

THE POLYMERIZATION OF ISOPRENE AND 2, 3-DIMETHYLBUTADIENE AND COPOLYMERIZATION WITH STYRENE AT -18°C . IN EMULSION¹

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ABSTRACT

The rate of polymerization increased with purification of the monomers. It was possible that the dienes formed cyclic compounds or dimers in side reactions. The 1,2 addition of the monomer decreased with decreasing polymerization temperature. A study was made of the copolymerization of isoprene and dimethylbutadiene with styrene at -18°C . From analyses of bound diene in the product at various conversions and initial diene to styrene ratios the reactivity ratios for these diene-styrene systems were calculated to be $r_1 = 1.30 \pm 0.02$ and $r_2 = 0.48 \pm 0.01$ for isoprene and styrene and $r_1 = 0.92 \pm 0.02$, $r_2 = 0.42 \pm 0.02$ for dimethylbutadiene and styrene (styrene always being considered monomer 2). Q and e values from the Alfrey-Price equation were calculated as $Q = 1.19$ and $e = -0.112$ for isoprene and $Q = 1.09$ and $e = -0.181$ for dimethylbutadiene relative to $Q = 1.0$ and $e = -0.8$ for styrene. From these and the values previously determined for butadiene, reactivity ratios for all combinations of the three dienes were calculated. The chain transfer reaction between dienyl radicals and mixed tertiary mercaptans was studied and it was found that isoprenyl and dimethylbutadienyl radicals were much more reactive than butadienyl. The effect of this was illustrated by number and viscosity average molecular weights. Intrinsic viscosities of homo- and copolymers formed in a mercaptan-free recipe were measured and compared.

INTRODUCTION

General purpose chemical rubbers are produced by copolymerization of butadiene and styrene. It has been shown that a decrease in polymerization temperature yields a superior product (18, 19). Of interest also are the copolymers of styrene with the methyl substituted dienes, isoprene, and dimethylbutadiene. There has been little done in the study of the copolymerization of these dienes even at higher temperatures (7) and no published data are known obtained at lower temperatures. For this reason a study was undertaken of the copolymerization of these dienes with styrene at -18°C .

Recipes have been developed in this (15) and other (4) laboratories which permit copolymerization of butadiene and styrene at -18°C . without undue difficulty and it was felt that these recipes afforded an opportunity for a study of the polymerization behavior of the dienes under conditions in which side reactions and abnormal polymerization reactions are minimized.

EXPERIMENTAL TECHNIQUES

The polymerizations were conducted in 8 oz. peroxide bottles with punctured metal screw caps (5) in which the fiber gasket was replaced by a double rubber gasket consisting of an outer oil resistant Koroseal* sheet and an inner self sealing Butyl** gasket prepared from undercured unpigmented sheet. The techniques have been described in detail (15, 16).

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*Product of B. F. Goodrich Chemical Company.

**Product of Polymer Corporation Limited.

After the reaction was stopped, the degree of conversion of monomer to polymer was determined (8) and the unreacted monomers were removed from the latex by low pressure steam. The latex was filtered through glass wool to remove precoagulum and coagulated with isopropanol. The polymer was then purified in the conventional manner by reprecipitation from benzene with methanol.

Using the method of Saffer and Johnson (17) the degree of unsaturation was measured. From these results it was possible, in the case of a copolymer, to calculate its composition. The mercaptan in the latex was determined by amperometric titration with silver nitrate (10, 11). The intrinsic viscosities of the polymers formed were measured at 30°C. by dissolving the latex directly in an 80:20 benzene-isopropanol solution. Dilutions were then made with pure benzene so that intrinsic viscosities in pure benzene could be calculated (3, 6, 14).

Monomer purity	Source	Grade	Further treatment
Butadiene	Polymer Corporation Ltd.	Technical	None
Styrene	Polymer Corporation Ltd.	Technical	Steam distilled
Dimethylbutadiene	Polymer Corporation Ltd.		Fractionated
Isoprene	Phillips Petroleum Co.	Research	

Polymerization recipes

	I	II
Monomers	100 parts by wt.	100 parts by wt.
Mixed tertiary mercaptans	0.24	0.24
Water, distilled	157	224
Methanol	46	65.8
Potassium fatty acid soap flakes (Swift and Co.)	5.1	7.3
Daxad 11 (Dewey and Almy Chem. Co.)	0.05	0.07
Potassium sulphate	0.10	0.14
Ferrous sulphate heptahydrate	0.20	0.29
Arsenious oxide	0.2	0.17
Sequestrene AA (Alrose Chem. Co.)*	0.12	0.17
Paramenthane hydroperoxide (Hercules Powder Co.)	0.15	0.22
Ditertiary butyl hydroquinone	0.20	0.29
Benzene	5.0	7.2

*Ethylene diamine tetraacetic acid.

Initial attempts to synthesize polyisoprene using Recipe I failed. This was ascribed to lack of emulsification, which was immediately evident upon examination of the contents of the bottles. The contents always showed distinctly two phases and never an homogeneous emulsion. This was remedied by increasing the soap and water solution to that amount shown in Recipe II whereupon 40% conversion was obtained in 17 hr. using distilled isoprene. This yield later proved to be decidedly irreproducible, presumably depending on the purity of the sample used. Recipe II was used in all succeeding studies on both isoprene and dimethylbutadiene.

EXPERIMENTAL

Effect of Diene Purity

Two samples of isoprene were obtained, one technical grade analyzing 95% isoprene, and the other Phillips 99 mole % pure research grade. Both samples were fractionated in the usual manner so that the final product had a boiling point range of 0.1 to 0.2°C. On polymerization of these to polyisoprene, 29.4%

conversion was obtained for the sample derived from the technical grade as against 53.6% for the sample derived from the research grade. It was evident that there were impurities inhibiting polymerization which were not removed by fractionation. This experience was borne out with dimethylbutadiene. When samples fractionated from a technical grade were used, 17.5% conversion was obtained in 17 hr. However, when the dimethylbutadiene used was material which had been recovered from low conversion experiments and refractionated, i.e. it had been exposed to the action of free radicals at a low temperature, conversions up to 30% were obtained in the same time. This value was extremely irreproducible indicating that varying degrees of purity were obtained in this manner. Proceeding to the effect on the rates of conversion in the styrene-diene copolymer system, it was found that the effect of the inhibiting impurities was much more pronounced than in the homopolymerization systems. This is well indicated by an examination of the data shown in Table I for various dimethylbutadiene-styrene charge ratios using both dimethylbutadiene which had only been fractionated and dimethylbutadiene which had been refractionated after recovery from a low conversion polymerization reaction.

TABLE I
CONVERSION RATE FOR DIMETHYLBUTADIENE-STYRENE COPOLYMERIZATION

Charge ratio, DMB/styrene	Purification procedure	% Conversion/hour, average
75/25	Fractionated	1.1
25/75	Fractionated and recovered	4.7
50/50	Fractionated and recovered	3.5
75/25	Fractionated and recovered	3.0

It seems evident that a very large increase in rates results from use of recovered dimethylbutadiene. In general, the rate of conversion rises as the styrene content of the charge is increased if the purer form of diene is used. However with the more impure grade, the rate decreases as the styrene content is raised. This seems to indicate that the inhibitors normally found in these dienes retard copolymer growth more than homopolymer formation. These results indicate the need for intensive purification of the monomers if any quantitative results are to be deduced from rates of monomer disappearance and if reproducible conversion curves are required for viscosity, residual mercaptan, and other measurements.

Side Reactions

The possibility of side reactions became apparent during the first experiments when a high boiling oil was isolated from reaction mixture in which only low boiling monomers and quite higher molecular weight polymers should have been present. In all experiments these steam volatile compounds were present. From isoprene polymerizations a yellow oil (n_D^{25} 1.493) was obtained together with traces of yellow crystals of a higher melting compound. From dimethylbutadiene polymerizations, larger quantities of the yellow crystals resulted. Since these products were formed in systems where the intrinsic viscosity of the high polymer formed was as high as 6, it was felt unlikely that they could

be low molecular weight linear polymers which would necessarily comprise the lower end of the molecular weight distribution curve. It was thought that they might be cyclic compounds, since it was known that these dienes showed a tendency to cyclize (20).

Effect of Oxygen on Conversion Rates

In the homopolymerizations of butadiene, isoprene, and dimethylbutadiene, the effect of oxygen on the reaction rates was tested (Table II). In the two latter cases oxygen had no effect on the conversion rates and no effect on the intrinsic viscosity of polyisoprene. With butadiene, however, addition of oxygen decreased the rate markedly although little or no change was noted in the intrinsic viscosity.

TABLE II
EFFECT OF OXYGEN ON RATE OF POLYMERIZATION AND VISCOSITY OF POLYMER

Monomer	Cc. air/100 gm. monomers	% Conv. (17 hr.)	$[\eta]$
Butadiene	0	37.5	5.9
	5	18.6	5.1
Isoprene	0	29.4	5.9
	5	33.0	6.0
Dimethylbutadiene	0	17.5	5.5
	5	21.8	—

1,2 and 1,4 Addition

It is known that dienes have alternative methods of chain propagation. Owing to their conjugated structure both 1,2 (or 3,4) and 1,4 addition are possible. Unless the activation energies of the two reactions are identical, the ratio of 1,2 (and 3,4) to 1,4 addition should be a function of temperature. A method (17) has been published whereby this ratio may be determined by measuring the consumption of perbenzoic acid by the polymer as a function of time. Since the acid adds to the 1,4 addition product much more rapidly than to the 1,2 addition product, it is possible to estimate the amount of 1,4 addition. The one difficulty in this method is that in the presence of any 1,2 addition product and of large excess of perbenzoic acid, higher results are obtained for the value of 1,4 addition. This is avoided by obtaining values of the percentage 1,4 addition using different concentrations of perbenzoic acid. From the absolute values of the 1,4 addition and the rate of change of these values with % excess perbenzoic acid, it is in practice quite possible to make a fairly reliable estimate of the true value. This is illustrated by the results obtained using polyisoprene and polydimethylbutadiene synthesized at -18°C . (Table III). It is thus seen that a rather small change in the value occurs with polyisoprene. At 35% excess perbenzoic acid this value is 95% 1,4 addition. From the original work done on the method a value close to the true one would be expected at this perbenzoic concentration. The small change in the value of 1,4 addition supports this view inasmuch as a small amount of 1,2 and 3,4 addition might be expected.

TABLE III
 VALUES OF 1,4 ADDITION ON POLYDIENE

Polymer	% Excess perbenzoic acid	% 1,4 Addition
Polyisoprene	115	103
	65	103
	35	95
Polydimethylbutadiene	72	101
	39	101
	32	99.8

For polydimethylbutadiene, there was no significant trend in the value for the % 1,4 addition with all the values close to 100%. This indicates that within the error of this investigation, no 1,2 addition occurs in dimethylbutadiene at this temperature. It is interesting to compare these values with values determined on polymers synthesized at 50°C. This is shown in Table IV. It is thus evident that (i) 1,2 addition decreases more with polymerization temperature with dimethylbutadiene than with isoprene, (ii) 1,2 addition relative to polybutadiene is suppressed at both temperatures by

 TABLE IV
 CHANGE IN 1,4 ADDITION WITH TEMPERATURE

Polymer	Polymerization temperature, °C.	% 1,4 Addition
Polyisoprene	-18	95
	50	86
Polydimethylbutadiene	-18	95
	50	100
		88

the presence of the methyl groups, presumably because of steric hindrance, and (iii) a product very similar to natural rubber in so far as 1,2 and 1,4 addition is formed at -18°C.

Measurement of Bound Monomer Ratios and Reactivity Ratios of Dienes with Styrene

Measurements of this nature have already been made at -18°C. with butadiene-styrene copolymers (16). The investigation of 1,4 addition by perbenzoic acid addition offered a convenient method for analysis of diene-styrene copolymers by measurement of the total 1,4 unsaturation. In the case of isoprene-styrene copolymers this value was corrected for the fact that only 95% of the isoprene in the copolymer was in the 1,4 configuration. In the dimethylbutadiene-styrene copolymers, however, the 1,4 unsaturation gave the dimethylbutadiene content of the polymer directly. The values obtained at various conversions and charge ratios for the two dienes shown are in Figs. 1 and 2. A statistical analysis of the data shown in these figures gave an average probable error in the results of 0.7% bound diene.

The composition of the copolymer as measured is related to the amount of monomers in the charge at the time of formation of the copolymer by the well-known copolymerization equation. The reactivities of the monomers are ex-

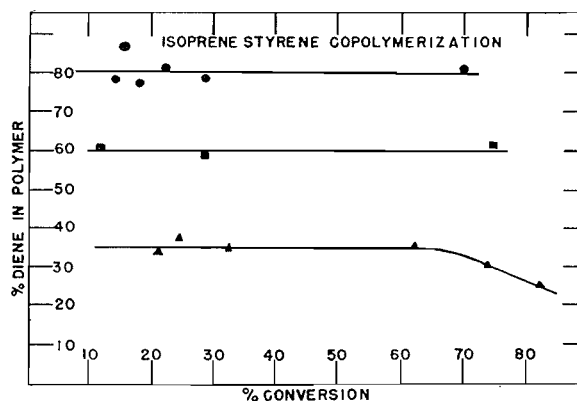


FIG. 1. Bound isoprene for • 75/25, ■ 50/50, and ▲ 25/75 isoprene/styrene charge ratio.

pressed as a ratio. The reactivity of monomer-1 (r_1) of a pair is the ratio of the rate of reaction of a free radical chain ended in a monomer-1 residue with monomer-1 to the rate with monomer-2. The reactivity ratio of monomer-2 (r_2) is then the ratio of the rate of reaction of a free radical chain ended in monomer-2 with monomer-2 and the rate with monomer-1. The reactivity ratios were calculated by extrapolation of the bound monomer curves to 0% conversion and substitution of the values obtained in the copolymerization equation. This method was made necessary because it was only here that the actual ratio of monomers was known in the absence of quantitative data on the possible side reactions. If the diene is considered as monomer 1, then the reactivity ratios obtained were $r_1 = 1.30 \pm 0.02$ and $r_2 = 0.48 \pm 0.01$ for isoprene-styrene, and $r_1 = 0.92 \pm 0.02$ and $r_2 = 0.42 \pm 0.02$, for dimethylbutadiene-styrene. The limits of error were determined by the degree to which the results from each charge ratio checked with each other.

Recalling $r_1 = 1.37$ and $r_2 = 0.38$ for the butadiene-styrene system at this

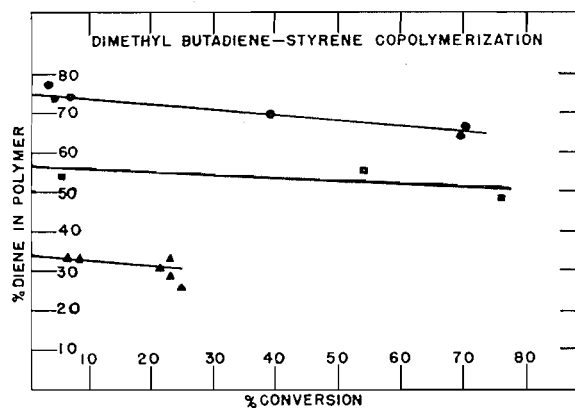


FIG. 2. Bound dimethylbutadiene for • 75/25, ■ 50/50, and ▲ 25/75 DMB/styrene charge ratio.

temperature (16) it is evident that as the number of methyl groups on the diene increase, r_1 shows a continual decrease. This means that with increasing substitution, the dienyl free radicals show an increasing preference to attack styrene over attacking a diene molecule; r_2 seems to rise to a maximum for isoprene.

An attempt to describe all copolymerization characteristics of a monomer in terms of two constants Q and e has been recently made by Alfrey and Price (1) which are defined in terms of the equations

$$r_1 = \frac{Q_1}{Q_2} e^{-e_1(e_1-e_2)} \text{ and } r_2 = \frac{Q_2}{Q_1} e^{-e_2(e_2-e_1)}.$$

Q is a measure of the reactivity of the monomer and e a measure of its polar character. For purposes of this treatment Q and e for styrene were arbitrarily chosen as 1.0 and -0.8 respectively.

Solving the above equations we obtain a $Q = 1.09$ and $e = -0.181$ for dimethylbutadiene and $Q = 1.19$, $e = -0.112$ for isoprene. Recalling that butadiene (16) shows a $Q = 1.38$ and $e = +0.008$ it is evident that addition of methyl groups causes a continuous decrease in the values of Q and e .

Possibly the most interesting use to which these constants could be put is a calculation of r_1 and r_2 for monomer pairs which had not been measured directly. This was done for the various diene combinations and the results are shown in Table V.

TABLE V
CALCULATED REACTIVITY RATIOS

Monomers	r_1	r_2
Butadiene and isoprene	0.94	1.06
Butadiene and dimethylbutadiene	1.26	0.78
Isoprene and dimethylbutadiene	1.18	0.84

Since the direct determination of these constants is subject to severe analytical difficulties, even an approximation, such as these values are, is of possibly greater accuracy than those which would be measured directly.

Bound Diene of Increment Polymer and Residual Unreacted Diene

The bound diene of the increment polymer is the average composition of the polymer formed over an increment of conversion. Since the composition of the unreacted monomers is continually subject to change, and side reactions are probably taking place, the composition of polymer formed changes as reaction proceeds. This chemical heterogeneity has a rather large effect on the properties of the polymer. In Table VI is shown bound diene of the increment polymer for dimethylbutadiene-styrene copolymers calculated from the smoothed curves of Fig. 2.

With isoprene the bound diene is constant over the conversion range at 80.5, 60.0, and 36.0 for 75/25, 50/50, and 25/75 diene/styrene charge ratios.

TABLE VI
BOUND DIENES OF INCREMENT POLYMER FOR DIENE-STYRENE COPOLYMERS

Diene	% Conv. range	% Diene in copolymer formed for initial diene/styrene charge ratio		
		75/25	50/50	25/75
Dimethylbutadiene	0-10	73	56	33
	10-20	71	54	31
	20-30	69	52	
	30-40	67	52	
	40-50	65	48	
	50-60	63	50	
	60-70	61	47	

With dimethylbutadiene the diene content of the increment polymer decreases more rapidly than with isoprene.

The per cent unreacted diene in the residual monomers, assuming no side reaction, was also calculated (Table VII).

TABLE VII
RESIDUAL UNREACTED DIENE

Diene	% Conversion	% Diene in residual monomer for initial diene/styrene charge ratio		
		75/25	50/50	25/75
Dimethylbutadiene	10	75	50	24
	20	76	49	23
	30	77	48	
	40	79	48	
	50	81	47	
	60	84	48	
Isoprene	10	74	49	25
	20	74	48	22
	30	73	46	20
	40	72	43	18
	50	70	40	14
	60	67	30	9
	70	63		

The values of the bound diene of the increment polymer should be related to the values for residual diene in the unreacted monomers and the reactivity ratios r_1 and r_2 by the equation $\frac{dD}{dS} = \frac{D}{S} \left(\frac{r_1 D/S + 1}{D/S + r_2} \right)$ where S is the concentration of styrene and D the concentration of diene. When the calculated unreacted diene in the residual monomer is plotted against the calculated increment polymer composition, for a given set of reactivity ratios, the theoretical lines shown in Fig. 3 are obtained. When the observed values are plotted in this manner, it will be noted that only for 0% conversion do the values agree. At all finite values of conversion, there is a drift from the values predicted by the reactivity ratios. The cause of this is unknown but it should be noted that the drift is in the direction of a less random polymer, i.e. at higher conversions

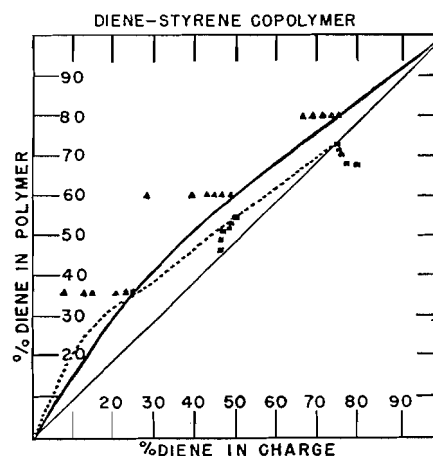


FIG. 3. Increment bound diene against residual diene in charge.
 — Calculated curve for isoprene-styrene $r_1 = 1.30$; $r_2 = 0.48$.
 - - - Calculated curve for DMB-styrene $r_1 = 0.92$; $r_2 = 0.42$.
 ▲ Observed values for isoprene-styrene copolymerization.
 ■ Observed values for DMB-styrene copolymerization.

there is a greater tendency to an alternating copolymer than the values of the reactivity ratios can account for except for r_1 of the dimethylbutadiene system which tends to increase. This type of behavior was also noticed in the butadiene-styrene system at this temperature (16) but in that case the values of r_1 and r_2 both tended to increase.

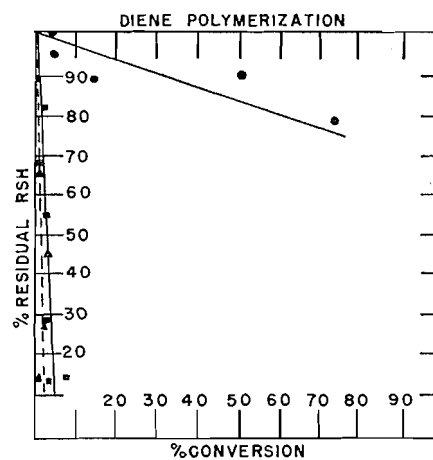


FIG. 4. MTM disappearance curves for:
 ● butadiene, ■ isoprene, and ▲ dimethylbutadiene.

Modifier Disappearance Curves

The reactivity of the free radical toward mercaptans is of considerable importance in the industrial applications of polymerization since this is one of the most widely used methods of regulating the molecular weight of the product. The rate of disappearance of mercaptan gives a measure of the relative impor-

tance of this chain transfer reaction. Three dienes, isoprene, butadiene, and dimethylbutadiene were investigated with MTM,* at a concentration of 0.39 parts MTM/100 parts monomers. The data for the three dienes are shown in Fig. 4. It is evident that the mercaptan disappears much more rapidly in the isoprene and dimethylbutadiene systems than it does in the butadiene systems. Assuming that the logarithm of the % residual mercaptan is linear with respect to % conversion, the slopes of the lines were calculated. These are the regulating indices given in Table VIII.

TABLE VIII
REGULATING INDEX FOR MTM

Monomer	Regulating index
Butadiene	0.4
Isoprene	40
Dimethylbutadiene	52

Two factors influence this regulating index, (i) the absolute rate of the chain transfer reaction, (ii) the rate of diffusion of the mercaptans to the growing polymer free radicals. In the event of a rapid diffusion the regulating index then becomes a measure of the reactivity of the free radical toward the mercaptan. In this particular recipe, diffusion must be relatively rapid since the regulating index is high. This indicates that isoprenyl and dimethylbutadiene radicals show a reactivity of at least 90 to 100 times greater toward MTM than do butadienyl radicals. This result is supported by work on dimethylbutadiene (12) which indicates that less modifier is required to synthesize a polymer of a given Mooney viscosity than is the case for butadiene systems and by observations that isoprene in the presence of chain transfer agents yields oils (2). No work has been done on diene-styrene copolymerization systems but there

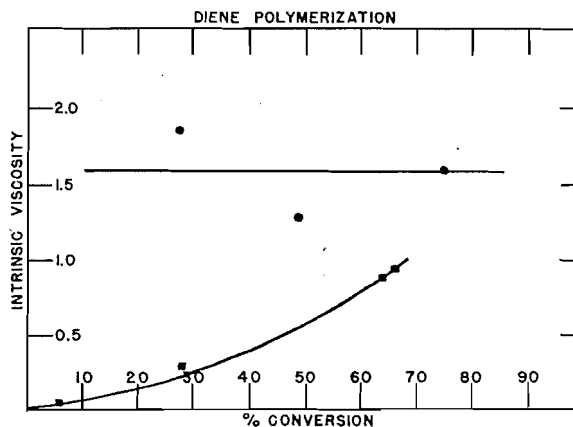


FIG. 5. Intrinsic viscosity with 0.39 parts MTM of:
● polybutadiene and ■ polyisoprene.

* A mixed tertiary mercaptan consisting of 60% C_{12} , 20% C_{14} , 20% C_{16} average molecular weight, 220. Phillips Petroleum Company.

is no reason to believe that this increase in modifier consumption will not also be characteristic of the copolymerizing systems.

It is interesting to note the effect of this increased mercaptan consumption on the intrinsic viscosity of the polymer produced. This is shown in Fig. 5 for butadiene and isoprene. It will be noted that the intrinsic viscosity for polybutadiene is relatively constant (see also Reference 16) while that for polyisoprene begins at a very low value and slowly rises. This increase is due to the fact that at 10 to 15% conversion, all the mercaptan has been consumed and the polymer is then being formed in a mercaptan free medium. Although the data are very scattered, it is of interest to calculate the intrinsic viscosity of the increment polymer being formed and show how it increases when the mercaptan has been consumed. This is shown below in Table IX using the smoothed curves of Fig. 5 for isoprene.

TABLE IX
INCREMENT INTRINSIC VISCOSITIES FOR POLYISOPRENE

% Conversion range	Intrinsic viscosity
0-10	0.05
10-20	0.15
20-30	0.40
30-40	0.80
40-50	1.25
50-60	1.85
60-70	3.20

It may be seen (Fig. 5) that the increment intrinsic viscosity in polybutadiene is constant at 1.60. This is also characteristic of butadiene-styrene copolymers at this temperature (16). However the increment intrinsic viscosity of the polyisoprene slowly rises, indicative of the fact that the mercaptan is disappearing exceedingly rapidly. There is no apparent reason why there is not a sharp increase in this increment intrinsic viscosity to a value which would be characteristic of a mercaptan free system when the mercaptan is consumed.

Number Average Molecular Weights

Assuming that the only chain terminating step is that due to mercaptan it is possible to compare number average molecular weights for the two systems. The number average molecular weights for polybutadiene calculated from the smoothed curve of Fig. 5 is 1.1×10^5 . The data for polyisoprene are in Table X.

TABLE X
CALCULATED MAXIMUM NUMBER AVERAGE MOLECULAR WEIGHTS FOR POLYISOPRENE

% Conversion	\bar{M}_n
2	2.8×10^3
4	3.2×10^3
10	5.6×10^3

For isoprene, however, \bar{M}_n increases after the total consumption of the mercaptan, the increment \bar{M}_n to a value representing other types of termination.

Intrinsic Viscosities with a Mercaptan Free Recipe

One characteristic of $-18^{\circ}\text{C}.$ reactions is that it is possible to prepare soluble diene polymers and copolymers in mercaptan free recipes. This is not possible at higher temperatures where the greater proportion of cross linking and branching gives insoluble polymers. The intrinsic viscosity was measured at different charge ratios and conversions. The data for isoprene-styrene copolymerization reactions are shown on Fig. 6. It will be noticed that for the higher diene con-

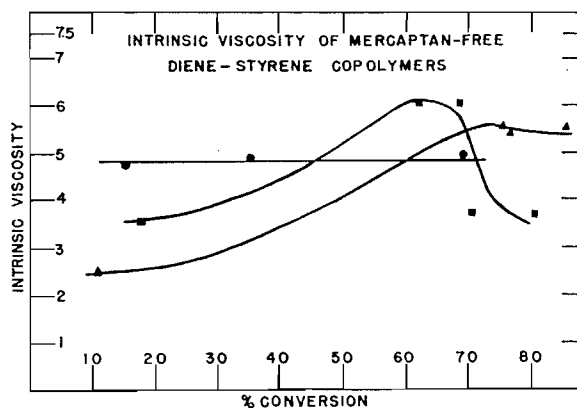


FIG. 6. Intrinsic viscosities for:
●, ■, ▲ 75/25, 50/50, and 25/75 isoprene-styrene.

tents, the intrinsic viscosity seems to be independent of conversion but a peak at about 50% conversion may have been missed. At higher styrene contents (50/50 and 25/75 diene/styrene charge ratio) this is no longer the case. The curves seem to pass through maxima. Some data for dimethylbutadiene-styrene copolymerization reactions are in Table XI.

TABLE XI
INTRINSIC VISCOSITIES OF UNMODIFIED DIMETHYLBUTADIENE-STYRENE COPOLYMERS

Charge ratio	% Conversion	[η]
75/25	23.5	3.3
	31.7	2.6
50/50	14.4	2.0
	31.7	3.5
25/75	29.4	3.2
	31.2	3.9

It may be seen that the intrinsic viscosities of the three polydienes prepared in mercaptan free recipes are very nearly equal (Table II). The initial intrinsic viscosity of the polymer formed becomes lower as the styrene content of the polymer increases. This is shown in Table XII for isoprene-styrene copolymers.

The intrinsic viscosities for dimethylbutadiene-styrene copolymers were always lower than the corresponding isoprene-styrene copolymers. (Compare Table XI with Fig. 6.) The change in $[\eta]$ between 75/25 and 50/50 charge ratio also seemed to be less than the corresponding change in the isoprene-styrene system.

TABLE XII
INTRINSIC VISCOSITIES AT 0% CONVERSION FOR ISOPRENE-STYRENE COPOLYMERS

Charge ratio isoprene/styrene	Intrinsic viscosity at 0% conv.
100/0	6.0
75/25	4.9
50/50	3.4
25/75	2.4

Viscosity Average Molecular Weights of Polyisoprene

If we assume that K and a for the polydienes are not appreciably different, and since K and a for polybutadiene synthesized at this temperature is suggested to be $K = 10.6 \times 10^4$ and $a = 0.63$, it is possible to calculate viscosity average molecular weights (9) for the modified polybutadienes and polyisoprenes. These are in Table XIII for polyisoprene.

TABLE XIII
VISCOSITY AVERAGE MOLECULAR WEIGHTS OF MODIFIED POLYISOPRENE

% Conversion	Polyisoprene
10	4.6×10^3
20	1.3×10^3
30	4.0×10^3
40	9.7×10^3
50	1.8×10^4
60	5.0×10^4
70	6.3×10^4

The viscosity average molecular weight of polybutadiene is constant at 1.1×10^5 assuming a horizontal line in Fig. 5. However, the viscosity average molecular weight of polyisoprene increases quite rapidly as would be expected from the modifier disappearance data, Fig. 4, and as calculated from the smoothed curve of Fig. 5.

DISCUSSION

The change in Q and e values as the number of methyl groups increase is interesting; e is usually defined as C/\sqrt{DkTr} (1) where

- C is charge on double bond,
- r is radius of activated complex,
- D is dielectric constant,
- k is Boltzmann's constant, and
- T is the absolute temperature.

If r is assumed to be constant for the different dienes, then C must become increasingly more negative with the addition of methyl groups since a change in the dielectric constant D has been shown not to affect reactivity ratios. Recalling that e was +0.008, -0.112, and -0.181 for butadiene, isoprene, and dimethylbutadiene respectively, it may be seen that the Δe caused by addition of a methyl group decreases from -0.120 for the first methyl group to -0.069 for the second.

A survey of the data in a recent comprehensive review by Mayo and Walling (7) was made. There appeared to be two series in which comparisons of monomers and their methyl analogue could be made. The first is in Table XIV in which the reactivity ratios for methyl acrylate and methyl methacrylate in combination with a number of reference monomers is shown. It will be observed that in all cases r_1 increases and r_2 decreases with methyl substitution; quite contrary to our observations.

TABLE XIV
COMPARISON OF REACTIVITY RATIOS

$M_1 \backslash M_2$	Methyl acrylate			Methyl methacrylate		
	r_1	r_2	$r_1 r_2$	r_1	r_2	$r_1 r_2$
Allyl acetate	5	0		23	0	
Butadiene	0.05	0.76	0.038	0.25	0.75	0.19
2-Chloroallyl acetate	0.7	0		1.0	0	
2-Chlorobutadiene	0.081	11.1	0.90	0.083	6.12	0.51
2, 5-Dichlorostyrene	0.15	3.4	0.51	0.44	2.25	0.99
Maleic anhyd.	2.8	0.02	0.056	6.7	0.02	0.13
Trichloroethylene	3.5	0		81	0	
Vinyl chlor.	9.0	0.083	0.74	13	0	
Styrene	0.206	0.775	0.18	0.49	0.56	0.27

The second series shows the reactivity ratios for a number of monomers and their methyl derivatives towards styrene and methyl methacrylate as reference monomers, Table XV. Again r_1 and r_2 increase and decrease respectively except for butadiene, styrene, and vinyl acetate in which the opposite tendency is shown. The only distinguishing feature of these three monomers is the negative "e" value. Whether this is a general rule and whether it has a satisfactory explanation should be left for further data.

TABLE XV
COMPARISON OF REACTIVITY RATIOS

	r_1	r_2	$r_1 r_2$	Methyl analogue		
				r_1	r_2	$r_1 r_2$
Styrene = M_2						
Butadiene	1.83	0.65	1.2	1.68	0.80	1.3
Acrylic acid	0.25	0.15	0.038	0.7	0.15	0.11
Acrylonitrile	0.03	0.42	0.012	0.18	0.30	0.27
Allyl acetate	0	90		0	71	
Allyl chloride	0.016	31.5	0.50	0	22	
Methyl acrylate	0.206	0.775	0.16	0.49	0.56	0.27
Methyl methacrylate = M_2						
Vinyl acetate	0.015	20	0.30	0.017	30	0.51
Acrylonitrile	0.18	1.35	0.24	0.65	0.67	0.44
Allyl acetate	0	23		0	10	
Allyl chloride	0	41		0	7.5	
Styrene	0.56	0.49	0.27	0.14	0.50	0.07

Considerably less data are available on the changes of Q and e values with methyl substitution so that the data in Table XVI might be considered as indicative of possible trends. In this field many more data are required.

TABLE XVI

COMPARISON OF Q AND e VALUES

	Q	e	Methyl analogue	
			Q	e
Butadiene	1.38	0.008	1.09	-0.181
Styrene	1.0	-0.8	0.58	-1.0
Methyl methacrylate	0.42	0.6	0.74	0.4

A method has recently been published (13) whereby an estimate of the heterogeneity of the molecular weight of a polymer may be made if viscosity average and number average molecular weights are known. For GR-S the relationship was calculated as

$$\beta = 2.35 \sqrt{\log R} \text{ and } M_0 = \bar{M}_n R^{-0.60} \text{ where } R = \frac{\bar{M}_v}{\bar{M}_n}.$$

β is a measure of the heterogeneity of the polymer and M_0 is that molecular weight at which the peak occurs in the distribution curve. It may be seen from the data that for polybutadiene $\beta = 0$ and $M_0 = \bar{M}_v = \bar{M}_n = 1.1 \times 10^5$. This indicates the highly improbable condition of a completely homogeneous polymer. Polyisoprene showed $\bar{M}_v < \bar{M}_n$. This obviously cannot be the case and indicates that the experimental errors involved are very large or the considerations do not apply under the experimental conditions used.

From the theoretical side it is evident that some means of expressing reactivities which takes into account the "activity" of the double bond and the effect of temperature is required. Perhaps then the effect of substitution adjacent to the double bond can be predicted with more certainty as a function of the activity of the original structure. In the more practical field it has been shown that isoprene and dimethylbutadiene polymerize and copolymerize much like butadiene but are more sensitive to monomer impurities, less sensitive to oxygen, and more difficult to modify to form a product of more uniform molecular weight. On the other hand there is more tendency towards a linear structure so that high conversion linear polymers should be possible as well as soluble polymers of very high molecular weight.

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