroxide. Thermal polymerization takes place much more easily in the presence of oxygen. In this case, oxygen is an activator according to the mechanism presented in Fig. 36. In all cases soluble polymers with molar masses lower than 1200 are obtained.

The radical polymer has an *a*-type structure (Fig. 35) having also dihydroanthracenic structures (*c*, Fig. 35) which appear as a "wrong" addition during their polymerization and/or isomerization.

The anthracene group of 9EA can act as an inhibitor of radical polymerization, adding the radicals at the free mesoanthracenic position. In this way, an inactive dibenzylid radical is formed, stabilized by the two lateral phenylic rings. This reaction is similar to chain termination (Fig. 37).

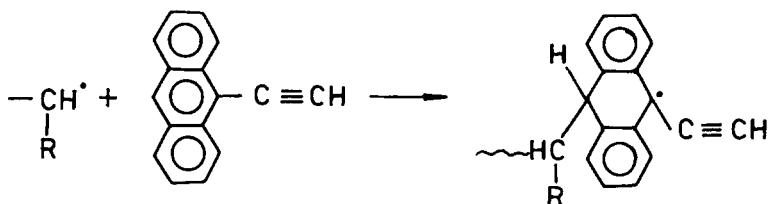


FIG. 37. Mechanism proposed for formation of dibenzylid inactive radical during radical polymerization of 9-ethynylanthracene (reference 236).

Radical isomerization gives also an inactive dibenzylid radical producing in this way also, dihydroanthracene structures (Fig. 38).

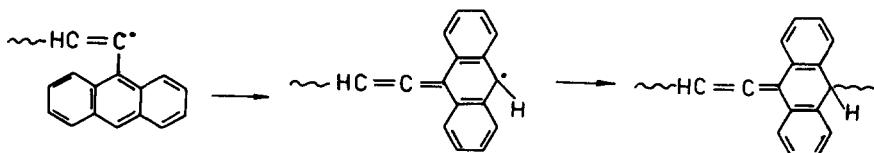


FIG. 38. Isomerization of 9-ethynylanthracene macroradical (reference 236).

9.3. Structure of poly(9-ethynylanthracene) obtained by cationic polymerization

Cationic polymerization of 9EA in the presence of Lewis acids takes place easily giving two polymer fractions: one insoluble in benzene and the other soluble in benzene but insoluble in methanol. When polymerization is carried out at temperatures lower than -50°C , only polymers soluble in benzene are obtained.^{236,243} The polymers obtained by the cationic mechanism present a structure based on monosubstituted anthracene sequences (a type, Fig. 35); disubstituted and dihydroanthracene sequences arise from normal 1,2 polymerization. Dihydroanthracene sequences arise from the isomerization of carbenium ion from α -carbon to the 10-anthracene carbon, which gives a more stable carbenium ion (Fig. 39).

Disubstituted anthracene sequences can arise both from acid or thermal isomerization of *c*-type structures giving *d*-structures (Fig. 35) and through polyalkylation reactions giving structures of the type presented in Fig. 40.

A decrease of polymerization temperature leads to an increase in 9,10-disubstituted anthracene and dihydroanthracene sequence concentration, which increases the polymer solubility.^{236,243}

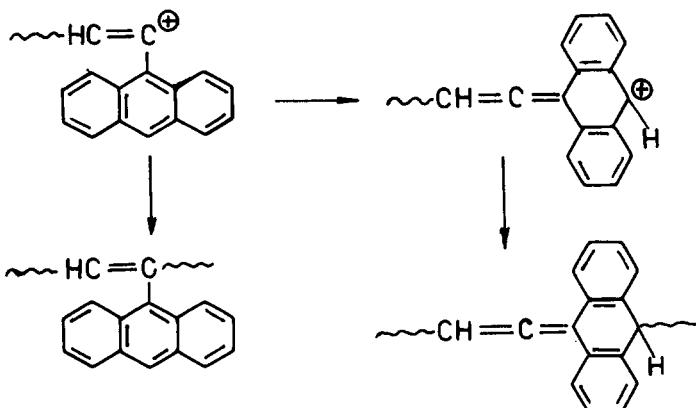


FIG. 39. Cationic polymerization of 9-ethynylanthracene (reference 236).

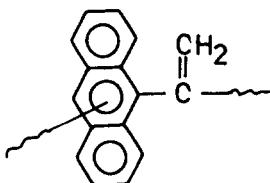


FIG. 40. Disubstituted anthracene sequences obtained by cationic polyalkylation (reference 246).

9.4. Structure of poly(9-ethynylanthracene) obtained by coordinative polymerization

9-vinylnanthracene polymerization with Ziegler-Natta catalysts is impossible, due to steric hindrances between the hydrogens of the double bond and hydrogens 1 and 8 of the anthracene.²⁴⁴⁻²⁴⁶ In the case of 9EA, due to the replacement of the double bond by the triple bond, with consequent elimination of two hydrogen atoms steric hindrances are smaller, which makes possible polymerization in the presence of Ziegler-Natta catalysts as: $\text{AlEt}_3/\text{VO}(\text{acac})_2$, $\text{AlEt}_3/\text{Fe}(\text{acac})_3$, $\text{AlEt}_3/\text{Co}(\text{acac})_3$ and $\text{AlEt}_3/\text{Fe}(\text{dmg})_2 \cdot 2\text{Py}$.^{162, 236-238} In all cases, two polymer fractions are obtained: one black, insoluble in benzene and one dark brown, soluble in benzene, but insoluble in methanol. Both fractions are amorphous and present an α -type structure with cis-cisoidal configuration. The fraction soluble in benzene also contains small quantities of cyclic trimers.

9EA polymerization in the presence of phosphinic, arsenic and stibinic complexes of VIII-th group transitional metals, easily proceeds in a $\text{EtOH}-\text{THF}$ mixture (9/1, v/v) at reflux temperature.²³⁶⁻²³⁹ In all cases, two polymer fractions are obtained, insoluble and soluble in benzene. Their structure is of α -type with a cis-cisoidal configuration. Unlike the insoluble fraction, the polymer soluble in benzene also

contains small quantities of dihydroanthracene sequences which appear from a radical mechanism, probably due to impurification with polymer obtained through pure thermal polymerization.^{236,239}

The cis polymer obtained with phosphinic, arsenic and stibinic complexes proves that for 9EA also, as in the case of acetylene polymerization, the triple bond is opened in the cis position. In the case of 9EA the very bulky substituent and the steric hindrances require a cis-trans isomerization heat higher than that resulting from the heat of polymerization together with the temperature of polymerization. However, in polymers obtained with phosphinic, arsenic and stibinic complexes, the cis content estimated from the exothermic heat of thermal isomerization is lower than in polymers obtained with classical Ziegler-Natta catalysts.²³⁶

Like the other polyarylacetylenes, poly 9EA with cis-cisoidal structure presents in its electronic absorption spectrum, besides the characteristic anthracene ring absorption in the UV domain, an absorption maximum located at 550 nm, followed by a continuous decreasing absorption up to 650 nm.

The other 9EA polymers, containing also *a*-type sequences with trans-cisoidal configuration, together with dihydroanthracene or other type structures, present in the visible domain only a continuous absorption up to *ca.* 600 nm.²³⁶

10. SYNTHESIS AND STRUCTURE OF POLY(9-ETHYNYLPHENANTHRENE) AND POLY(3-ETHYNYLPHENANTHRENE)

10.1. *Synthesis and structure of poly(9-ethynylphenanthrene)*

9-ethynylphenanthrene polymerization was performed only by radical mechanism, initiated thermally or by means of AIBN.²⁴⁷⁻²⁴⁹ For thermal polymerizations, when increasing the polymerization temperature, an increase of the yield and of the molar mass occurs up to 150°C. Above 150°C the conversion remains constant, but the molar mass decreases, probably due to thermal degradation, from 1400 (at 150°C) to only 668 (at 200°C). With AIBN, the decrease of the molar mass takes place at lower polymerization temperatures. Thus, at 70°C, molar masses of 2500 are obtained, and at 90°C the molar mass does not surpass 2000, over a large range of initiator concentrations. Unlike the thermal polymerization of PA, in this case initiator concentration influences the polymerization degree, as with vinylic monomers.

The structure of the polymers obtained is trans.

10.2. *Synthesis and structure of poly(3-ethynylphenanthrene)*

Polymerization of 3-ethynylphenanthrene was performed by thermal initiation, in the presence of Ziegler-Natta coordinative catalysts and in the presence of phosphinic complexes of VIII-th group transitional metals.^{236,250,251}

Soluble Ziegler-Natta catalysts give two polymer fractions. The fraction insoluble in benzene is red and has a cis-cisoidal structure, whereas the fraction soluble in benzene and insoluble in methanol is red-brown and has a cis-transoidal structure. Both fractions are amorphous. Insoluble Ziegler-Natta catalysts ($\text{AlEt}_3/\text{TiCl}_4$) produce cyclic trimers and a polymer soluble in benzene with cis-transoidal structure.

Thermal polymerization, and polymerization in the presence of phosphinic complexes, give only soluble polymers with trans-cisoidal structure, having small amounts of cis-transoidal sequences.²⁵¹ This proves that not only in coordinative polymerization, but also in pure thermal polymerization, the opening of the triple bond occurs in the cis position.

It is to be noted that, unlike all other polyacetylenes, the electronic absorption spectra of poly(3-ethynylphenanthrene) present only a continuous absorption from the UV into the visible domain, independent of polymer configuration.²³⁶ This implies a high polydispersity of conjugated sequence lengths, even in the case of stereoregular polymers. The sole explanation for this behaviour can be the presence of phenanthryl substituents assymmetrically substituted introducing a new locus of structural irregularity, as can be seen in Fig. 41.

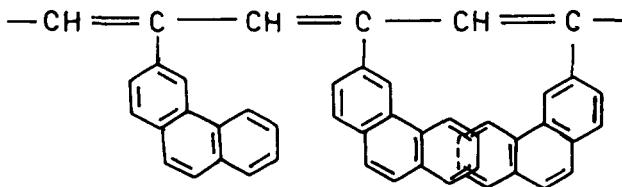


FIG. 41. Steric hindrances occurring in the poly(3-ethynylphenanthrene) chain, as a consequence of assymetric substitution of phenanthrene ring (reference 236).

11. POLYMERIZATION OF AROMATIC PROPIO LIC ESTERS

9-anthrylmethylpropiolate, 9-fluorenylpropiolate and 9-(2,4,7-tri-nitrofluor- enyl)propiolate were recently synthesized by coupling of corresponding aromatic diazoderivatives with propiolic acid.²⁵² The monomers readily polymerize by radical (with AIBN) and anionic (with NaSCN) mechanisms. In the presence of electron-donor compounds such as triethylamine, all monomers spontaneously polymerize by a CTC mechanism.²⁵² The configuration of the polymers obtained is trans-cisoidal. 9-anthrylmethylpropiolate polymerizes in the presence of Lewis acids by a Diels-Alder mechanism giving a polymer with the structure²⁴¹ presented in Fig. 42. This is the sole way to synthesize polymers having the structure presented in Fig. 35b.

The properties of these polymers have not yet been studied.

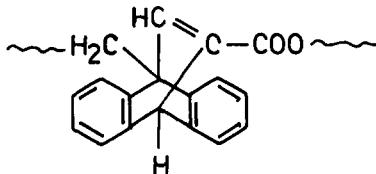


FIG. 42. Polymer structure obtained by Diels–Alder polymerization of 9-anthrylmethylpropionate (reference 241).

12. PROPERTIES OF POLYARYLACETYLENES

12.1. *Cis-trans thermal isomerization*

The thermal behaviour of polyarylacetylene isomers studied by DTA or DSC^{169,–43,44,253} has the following peculiarities. All cis polymers present on DTA or DSC curves an exothermal peak in a temperature range depending on polymer nature and microstructure. This effect is irreversible. The trans polymers do not give such exothermal effect.²⁵⁴ These exothermal effects are not accompanied by weight losses, except with N-ethynylcarbazole and 9-ethynylanthracene polymers. In these cases the weight loss depends on polymer cis content, being between 1 and 10% of the sample.

It is to be noted that for N-ethynylcarbazole and 9-ethynylanthracene polymers with trans-cisoidal structure, the first step of the thermal degradation is not accompanied by thermal effects. The UV, IR, ¹H-NMR and XRD spectra proved that these exothermal peaks are due to cis–trans isomerization, which changes the cis insoluble or soluble, crystalline or amorphous polymer into a polymer with trans-cisoidal structure, soluble and amorphous. Only for N-ethynylcarbazole polymers, the exothermal peaks occur in a temperature range between 200 and 300°C. The isomerization temperature value is dependent in this case on the cis–transoidal, cis–cisoidal and trans–cisoidal stereoblock ratio. It is difficult to decide only by ¹H-NMR spectroscopy if for polymers with substituents larger than phenyl, the isomerization reaction is accompanied by intramolecular cyclization, as for PPA. This difficulty arises from the very small ratio of methynic protons from cyclohexadienic structures and the other protons, including the aromatic ones. In our opinion, steric effects given by substituent size, probably hinder cyclization reactions.

It is difficult to explain now why, except for trans polyacetylene, all other trans polymers are amorphous.

In almost all cases when the cis–trans thermal isomerization is not accompanied by side reactions, the enthalpic changes associated with exothermal effects include: cis–trans isomerization (exothermal phenomenon), in–plane disordering of molecular chains (endothermal phenomenon) and rearrangements in a new conformation (exothermal phenomenon). The enthalpic changes are presented in Table 10.

TABLE 10. Enthalpy changes associated with the thermal isomerization exotherm phenomenon of polyacetylenes (reference 44).

Polymer	Polymer structure	Isomerization range °C	Temp. of exothermic peaks °C	Enthalpy change kcal/mole
PA	high crystalline 88% cis content	145	145	1.85
PPA	c-t, amorphous, 90% cis content	100–235	145, 155, 182	2.49
PDPA	c-t, amorphous 81% cis content	112–228	143, 156, 181	2.34
PDPA	amorphous, very low cis content	130–285	231, 236	6.83
PEFc	c-t	130–226	172	3.78
P α -EN	c-c, 80% crystallinity	225–264	245	1.70
P β -EN	c-c, 60% crystallinity	186–258	238	5.86
PEK	c-c/c-t, 60% crystallinity	275–360	320	19.80
P-9-EA	c-c, amorphous	266–370	338	12.40
P-3-EPh	c-c, amorphous	203–277	243	10.20
P-3-EPh	c-t, amorphous	142–257	226	7.70

It is now impossible to determine separately the cis-trans isomerization heat from the apparent enthalpy change, at least due to the different polymer crystallinities. However, as can be seen in Table 10, the enthalpic changes at cis-trans isomerization temperature increase when increasing substituent size. The highest thermal effect was observed for N-ethynylcarbazole polymers and can be explained by the high rigidity of the polymer chain. On the other hand it is not possible to determine spectrally the cis content of the polymers having bulkier substituents than phenyl, especially for insoluble polymers. The thermal effects presented in Table 10 are the highest values obtained for many series of polymers having different cis contents. This proves that in all cases, the cis content is higher than 90%.

12.2. Polyarylacetylenes paramagnetism

In 1967, Ehrlich *et al.*¹⁶⁶ showed that, whereas the paramagnetism of PPA obtained by the thermal mechanism follows the Curie law in the range -100 to +130°C, both in solution and in solid state, the crystalline polymer obtained with Ziegler-Nattat catalysts exhibits an increase of the paramagnetic centre concentration between 70 and 130°C, then it remains constant up to the melting temperature (180–190°C). This change of paramagnetic centre concentration is associated with an irreversible order-disorder transition.²²⁵ Indeed, in this temperature interval, the crystalline structure of PPA is changed into an amorphous structure, the polymer becomes soluble and the configuration changes from cis-cisoidal to trans-cisoidal.

Also, Ehrlich *et al.*²⁵⁶ showed that at 120°C the PPA paramagnetism reaches a

maximum. On cooling, the ESR signal obeys the Curie law. The authors proposed that structural defects of biradical type, which arise from the π -electrons on π -bonds breaking, are the origin of the paramagnetism. The ESR spectrum in xylene solution has a hyperfine structure for a solution of crystalline PPA at 120°C.²⁵⁷ If the increase in paramagnetic centres is explained as above, this hyperfine structure is, more likely, due to the cyclohexadienic radicals arising during intramolecular cyclization reaction.

Ehrlich *et al.*^{258,259} were also the first to show that the cis PPA paramagnetic centres reach a maximum concentration at 120°C, even if the thermal treatment is made in solution. Polymer paramagnetism is independent of molar mass.

Simionescu *et al.*²¹⁸ showed that the paramagnetism is also independent of the molar mass for trans-cisoidal poly(α -ethynylnaphthalene).

The study of paramagnetism of cis-cisoidal, cis-transoidal and trans-transoidal isomers of PPA, poly(α -ethynylnaphthalene), poly(β -ethynylnaphthalene) and poly(N-ethynylcarbazole) evidenced the following^{43,44,260,261}:

The paramagnetic centre concentration of the crystalline polymers of PA and β -ethynylnaphthalene is one or two orders of magnitude smaller than that for amorphous polymers. Moreover, the ESR spectrum of cis-cisoidal poly(β -ethynyl-naphthalene) just prepared at -78°C, demonstrates that the polymer is diamagnetic, even at room temperature.²⁶² On keeping the sample a few hours at room temperature, the polymer becomes paramagnetic, probably due both to CTC formation with oxygen and to structural defects from cis-trans isomerization.

Both in solution and in the solid state, the unpaired spin concentration of cis polymers has a maximum at the cis-trans isomerization temperature. The maximum value is proportional to the cis content of the polymer. For all cis polymers, the Curie law is obeyed at temperatures lower than the temperature which changes polymer configuration.

All trans-cisoidal polymers obey the Curie law both in solution and in solid state, in a temperature interval between 20 and 200°C, i.e. above their melting temperatures.

Consequently, one can consider the nature of paramagnetic centres in polyarylacetylenes to be similar to polyacetylene paramagnetism, being due to the structural defects in the polymer chain.

12.3. Electrical properties of polyarylacetylenes

The electrical properties of polyarylacetylenes were excellently reviewed by Kryszewski in the book published in 1980.⁴² Here, only a few recent data will be shortly presented.

The most representative results referring to PPA structure were published beginning with 1977. Consequently, the electrical properties of PPA, whose cis form is unstable even at room temperature, and whose trans isomer was only recently synthesized by chemical isomerization, were studied on polymers having

unknown structure. It is not difficult to understand, therefore, the differences of eight orders of magnitude between the electrical conductivity values reported by different authors.²⁶³

Recent electrical measurements performed by Simionescu *et al.*^{163, 263} on cis and trans isomers of PPA, poly(α -ethynylnaphthalene), poly(β -ethynylnaphthalene) and poly(N-ethynylcarbazole) showed that all polymers have electrical conductivities higher than $10^{-12} \Omega^{-1} \text{cm}^{-1}$, being therefore insulators.

There is, however, a difference of mostly 4 orders of magnitude between the conductivity of amorphous and crystalline polymers. In all cases, amorphous polymers have a smaller electrical conductivity. Moreover, cis-trans thermal isomerization carried out during electrical measurements causes a decrease in electric conductivity, if the cis polymer is crystalline.²⁶³ It was also proved that electrical conductivity is independent of polymer molar mass.²¹⁸

As for polyacetylene, the charge carriers of polyarylacetylenes can arise only from a CTC which cannot be avoided unless the polymer is handled in the absence of oxygen. Due to the higher ionization potential of polyarylacetylenes as compared with polyacetylene (due to the conjugation differences of the two types of polymers), the oxygen creates only a weak CTC with polyarylacetylenes. The consequence is the very small electrical conductivity. In this context, the conduction mechanisms explained on the basis of intrinsic charge carriers from polyarylacetylenes have no physical significance²⁶⁴⁻²⁶⁸ as for polyacetylene.

Indeed, studies on weak CTC of PPA indicate increase of electrical conductivities of 8-9 orders of magnitude.²⁶⁹⁻²⁷² But, unlike polyacetylene CTC, PPA CTC are weaker and the halogen can be completely recovered by application of vaccum.²⁷²

Strong CTC of a salt type were realized by Berlin *et al.*²⁷³⁻²⁷⁵ and Simionescu *et al.*²⁷⁶ using poly(2-ethynylpyridine) and poly(4-ethynylpyridine). The conductivities of these complexes are of the same order of magnitude as that of the complexes obtained with corresponding vinylic polymers. This behaviour can be explained by cyclohexadiene-type microstructure of 2- and 4-ethynylpyridine polymer chains obtained by radical mechanism.²¹¹

There are no doubts that the use of strong electron-acceptors, (e.g. AsF_6^-) will confer very good electrical properties on polyarylacetylenes.

12.4. Energy migration and transfer in polyarylacetylenes

Davydov *et al.*²⁷⁷ and North *et al.*^{278, 279} studied energy migration and transfer in a PPA probably having mainly cyclohexadienic sequences. North's results⁶⁵ showed that down-chain energy migration is very efficient, especially in dilute solutions where it is limited only by polymer chain length. The same author considers that PPA, which has a broad absorption spectrum and presents high efficacy in energy migration and transfer, can be used as an effective additive for energy transfer in vinylic polymers. Probably, polyenic polyarylacetylenes have much better properties than the above polymers.

13. CONCLUSIONS

The acetylene polymers field is very complex. Polyacetylenes study is approached by specialists in catalysts, polymerization mechanism, polymerization kinetics, structural analysis, chemistry and physics of solid state. Unfortunately, there are no research groups which study the same problems with the same purpose. However, the progress achieved in this polymer class in the last 3–4 years is much higher than that realized in the preceding 20 years.

The general phenomenon of studying the properties which make a polymer useful, before resolving the basic research problems, was evidently manifested in this polymer class. Thus, although intensive theoretical studies which explain properties of polyacetylenes or polyarylacetylenes were published in recent years, and only very recently Wegner *et al.* and Simionescu *et al.* demonstrated that in fact the then supposed structure of polyacetylene and polyarylacetylenes was not real.

The aim of this review was to reconsider some of the most significant data regarding polyacetylene synthesis and structure. We believe that a comparison between polyacetylene and polyarylacetylene structure and synthesis design can be very useful for those working in this field, with many problems to be solved.

Details on polyarylacetylenes microstructure can be obtained due to the solubility of some polymer configuration. These results will facilitate polyacetylene microstructure elucidation.

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