Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Léonard, J. and Malhotra, S. L.(1977) 'Ionic Polymerization of α-lsopropyl-a-methylstyrene', Journal of Macromolecular Science, Part A, 11: 11, 2087 — 2112
To link to this Article: DOI: 10.1080/00222337708061351
URL: http://dx.doi.org/10.1080/00222337708061351

J. MACROMOL. SCI.–CHEM., A11(11), pp. 2087-2112 (1977)

Ionic Polymerization of p-Isopropyl-α-methylstyrene

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ABSTRACT

The polymerization of p-isopropyl-α-methylstyrene was carried out with anionic and cationic initiators. Polymers prepared in bulk through an anionic mechanism yielded narrowly dispersed products whereas those prepared with sodium-naphthalene complex in solution as well as with cationic initiators gave broad or bimodal distributions when analyzed with gel-permeation chromatography. The presence of microgels was also detected in these latter polymers and has been attributed to chain transfer reactions leading to branching and possibly crosslinking. The comparison of the proportions of different protons in these polymers, as computed from their nuclear magnetic resonance and infrared spectra, with those obtained for a polymer of regular structure suggests that reactions originating from the isopropyl group, along with substitutions on the benzene ring, are responsible for the anomalous structures.

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INTRODUCTION

The polymerization of styrene and substituted styrenes has been investigated by a number of research workers, and the effect of substituents on various aspects of polymerization is well known. Recently it was reported that during the cationic polymerization of p-methylstyrene [1] and o-isopropylstyrene [2] anomalous structures appear in the final product. These were correlated with isomerization polymerization, where the chain propagation is accompanied by simultaneous migration of a mobile hydrogen atom or a group of atoms. These claims have already been questioned by other workers [3, 4] who have polymerized the two monomers and, based on their interpretation of infrared and NMR spectra, have ruled out the possibility of such a polymerization for p-methylstyrene and even for p-isopropylstyrene, where migration would be favored energetically.

Polymerization of p-isopropyl-α-methylstyrene has been reported in the literature [5, 6], but very few data are available. The anionic and cationic polymerization of this monomer was carried out in this laboratory. Since the anionic polymerization could lead to an equilibrium between monomer and active polymer chains, which may form the subject of further studies, these were carried under conditions similar to those encountered in the equilibrium polymerization. Under those specific conditions of reaction, irregularities in the polymer structure were observed through infrared and nuclear magnetic resonance spectra, and the results are reported in the present paper.

EXPERIMENTAL

Materials

p-Isopropyl-α-methylstyrene (Aldrich Chemical Co.) was kept over calcium hydride and degassed on the vacuum line for two weeks. It was distilled under vacuum, the head and tail fractions being discarded. Vapor-phase chromatography of the middle fraction showed that there were no impurities present. This was further confirmed by infrared and NMR spectra. Before use, the monomer was further purified by distilling it on to a mirror of sodium or potassium metal. However a sodium-potassium alloy initiated polymerization rapidly and hence was not suitable as a long-term drying agent. Tetrahydrofuran (THF) was purified in the same manner.

n-Butyllithium (BuLi) (Foote Mineral Co.), potassium metal (Matheson Coleman & Bell), methylene chloride (CH_2Cl_2) (Fisher Scientific ACS), aluminum chloride ($AlCl_3$) (Fisher Scientific ACS), and triphenylmethyl hexafluorophosphate [$(C_6H_5)_3C^+PF_6^-$] (Alfa Inorganics) were used directly without further purification. N,N,N',N'-Tetramethyl-1,2-ethylenediamine (TMEDA) (Aldrich Chemical Co.) was dried over molecular sieves and distilled on a vacuum line from time to time before use.

Polymerizations

Bulk anionic polymerization of p-isopropyl-α-methylstyrene, with BuLi-TMEDA complex as initiator, was carried out in screw-capped bottles inside a dry box. These bottles were washed with a sodium dichromate-sulfuric acid mixture, distilled water, methanol, dried in an oven and finally cooled in an atmosphere of nitrogen. Monomer, TMEDA and butyllithium were injected into the bottles in that order till the red color of the solution persisted. The bottles were capped and immersed in a bath set at -25°C for the desired time.

Polymerizations with a potassium-sodium alloy as initiator were carried out in a Pyrex tube provided with a joint at the top. Freshly cut sodium and potassium were introduced into the ampoule under nitrogen inside a dry box. The ampoule was connected to the vacuum line, degassed and the two metals were melted with a flame. After cooling, p-isopropyl-α-methylstyrene was distilled onto the alloy. The ampoule was sealed off from the line and immersed in a bath set at the desired temperature.

Polymerizations with potassium alone were carried out in a similar fashion as described above as well as in a fashion described elsewhere [7]. These were carried out in Pyrex ampoules provided with a side tube for making a mirror of pure metal and distillation of tetrahydrofuran followed that of the monomer. With naphthalene-sodium as initiator, polymerizations were carried out in Pyrex tubes which had a side tube containing naphthalene-sodium in THF and which was connected with the main tube through a break seal. The rest of the procedure was the same as above.

For the cationic polymerizations, aluminum chloride or triphenylmethyl hexafluorophosphate was added to a Pyrex tube with a joint on the top, inside a dry box, under a continuous flow of nitrogen gas and was degassed on the vacuum line. The required amounts of methylene chloride and p-isopropyl-α-methylstyrene were distilled in, in that order. The ampoule was sealed off from the line. Initiation was rapid and the reaction was exothermic. The ampoule was immersed in a bath at -25°C. All polymerizations were carried out for a period of approximately 24 hr. After the polymerizations were over, the polymers were precipitated out of methanol. The filtrate was evaporated to recover the methanol-soluble fraction of the polymer, and the residue thus obtained was added to the precipitated polymer.

Analysis of the Polymer

Gel-Permeation Chromatography (GPC)

The GPC molecular weight distributions of poly-p-isopropyl-α-methylstyrene were obtained with a Waters Associates (model 200) gel permeation chromatograph equipped with three columns connected in series, each one being packed with crosslinked polystyrene gel having, according to the Waters' method, a maximum rated porosity of 1×10^6, 1.5×10^5, and 3×10^3 Å, respectively. The flow of solvent (THF purged with nitrogen) was maintained at 1 ml/min while the concentration of polymer was limited to 0.125% in order to avoid "concentration effects" on the peak positions in the chromatograms. The calibration of the instrument was performed with narrowly distributed polymer samples of poly-p-isopropyl-α-methylstyrene. Molecular weights were computed by the method discussed in the Waters Associates Instruction Manual [8].

NMR Spectroscopy

Nuclear magnetic resonance spectra of 15% polymer solutions in o-dichlorobenzene with tetramethylsilane as internal standard were run at 100°C in a 220 MHz Varian spectrometer.

Infrared Spectroscopy

IR spectra of polymer samples were recorded with a Beckman infrared spectrophotometer as well as a Perkin-Elmer 457 grating spectrophotometer. The spectra were run on KBr pellets or directly from thin films of polymer.

Viscosity

Viscosity of polymer solutions in toluene was measured at 25°C with a modified Ubbelohde viscometer [9].

RESULTS AND DISCUSSION

Polymerization and Gel-Permeation Chromatographic Analysis

Anionic Polymerization

GPC chromatograms of polymers prepared in THF with potassium metal alone as well as with sodium naphthalene complex are shown in Fig. 1. $\overline{M}_w$ and $\overline{M}_n$ as computed from these curves and other data are

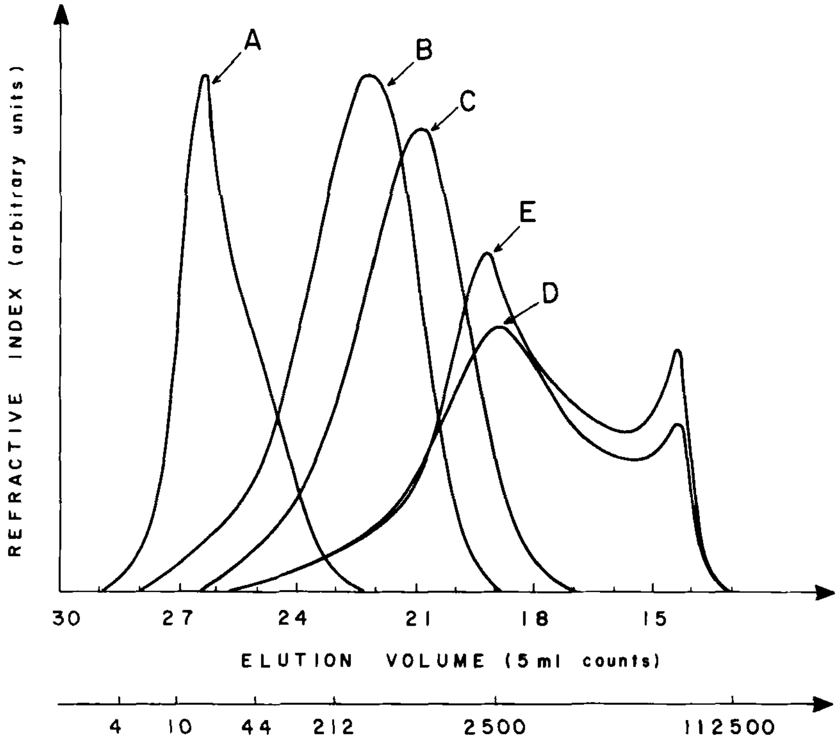


FIG. 1. GPC chromatograms of poly-p-isopropyl-α-methylstyrene prepared in tetrahydrofuran with potassium metal (A, B, D) and sodium naphthalene (C, E) as initiators.

presented in Table 1. From Table 1 it is quite obvious that the polydispersity of samples A, B, and C increases with increasing degree of polymerization ($\overline{DP}$). Polymers E and D having very high molecular weights and broad distributions exhibit a peak at an elution volume of 75 ml corresponding to a $\overline{DP}$ value in the vicinity of 100,000. These high molecular weight polymers (microgels) represent from 10 to 20% by weight of the total polymer. If the polymer chains are allowed to grow beyond that $\overline{DP}$, complete gelling occurs. This gel was recovered in the form of a flexible rubberlike rod by breaking the glass ampoule and was found to be insoluble in all solvents but did swell when kept in a solvent over a long time. All these observations suggest that during polymerization chain branching takes place which eventually leads to crosslinking and yields anomalous structures.

TABLE 1. Cationic and Anionic Polymerization of p-Isopropyl α-methylstyrene

Sample	Solvent	[Monomer]$_0$ (mole/ liter)	Initiator	[C] (mole/ liter)^a	Polym. temp (°C)	Polymer (base-mole/ liter)	[η] (in toluene, 25° C)	$\overline{M}_w \times 10^{-5}$ (GPC)^b	$\overline{M}_n \times 10^{-5}$ (GPC)^b	$\overline{M}_w/\overline{M}_n$
A	THF	4.13	Potassium	0.040	30	0.40	0.042	0.053	0.031	1.7
B	THF	1.16	Potassium	0.005	-5	0.35	0.168	0.60	0.21	2.9
C	THF	0.70	Na-Naphth	0.002	-20	0.36	0.320	1.70	0.56	3.0
D	THF	2.03	Potassium	0.0015	-5	0.86	0.602	5.10 (87%) 67.00 (13%)	1.60 61.00	3.2 1.1
E	THF	1.00	Na-Naphth	0.001	-20	0.71	1.178	5.10 (80%) 66.00 (20%)	1.60 59.00	3.2 1.1
S-3	None	6.25	BuLi-TMEDA	0.228	-25	7.20	0.073	0.13	0.10	1.3
S-20	None	6.25	BuLi-TMEDA	0.151	-25	7.20	0.120	0.21	0.155	1.3
S-17	None	6.25	BuLi-TMEDA	0.063	-25	7.20	0.255	0.93	0.35	2.7
S-25	None	6.25	BuLi-TMEDA	0.017	-25	7.20	0.601	4.31	1.32	3.3
K-1	None	6.25	Na-K alloy	-	25	-	0.320	-	-	-
F-4	None	6.25	Na-K alloy	-	25	-	0.870	7.23	1.80	4.0
M-24	CH_2Cl_2	0.80	$AlCl_3$	0.010	-25	0.60	-	0.038	0.019	2.0
M-27	CH_2Cl_2	1.20	$(C_6H_5)_3C^+PF_6^-$	0.010	-25	0.75	0.087	0.26	0.024	11.0
M-20	CH_2Cl_2	2.50	$(C_6H_5)_3C^+PF_6$	0.010	-25	2.15	0.285	1.10	0.068	16.0
M-23	CH_2Cl_2	4.00	$(C_6H_5)_3C^+PF_6$	0.010	-25	3.80	0.320	1.30	0.12	11.0

[a] The concentration of active chain ends, [C], is computed from $\overline{M}_n$ on assuming two active centers per chain in the cases of samples A to E.

[b] $\overline{M}_w$ and $\overline{M}_n$ computed according to the method described in Water's Associates Instruction Manual [8].

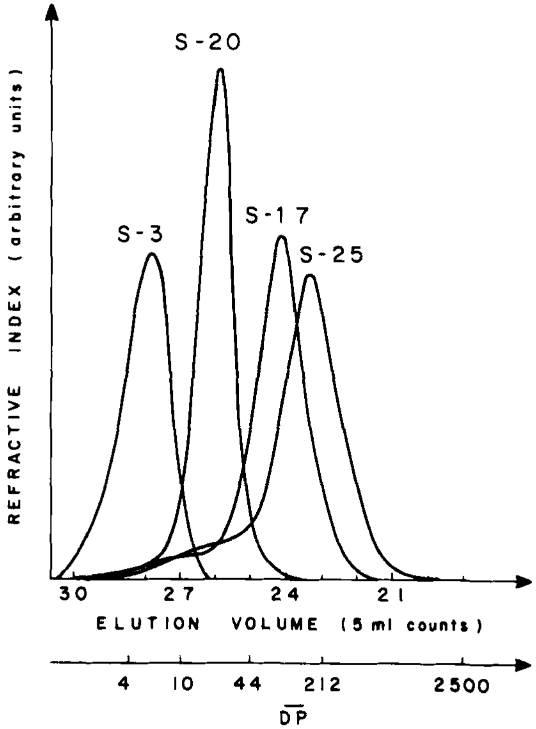


FIG. 2. GPC chromatograms of poly-p-isopropyl-α-methylstyrene prepared in bulk with BuLi-TMEDA complex as initiator.

On the other hand, low molecular weight polymers obtained from bulk polymerization using the BuLi-TMEDA complex as initiator, seem to have unimodal distributions (Fig. 2) and low polydispersity, hence maximum possibility of having a regular structure.

As mentioned above in the experimental section, polymerization was initiated when pure monomer was left in the presence of a mirror of a sodium-potassium alloy. The chromatogram of polymer K-1 thus obtained after one week and separated from its gel is shown in Fig. 3. In addition to branching and crosslinking reactions, the presence of polymer species with molecular weights ranging from 10^3 to 10^7 and the exceptional broadening of the GPC curve can be attributed, for this particular case, to the nonhomogeneous distribution of living ends within the solution of the polymer in its own monomer where higher concentration of living ends are expected to be found in the vicinity of the mirror. Polymer sample K-1 was fractionated, and one of its high molecular weight fractions F-4 was retained for the present study.

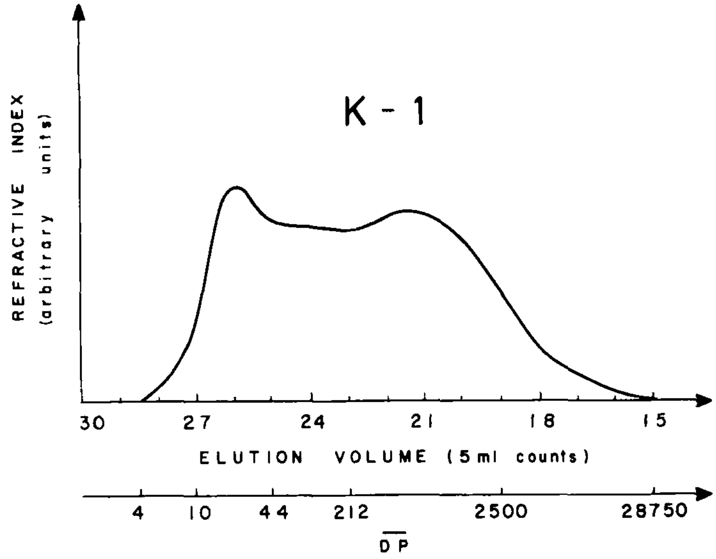


FIG. 3. GPC chromatogram of poly-p-isopropyl-α-methylstyrene prepared in bulk with Na-K alloy as initiator.

Cationic Polymerization

Figure 4 shows the GPC results for polymers prepared with aluminum chloride (M-24) and triphenylmethyl hexafluorophosphate (M-23, M-20 and M-27) as initiators in the presence of small amounts of CH_2Cl_2. Sample M-24 has most probable distribution, with an average degree of polymerization of about 12. Samples M-23, M-20, and M-27 all show bimodal distributions, with the lower molecular weight polymer having the same $\overline{DP}$ of 12, whereas that of the higher molecular weights is different in the three samples. The relative proportion of the low and high molecular weight species as well is different in the three samples. Bimodal molecular weight distributions have also been reported by Higashimura and co-workers [10, 11] as well as by Pepper [12] in their studies of styrene polymerizations with perchlorates in methylene dichloride as solvent. These authors have explained these bimodal distributions on the basis of the concept that two or more kinds of propagating species participate simultaneously in the propagation reaction.

Similar arguments may be put forward to explain the bimodal distributions in the present study. However, there is yet another way to explain the formation of low molecular weight species in the case of polymers M-20, M-23, and M-27 prepared with triphenylmethyl

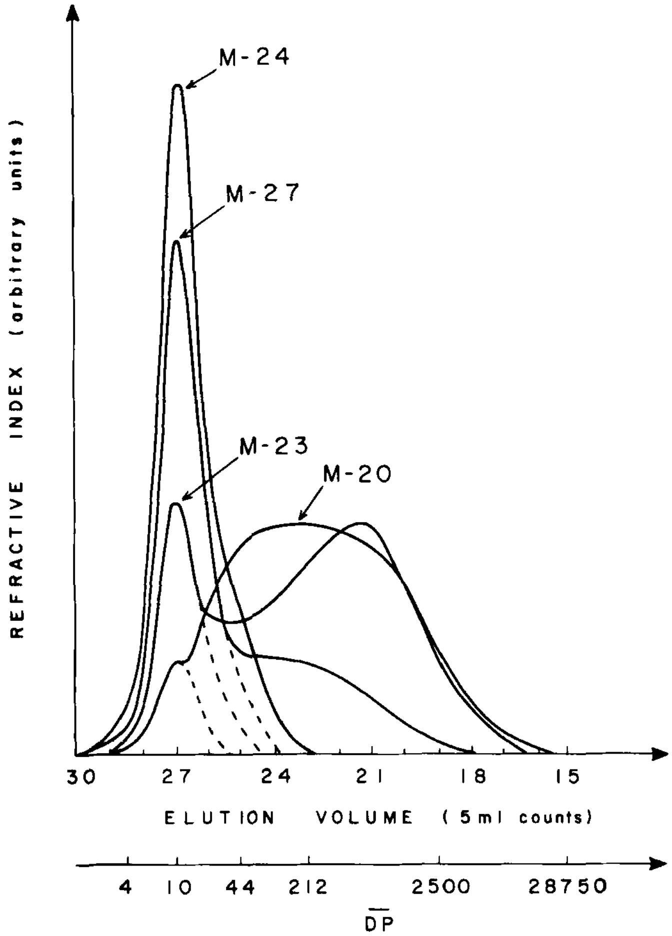
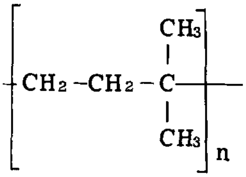


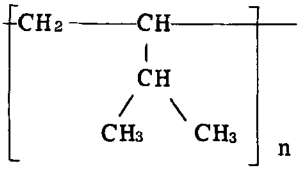
FIG. 4. GPC chromatograms of poly-p-isopropyl-α-methylstyrene prepared in CH_2Cl_2 with $AlCl_3$ (M-24) and $(C_6H_5)_3C^+PF_6^-$ (M-20, M-23, and M-27) as initiators.

hexafluorophosphate. These species, which elute at the same count as that for polymer M-24 prepared with $AlCl_3$, may have their origin from a different type of mechanism similar to the one reported by Kennedy and co-workers [13] in the $AlCl_3$-initiated polymerization of methylbutene-1. These workers reported that the NMR analyses of the polymers revealed them to have the structure



$$\left[-CH_2-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}- \right]_n$$

rather than the expected



Here despite their different GPC distributions, polymer samples C, K-1, and M-23 all have an intrinsic viscosity of 0.32. This illustrates the fact that interpretations based solely on intrinsic viscosity results without reference to molecular weight distribution can be misleading.

NMR Spectra

Figures 5-7 show 220 MHz NMR spectra of polymer samples prepared through anionic and cationic polymerizations. Since the spectrum of sample F-4 was similar to those of S-25 and M-23, it is not shown here, although the values obtained from its spectrum are presented in Table 2. Assignment of the various proton resonances has been given elsewhere [14] and are as follows: benzene protons (H_B), $\tau = 3.0$-3.6; methine protons (CH), $\tau = 7.05$-7.4; methylene protons (CH_2), $\tau = 7.9$-8.6; methyl protons of the isopropyl group (iso-CH_3), $\tau = 8.7$-8.9; α-methyl protons (αCH_3), $\tau = 9.0$-9.9.

In a polymer with a regular structure, relative abundances of the different protons may be expressed in the form of ratios. In poly-p-isopropyl-α-methylstyrene there are ten different possible combinations of proton/proton ratios and these are shown in Table 2. The relative abundances of protons for four polymer samples are also given in Table 2.

From Table 2 it can be seen that the experimental ratios do not coincide with the ones that should be obtained for a polymer with the regular structure I. This implies that there is at least one side reaction taking place which brings about a change in the proton/proton ratios. In order to identify this reaction, one may consider

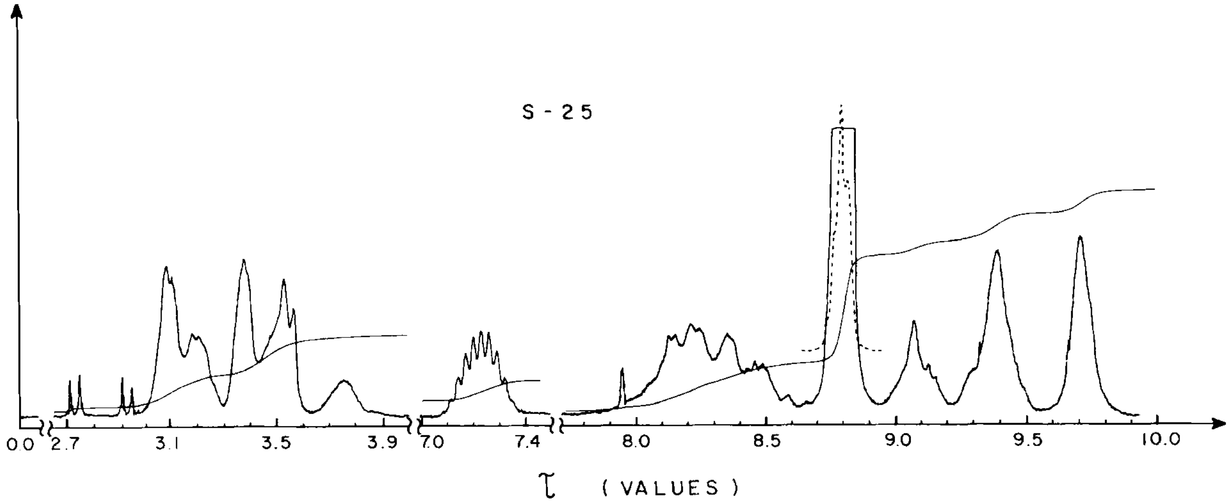


FIG. 5. 220 MHz resonance spectrum of poly-p-isopropyl-α-methylstyrene prepared in bulk with BuLi-TMEDA complex as initiator.

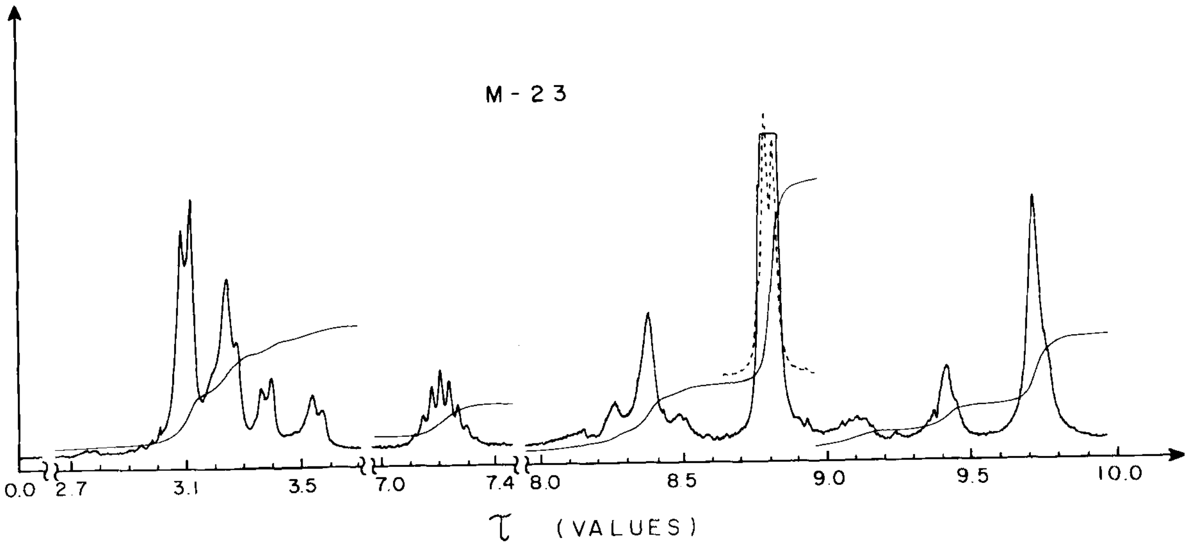


FIG. 6. 220 MHz resonance spectrum of poly-p-isopropyl-α-methylstyrene prepared in CH_2Cl_2 with $(C_6H_5)_3C^+PF_6^-$ as initiator.

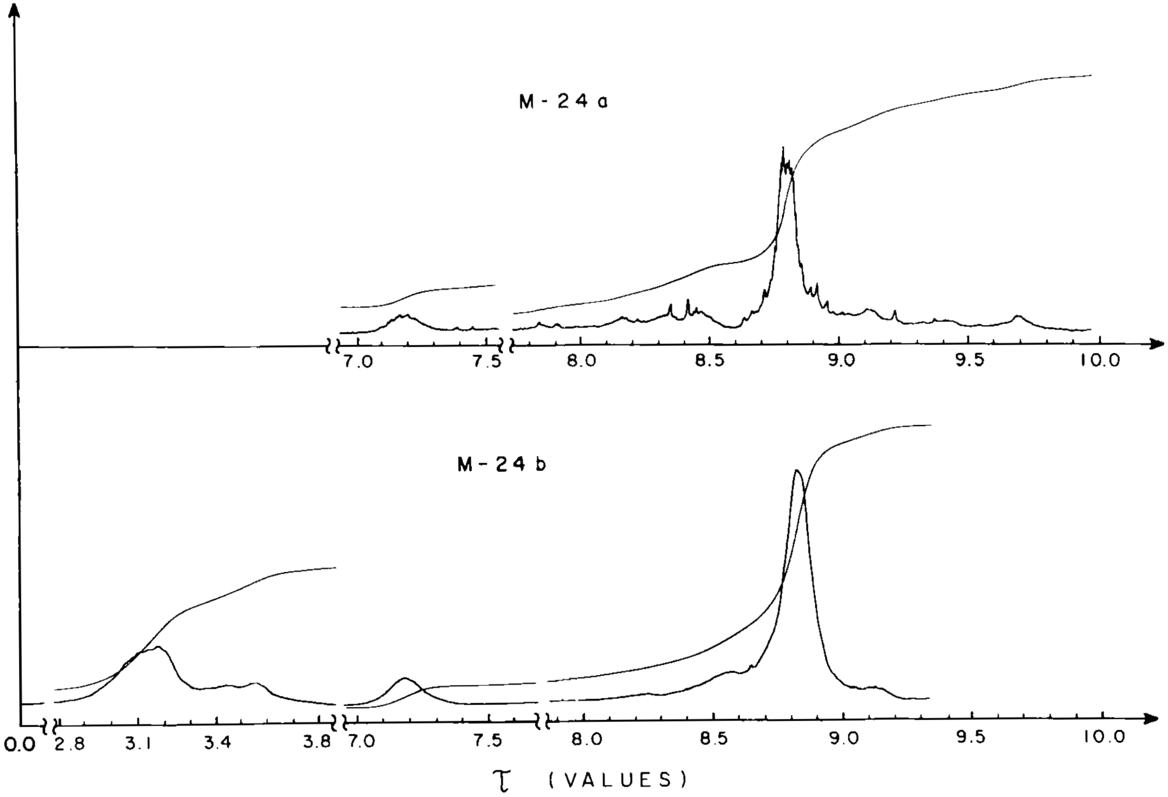
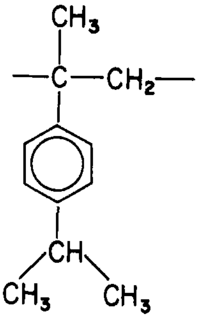


FIG. 7. 220 MHz resonance spectra of low molecular weight poly-p-isopropyl-α-methylstyrene: (a) 100°C; (b) -50°C in carbon disulfide.

TABLE 2. Values of Proton-Proton Ratios obtained from NMR Spectra for Poly-p-isopropyl-α-methylstyrene

	Ratio	Regular	F-4	S-25	M-23	M-24
1	iso-CH_3/H_B	1.5	1.7	1.5	1.6	-
2	iso-$CH_3/\alpha CH_3$	2	1.6	1.6	1.6	-
3	iso-$CH_3/\beta CH_2$	3	2.5	2.4	2.4	-
4	iso-CH_3/CH	6	6	5.8	6	-
5	$H_B/\alpha CH_3$	1.3	0.9	1.0	1.0	-
6	$H_B/\beta CH_2$	2	1.4	1.5	1.5	2.1
7	H_B/CH	4	3.5	3.8	3.8	5.7
8	$\alpha CH_3/\beta CH_2$	1.5	1.6	1.5	1.5	-
9	$\alpha CH_3/CH$	3	3.8	3.6	3.8	-
10	$\beta CH_2/CH$	2	2.4	2.4	2.5	2.7

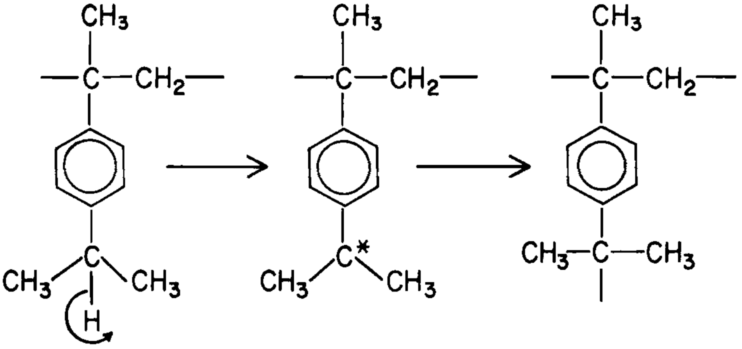


I

various hypothetical structures, estimate qualitatively the variation in the ratios related to the newly formed structure and see how this variation compares with the experimentally observed ratios obtained from Figs. 5-7 and shown in Table 2. Two main types of reactions may be retained for consideration: (a) chain transfer and (b) isomerization.

Chain Transfer

The removal of a hydrogen atom may occur at various places within the polymer chain; an active center is then formed and a chain reaction initiated. This situation is illustrated below where the methine proton is removed from the isopropyl group, thus leading to the formation of structure II.



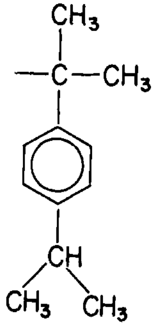
II

The asterisk on the carbon atom deprived of its proton denotes an active center which may be a carbanion, a carbenium ion, or a radical if all possible events are to be considered. This reaction could lead to formation of a side chain, and some of the proton/proton ratios would be altered thereby with respect to the regular structure. The number of methine protons and methyl protons of the isopropyl group decreases and if it is assumed that both methyl groups are equivalent to the α-methyl group, the number of α-methyl protons increases. The variation in the ratios is shown in Table 3, where a plus sign indicates an increase; a minus sign, a decrease; an equality sign, no change. A double sign indicates that both proton numbers of a given ratio vary in the same direction. An approximation sign indicates that both changes tend to cancel out. The removed hydrogen atom (or ion) may be transferred to a monomer and thus a new chain would be initiated, or it may react with an active center and in this case a chain would be terminated. In both cases, a chain is ended with a structure A or B. In order to account for the structures A or B resulting from each transfer reaction, one has to sum up the contributions of II and A or II and B, and these results are presented in Table 3 under headings IIA and IIB.

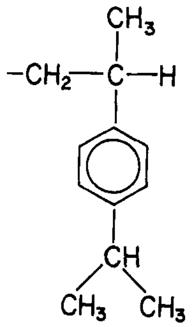
If a proton is removed from a methyl group of the isopropyl group, structure III would be formed. Assuming that the $-CH_3$ and $-CH_2-$ groups, from which the side chain originates, are equivalent to iso CH_3 and βCH_2 and that the methine remains unchanged, the variations in the ratios are those given in column III together with the combinations

TABLE 3. Comparison between Proton-Proton Ratios of Normal and Irregular Structures of Poly-p-isopropyl-α-methylstyrene

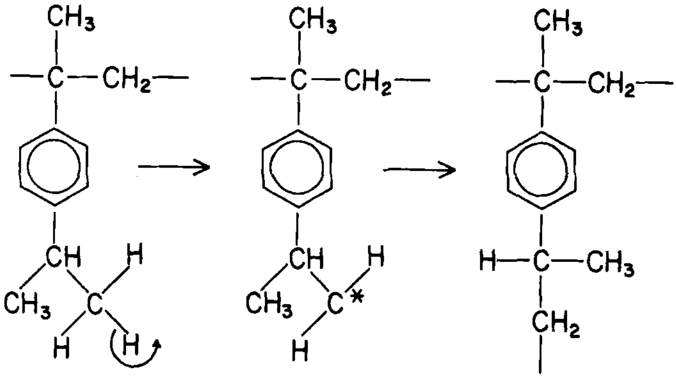
	Ratio	I	II	IIA and VI	IIB	III	IIIA and VII	IIIB and VIII, IX	IV	IVA	IVB	V	VA	VB
1	iso-CH_3/H_B	1.5	-	-	≃	-	-	≃	=	=	+	+	+	++
2	iso-$CH_3/\alpha CH_3$	2	--	--	≃	-	--	+	+	≃	++	=	-	++
3	iso-$CH_3/\beta CH_2$	3	-	≃	≃	--	-	-	-	≃	≃	=	+	+
4	iso-CH_3/CH	6	≃	≃	-	-	-	-	=	=	-	=	=	-
5	$H_B/\alpha CH_3$	1.3	-	--	≃	=	-	+	+	≃	++	-	--	≃
6	$H_B/\beta CH_2$	2	=	+	=	-	≃	-	-	≃	-	-	≃	-
7	H_B/CH	4	+	+	≃	=	=	-	=	=	-	-	-	--
8	$\alpha CH_3/\beta CH_2$	1.5	+	++	≃	-	+	--	--	≃	--	=	++	--
9	$\alpha CH_3/CH$	3	++	++	≃	=	+	--	-	≃	--	=	+	--
10	$\beta CH_2/CH$	2	+	≃	≃	+	≃	≃	+	≃	≃	=	-	-



Structure A



Structure B



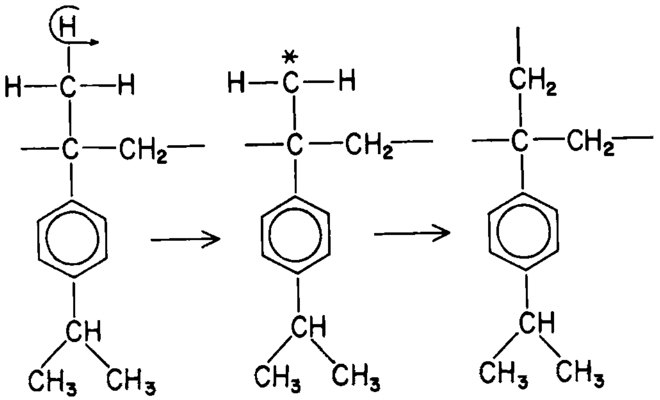
III

IIIA and IIIB. If on the other hand, the removal of one proton from the α-methyl is considered, this leads to structure IV where it is assumed that the CH_2 formed is equivalent to β methylene protons.

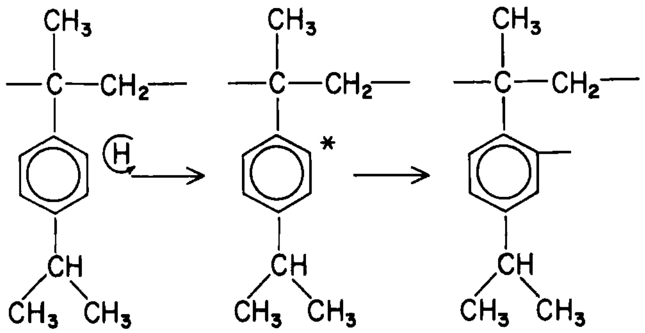
The removal of a benzene proton results in the formation of structure V, and the variations in the ratios as given in Table 3 under V, VA, and VB.

Isomerization

Structures different from the ones mentioned above may result from isomerization reactions and variations in the proton/proton ratios due to these reactions are evaluated in the manner described above. Isomerization takes place within the monomer unit bearing



IV

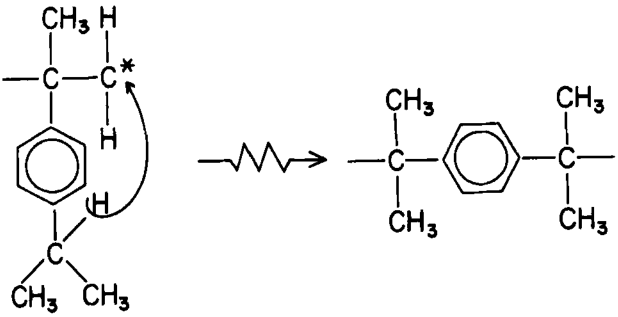


V

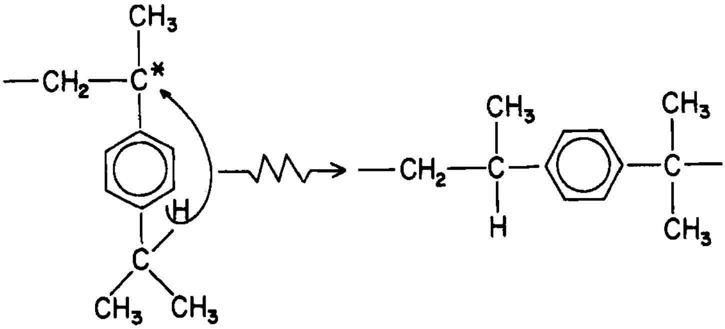
the active center. Because the ultimate unit bearing this active center is linked to the chain in head-to-head or head-to-tail fashion, every isomerization reaction may generate two different structural units.

Taking into consideration only the reactions that yield structures different from the above, various isomerization steps yielding structures VI to IX are discussed in the following paragraphs.

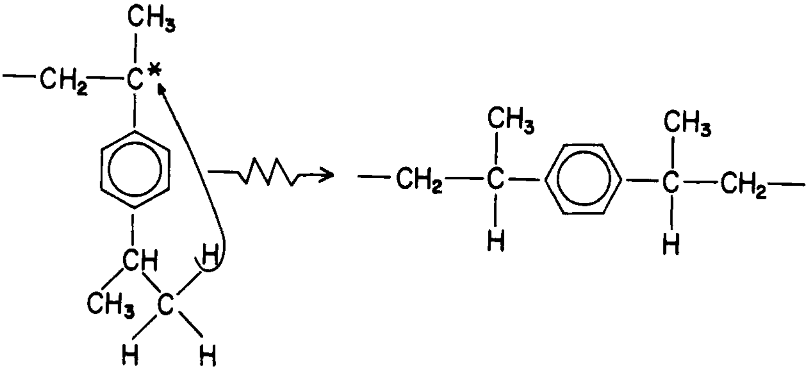
The results given in Table 3 are obtained by assuming that the methyl protons of a CH-CH_3 sequence are equivalent to iso-CH_3, all other methyl protons being equivalent to αCH_3. In accordance with this assumption, it is found that formation of structures VI, VII, VIII, and IX would cause variations in the ratios similar to the ones obtained for IIA, IIIA, and IIIB respectively. Ratio variations for



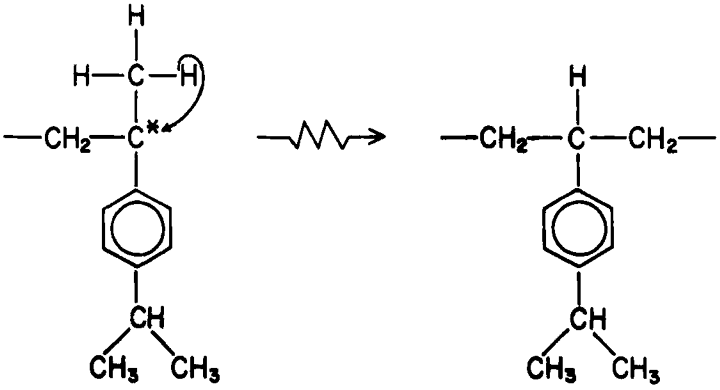
VI



VII



VIII



IX

structures VI to IX are those obtained for an hypothetical polymerization where isomerization only would take place as a side reaction.

From Table 2 it may be noted that ratios 2 (iso-CH_3/αCH_3) and 3 (iso-CH_3/βCH_2) both decrease, whereas ratios 9 (αCH_3/CH) and 10 (βCH_2 /CH) both increase. This result is a strong indication of proton abstraction from some of the methines of the isopropyl groups. In that event, the methyls of these isopropyl groups lose their characteristic and become equivalent to gem dimethyls. Then ratio 4 (iso-CH_3/CH) should remain approximately constant, which is verified experimentally (see Table 2). From Table 3 it can be seen that these five results can satisfy simultaneously only structure II on a qualitative basis. If this structure alone is present together with the regular structure, results for the five other ratios should agree which is not the case. All the four ratios involving the benzene protons show a lack of these protons. This shortage may come from an artefact in the spectra or from a side reaction. In the latter case the results would be in agreement with structure V, which represents substitution of a proton of the benzene ring. As the results for samples F-4, S-25, and M-23 are similar, the same consideration can be applied to the three cases.

The overall result of this analysis indicates the presence of irregular structures in the high molecular weight polymer obtained through anionic as well as cationic polymerization. The resulting structure of the polymer seems to be a combination of structures I, II and V. The decrease of the methine protons may be related to the formation of structure II. The decrease in the number of benzene protons (structure V) may be explained in various ways. In the case of the anionic polymerization with the butyllithium-TMEDA complex, metallation of the benzene ring is possible. In the case of cationic polymerization an intramolecular chain transfer mechanism which would bring about a decrease in the number of benzene protons has been suggested [6]. However these reactions alone would not fit the observed ratios listed in Table 2. Polymerizations of substituted α-methylstyrene seem to lead to polymers with irregular structures. Anionic polymerization of p-methyl-α-methylstyrene initiated with a sodium-potassium alloy has been reported to yield polymer with a structure equivalent to structure VII [15]. On the basis of this analysis all other structures can be rejected independently of the fact that some can be ruled out on the ground of energetic and thermodynamic arguments.

In the case of the low molecular weight polymer sample M-24, as has been mentioned earlier in the text, the abnormalities observed with this polymer might have their origin from isomerization or any other reaction leading to the same spectra because of its initiation with $AlCl_3$. The 220 MHz NMR spectra as recorded at 100°C as well as -50°C are shown in Fig. 7. At 100°C (M-24a), because of overlapping around a τ value of 9.0, it is impossible to separate the contributions of α-methyl protons from those of isomethyl protons. Figure 7 also shows that operating at -50°C (M-24b) did not improve the spectrum, thus making a precise measurement of proton/proton ratios impossible. The overlapping may be due to the fact that in some structures the protons of the methyl group are not equivalent to the protons of the regular structure as mentioned above. However from the partial results listed in Table 2, large values of the ratios H_B/CH and $\beta CH_2/CH$, for a normal $H_B/\beta CH_2$ ratio clearly indicate a decrease in the proportion of methine protons of the isopropyl group.

Infrared Spectra

Figure 8 shows the infrared spectrum of a polymer sample prepared with the BuLi-TMEDA complex. Except for the relative intensities of some absorption bands, all infrared spectra are similar, irrespective of the solvent and the initiator used for polymerization.

Infrared spectroscopy is often employed in order to elucidate the mechanism of reactions which yield polymers with irregular structures. This can be done by considering the relative number of protons or functional groups as an indication of the manner in which any initiator affects the structure of the chain during the process of polymer growth. As mentioned above, several possible irregular chain structures (II to IX) resulting from various assumed side reactions can be considered along with the regular structure I. Keeping in view these possible structures, except for case VI, there

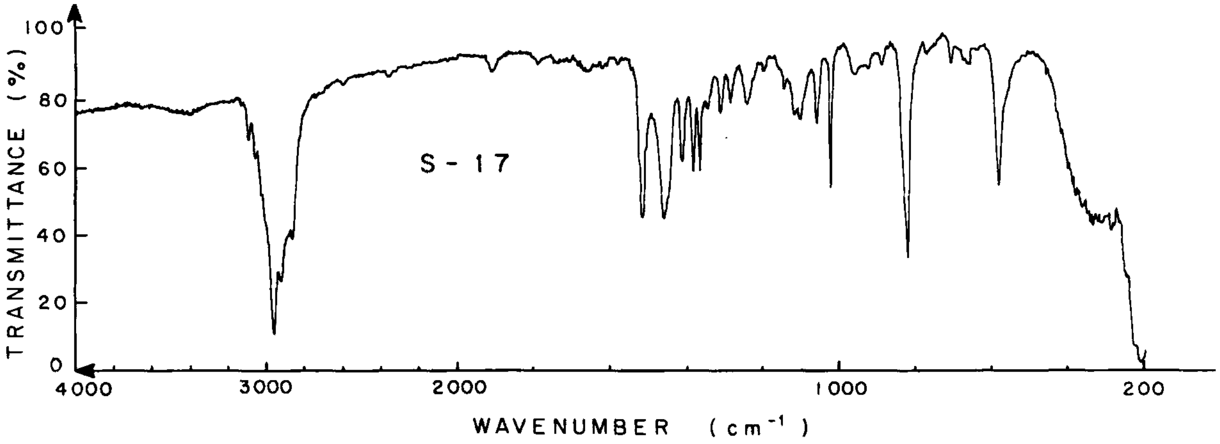


FIG. 8. IR spectrum of poly-p-isopropyl-α-methylstyrene prepared in bulk with BuLi-TMEDA complex as initiator.

does not seem to be any way in which the number of methyl groups can be larger than for the regular polymer. However there is always a possibility of their decrease due to chain transfer, isomerization or branching. The number of methylene groups should be constant or increase (except for case VI) because if methyl groups are involved in any transfer reaction they should be converted to methylene or methine. By the same token, a decrease in the number of methine protons is possible only in cases II and VI. If the ratio of aromatic over methyl, methylene or methine protons is low, this would mean that there is a strong possibility of substitution in the benzene ring.

It has been proposed [3] that the ratio of aromatic CH vibrations, D_{3100} (3100 cm^{-1}), to those of methyl, D_{2960}, and methylene groups, D_{2860}, can be used for a qualitative estimate of the relative abundance of the different protons. Except for the gel, the ratio D_{3100}/D_{2960} ranges from 0.06 to 0.11 in all cases listed in Table 4, and it is impossible to find any trend that could be related to any specific

TABLE 4. IR Intensity Ratios Measured at Various Wavenumbers for Poly-p-isopropyl-α-methylstyrene

	Intensity ratio	
Sample	D_{3100}/D_{2960}	D_{3100}/D_{2860}
A	0.086	0.20
B	0.11	0.26
C	0.093	0.23
D	0.078	0.24
E	0.11	0.25
S-3	0.06	0.19
S-20	0.057	0.18
S-17	0.078	0.21
S-25	0.077	0.21
M-24	0.07	0.18
M-27	0.058	0.15
M-20	0.076	0.21
M-23	0.11	0.28
Gel	0.21	0.28

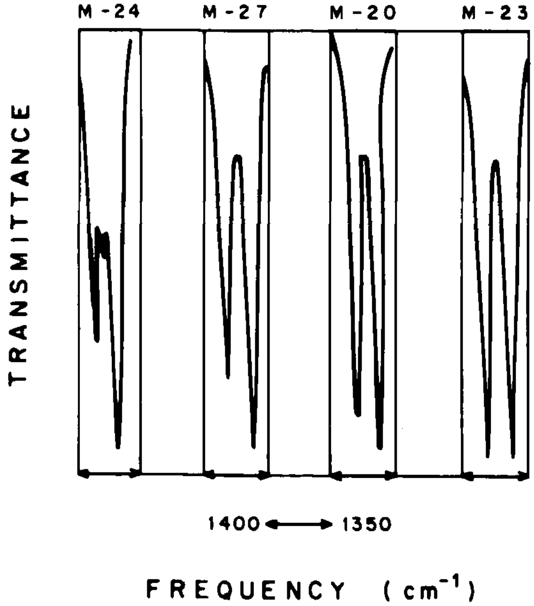


FIG. 9. Comparison of IR peak intensities measured at 1360 and 1380 cm^{-1} for poly-p-isopropyl-α-methylstyrene prepared through cationic polymerization.

type of polymerization. As for the gel, the ratio is 0.22; this would indicate that branching occurs through a methyl group, and a decrease in the ratio D_{3100}/D_{2860} is expected. However, this is not verified since the latter ratio is equal to 0.28 for all other polymers.

The infrared study may be complemented through examination of the bands at 1360 cm^{-1} and 1380 cm^{-1}. In a regular polymer where there is no isomerization, the isopropyl group gives a doublet at 1360 cm^{-1} and 1380 cm^{-1}; of the two peaks, the latter is the stronger one, indicating the predominance of isopropyl group over the geminal dimethyls [4]. However, in Fig. 9 it is observed that with cationic initiators the peak at 1360 cm^{-1} is more intense, indicating the possibility of occurrence of isomerization, or any other reaction leading to the same result. Furthermore it appears that as the average molecular weights of these samples increase, so does the intensity of the peak at 1380 cm^{-1}. The low molecular weight polymers have more of the irregular species than the high molecular weight ones, which may suggest that, either, in the IR spectra of the high molecular weight polymer the end-group effects cannot be detected or that the isomerization is more extensive at the early stages of the polymerization than at any other time.

CONCLUSIONS

A combined use of GPC, NMR, and IR analyses of the products obtained in the polymerization of p-isopropyl-α-methylstyrene with cationic as well as anionic initiators reveals the presence of important side reactions in this polymerization. NMR spectra show that irregular structures come from the isopropyl group, most likely from the methine proton. It appears also that reactions on the benzene ring take place and contribute to anomalous structures.

This can explain the fact that the experimental results do not fit a single model perfectly. The presence of gel in a certain number of polymerizations indicates that during polymerization chain branching takes place which eventually leads to crosslinking and yield anomolous structure.

GPC results show that low molecular weight polymers prepared with BuLi-TMEDA complex have low polydispersity index whereas in the cationic polymerization with $(C_6H_5)C^+PF_6^-$ the polymers have high polydispersity ratio. The IR analysis reveals that the low molecular weight polymers have more of the irregular species than the high molecular weight ones.

ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support from the National Research Council of Canada. S. L. M. wishes to thank the Université Laval for financial assistance.

This work has been carried out as part of the general research program of the Groupe de Recherche en Sciences Macromoléculaires at this university.

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Accepted by editor June 4, 1977
Received for publication June 24, 1977