

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Anionic Polymerization of α -Methylstyrene. IX. Nature of the Propagating Species

S. L. Malhotra^{ab}

^a D partement de g nie chimique Facult  des sciences et de genie, Universit  Laval Qu bec, Qu bec, Canada ^b Xerox Research Centre of Canada, 2480 Dunwin Drive, Mississauga, Ontario, Canada

To cite this Article Malhotra, S. L.(1981) 'Anionic Polymerization of α -Methylstyrene. IX. Nature of the Propagating Species', *Journal of Macromolecular Science, Part A*, 15: 4, 533 – 552

To link to this Article: DOI: 10.1080/00222338108056748

URL: <http://dx.doi.org/10.1080/00222338108056748>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Anionic Polymerization of α -Methylstyrene. IX. Nature of the Propagating Species

S. L. MALHOTRA*

Département de génie chimique
Faculté des sciences et de génie
Université Laval
Québec, Québec, G1K 7P4 Canada

ABSTRACT

The nature of the initiating and propagating species involved in the anionic polymerization of α -methylstyrene has been explored. The earlier hypothesis that multimodal GPC molecular weight distributions in polymers arise solely out of different reaction steps or different ion-pair mechanisms being involved has been modified for poly- α -methylstyrene. Multimodal GPC molecular weight distributions in poly- α -methylstyrene initiated with potassium at 25°C and polymerized at 25°C or higher in THF, p-dioxane, or cyclohexane as solvents have been ascribed to the presence of two different types of tetramers which grow simultaneously but at different rates, each responding to its own well-defined thermodynamic equilibrium and yielding dormant and living polymers. Reaction schemes describing the initiation (at 25°C) and propagation reactions (between -25 and 60°C) in the polymerization (in solution of THF as well as in bulk) of α -methylstyrene initiated with potassium-naphthalene, butyl-lithium, and butyllithium-tetramethylethylenediamine (TMEDA) have been presented. The role of coordinating agents naphthalene and TMEDA in changing irreversible propagations into reversible ones has been emphasized.

*Present address: Xerox Research Centre of Canada, 2480 Dunwin Drive, Mississauga, Ontario, L5L 1J9 Canada

INTRODUCTION

Studies on the anionic polymerization of α -methylstyrene have been reported earlier [1-9]. The gel permeation chromatographic (GPC) analyses of all those poly- α -methylstyrene samples which were initiated with potassium and potassium naphthalene in tetrahydrofuran (THF) [2, 3], p-dioxane [4], and cyclohexane [5] showed that irrespective of the solvent used, the polymers prepared at high temperatures ($> 25^\circ\text{C}$) and with high initial living end concentration $[\text{LE}]_0$ yielded multimodal molecular weight distributions made up of components having average degree of polymerization, $\overline{\text{DP}}$, ranging from 4 to 1000 and sometimes even greater than that. These molecular weight distributions were split into four components, viz., D, A, B, and C where D denoted a dead polymer, A the dormant polymer, and B and C denoted polymers due to different ion-pair mechanisms. Similar assignments have also been reported in the anionic polymerization of methyl methacrylate [10, 11] and styrene [12], as well as in the cationic polymerization of styrene [13-16] and α -methylstyrene [17] where bimodal GPC molecular weight distributions were observed.

Nuclear magnetic resonance studies [6, 7] on poly- α -methylstyrene prepared with anionic initiators [1-5] at high temperatures ($> 25^\circ\text{C}$) and having multimodal GPC molecular weight distributions built up of components, D + A (low molecular weight) and B + C (high molecular weight) showed that methylene and methyl protons associated with each of these two components appear at different τ values. The triad and tetrad analyses from the respective methyl and methylene protons of components D + A and B + C showed that their propagation follows Bernoullian statistics, the P_m value being in the range of 0.34 to 0.45 for the former and 0.26 for the latter component. The NMR analyses of poly- α -methylstyrene prepared at lower temperatures (5 to 25°C) [1-4] and having unimodal GPC distributions also showed the presence of component D + A whose propagation followed Bernoullian statistics but with a lower (0.25 to 0.35) P_m value. On further lowering the temperature of polymerization to -25 and -78°C [2, 3], the propagation statistics of component D + A changed from Bernoullian to first-order Markov. The propagation statistics of component B + C, on the other hand, were always Bernoullian with a P_m value of 0.26. On the basis of these observations it was concluded that different reaction steps were responsible for the formation of components D + A and B + C.

NMR studies of bimodal polymethyl methacrylate [11] samples initiated with the dianion of oligomeric α -methylstyrene showed that the isotactic, heterotactic, and syndiotactic triads of the low ($\overline{\text{DP}} = 190$) and high ($\overline{\text{DP}} = 670$) molecular weight fractions of the polymer appear at the same τ values. However, while the propagation statistics for the high molecular weight fraction obeyed Bernoullian

statistics with $P_m = 0.22$ ($mm = 0.05$, $mr = 0.33$, and $rr = 0.62$), the propagation statistics for the lower molecular weight fraction were non-Bernoullian ($mm = 0.29$, $mr = 0.43$, and $rr = 0.28$) with $P_{m/r} = 0.43$ and $P_{r/m} = 0.43$. These results led Warzelhan and Schulz [11] to indicate that two active species added the monomer stereospecifically in a different way.

^{13}C NMR studies of bimodal polystyrene [13] prepared with acetyl perchlorate showed that the low molecular weight fraction ($\bar{M} = 1.4 \times 10^3$) had 56% whereas the high molecular weight fraction ($\bar{M} = 2.3 \times 10^4$) had 62% racemic dyads associated with them respectively. These observations led Higashimura et al. [13] to propose the co-existence of two kinds of propagating species: 1) a loose ion-pair and/or a free ion which produced the high molecular weight polymer, and 2) a nondissociated species that yielded low molecular weight products.

Based on these earlier studies [1-17], one would be tempted to conclude that multimodal GPC molecular weight distributions in polymers arise primarily due to different ion-pairs being involved in the propagation reaction. This, however, may only be partly true, because it has not been clearly established whether these are different ion-pairs or different reaction steps which are responsible for adding the monomer stereospecifically in different ways. The concept of different reaction steps rather than ion-pairs being responsible for different stereospecificity of low and high molecular weight fractions of the bimodal polymer arises from the NMR analyses of poly- α -methylstyrene (prepared with potassium in THF [6] in three temperature ranges of a) $> 25^\circ\text{C}$, b) 25 to -25°C , and c) -25 to -78°C where contact ion-pairs, solvent separated ion-pairs, and free-ions, respectively, dominate [18]) which showed that the propagation reactions leading to the formation of high molecular weight component B + C always obeyed Bernoullian statistics with $P_m = 0.26$, irrespective of the nature of the ion-pair involved.

If one retains the possibility that more than one reaction step is involved in producing bimodal polymers whose two fractions have different tacticities, the next step is to determine the possible nature of these reaction steps. According to Korotkov et al. [19-22], in the sodium-naphthalene initiated polymerization of α -methylstyrene the propagation step is carried out by a "coordinate catalytic" mechanism [20-22] along with the stepwise mechanism. These could be the two reaction steps which yield low and high molecular weight polymers with different tacticities.

There is yet another possibility that the low and the high molecular weight components in poly- α -methylstyrene are derivatives of two different tetramers which do not grow at the same rates. According to Szwarc [23] and Vrancken et al. [24], a living tetramer may be prepared by the addition of the required amount of α -methylstyrene to living α -methylstyrene dimer in the presence of potassium or sodium-potassium alloy in THF. This tetramer is in equilibrium with the respective trimer and dimer.

On the other hand, relatively brief contact of a dilute THF solution of α -methylstyrene with metallic sodium gives an isomeric living tetramer [24, 25]. The structure of the two tetramers is not the same.

It is quite possible that the two tetramers always exist in solution whether the initiation is carried out with sodium or potassium or both. Keeping in mind the results of these earlier studies [1-25], it was thought of interest to reinvestigate the nature of the propagation species in the ionic polymerization of α -methylstyrene. A commercially available sample of poly- α -methylstyrene prepared via thermal polymerization and carrying oligomers as well as high molecular weight fractions has been examined by GPC and NMR. The data thus obtained as well as the earlier results [1-25] are put together and compared with a few others reported in the literature [26-40]. Based on the conclusions derived from their comparison, reaction schemes describing the initiation and propagation in the anionic polymerization of α -methylstyrene have been presented. The principal results of these studies form the subject of the present communication.

EXPERIMENTAL

Materials

Poly- α -methylstyrene (P α MeS-685, P α MeS-960 Aldrich Chemical Co.) samples were used as received. Polystyrene standards (PS) (Pressure Chemical Co.) were also used as received.

NMR Analyses

Nuclear magnetic resonance spectra of PS samples were recorded with a 220-MHz Varian Associates spectrometer at 75°C in CCl₄ whereas those of P α MeS were observed at 100°C in *o*-C₆H₄Cl₂. Tetramethylsilane was used in both cases as the internal standard.

IR Analyses

IR spectra of the polymers were recorded on KBr pellets as well as from thin films with a Perkin-Elmer model 520 grating spectrometer.

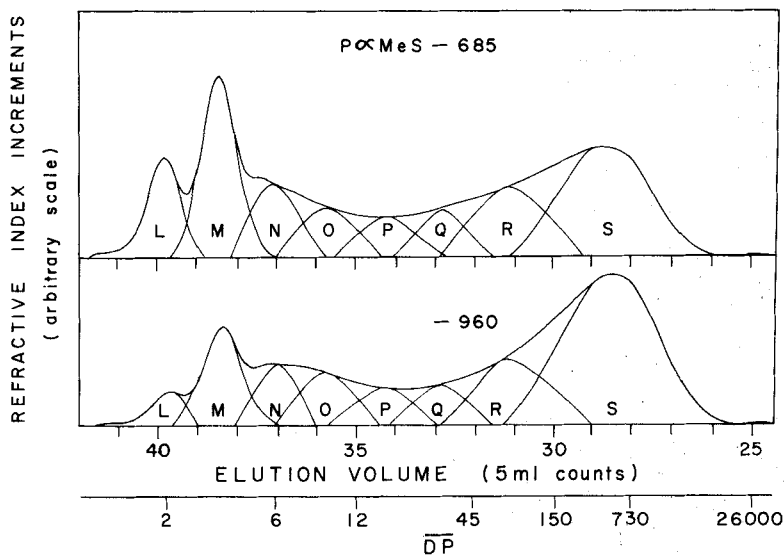


FIG. 1. GPC molecular weight distributions of poly- α -methylstyrene samples P α MeS-685 and P α MeS-960.

RESULTS AND DISCUSSION

Analysis of Commercial Poly- α -methylstyrene with Broad Molecular Weight Distribution

In Fig. 1 are shown the GPC molecular weight distribution curves of P α MeS-685 and P α MeS-960 samples. The component analysis of these curves is presented in Table 1 which lists their \overline{M}_w , \overline{M}_n , $\overline{M}_w/\overline{M}_n$, and % proportions. The principal difference in the composition of the two polymers lies in the proportion of components L, M, N and S in them whose respective proportions are 9.8, 18.8, 9.6, and 29.4% in P α MeS-685 and 3.1, 11.8, 7.1, and 44.5% in P α MeS-960. The % proportion of components O, P, Q and R in the two polymers is more or less the same. Based on the % proportion and \overline{M}_n values of each of the components in the two polymers, their overall \overline{M}_w and \overline{M}_n were as follows: P α MeS-685 ($\overline{M}_n = 9.35 \times 10^2$, $\overline{M}_w = 2.46 \times 10^4$) and P α MeS-960 ($\overline{M}_n = 1.6 \times 10^3$, $\overline{M}_w = 3.6 \times 10^4$).

In Fig. 2 are shown the IR spectra of P α MeS-685 and P α MeS-960

TABLE 1. Molecular Weights and % Proportion of Various Components in P α MeS-685 and P α MeS-960 Samples

Components	\bar{M}_w (GPC) $\times 10^{-2}$	\bar{M}_n (GPC) $\times 10^{-2}$	\overline{DP}	% Proportion	
				P α MeS-685	P α MeS-960
L	2.75	2.75	2	9.8	3.1
M	4.45	4.35	4	18.8	11.8
N	7.10	6.90	6	9.6	7.1
O	11.25	10.85	9	7.3	8.0
P	17.80	16.95	14	5.7	5.8
Q	36.20	34.15	29	6.2	5.8
R	107.50	89.20	75	13.1	13.9
S	767.0	391.0	330	29.4	44.5

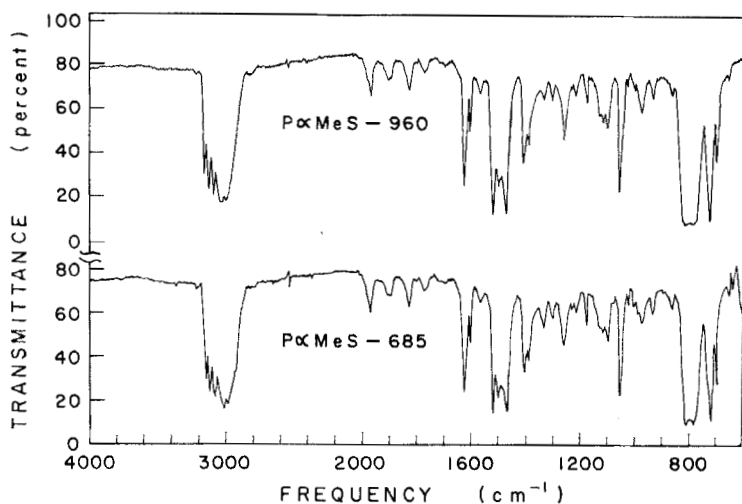


FIG. 2. IR spectra of P α MeS-685 and P α MeS-960.

samples. These spectra are identical, indicating that there is no structural difference between the two polymers.

In Fig. 3 are shown the 220 MHz NMR spectra of β -methylene and α -methyl protons of P α MeS-685 and P α MeS-960 observed in *o*-C₆H₄Cl₂ at 100°C in the range of 7.5 to 10.0 τ . These spectra resemble those

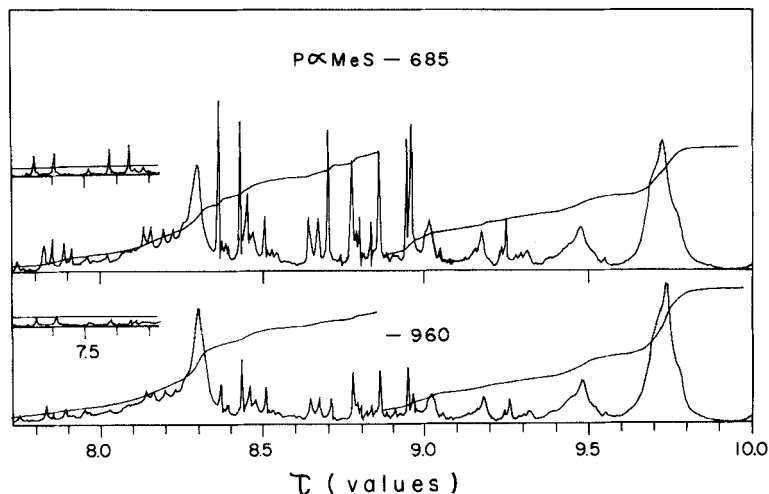


FIG. 3. 220 MHz NMR spectra of β -methylene and α -methyl protons of $P\alpha$ MeS-685 and $P\alpha$ MeS-960 observed in o - $C_6H_4Cl_2$ at $100^\circ C$ in the range of 7.5 to 10.0 τ .

reported earlier [6, 7] for anionic poly- α -methylstyrene samples carrying low molecular weight (D + A) and high molecular weight (B + C) fractions in them. The β -methylene protons of $P\alpha$ MeS-685 and $P\alpha$ MeS-960 are located between 7.3 to 8.5 τ whereas their α -methyl protons appear between 8.5 to 10.0 τ . Because of the presence of dimers and tetramers in $P\alpha$ MeS-685 and $P\alpha$ MeS-960 samples, there are more peaks between 8.3 and 9.0 τ than were present in the anionic poly- α -methylstyrene having bimodal GPC molecular weight distributions [6, 7].

In order to have a better idea of the placement of β -methylene and α -methyl protons associated with the dimers and tetramers of $P\alpha$ MeS-685 and $P\alpha$ MeS-960 samples, in Fig. 4 is shown a 220-MHz spectrum of $P\alpha$ MeS-685 observed in o - $C_6H_4Cl_2$ at $100^\circ C$ in the range of 8.3 to 9.0 τ . The highlights of this NMR spectrum along with those shown in Fig. 3 are summarized in Table 2. Assignments of τ values for CH_2 and CH_3 protons belonging to components (Q + R + S) are the same as those reported in the literature [7, 26, 29, 33, 35], and their NMR intensity (49%) calculated from the integral area agrees well with that (52%) given by GPC (Table 1). Assignments of τ values for CH_2 and CH_3 proton of components (N + O + P) are those listed in earlier publications from this laboratory for the low molecular weight component (D + A) of the multimodal anionic poly- α -methylstyrene [6, 7]. Assignments of τ values for CH_2 and CH_3 protons of components L and M are based exclusively on the availability of a reasonable match between their GPC and NMR intensities. Based on the results in

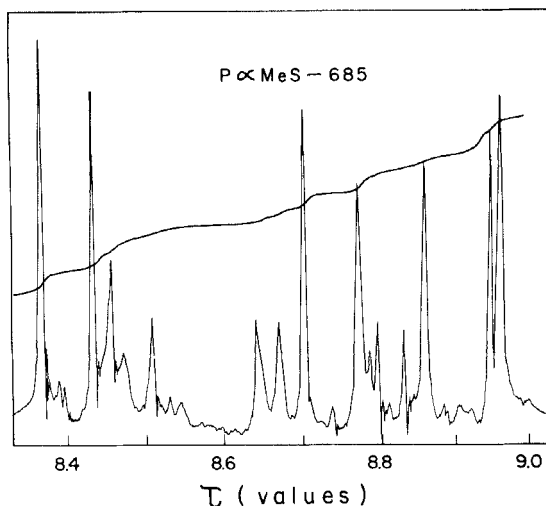


FIG. 4. 220 MHz NMR spectra of β -methylene and α -methyl protons associated with the oligomers (dimers and tetramers) of P α MeS-685 observed in o -C₆H₄Cl₂ at 100°C in the range of 8.3 to 9.0 τ .

Table 2 it would appear that as the molecular weight of a component increases, its β -methylene and α -methyl protons follow an ascending order of magnetic field. In earlier publications [6, 7] it was shown that the downfield magnetic shift of certain protons of the lower molecular weight fraction in a polymer arises due to changes in the environment of these protons and not due to their low molecular weights. This would mean that even in the thermally initiated poly- α -methylstyrene samples P α MeS-685 and P α MeS-960, the low molecular weight polymers may have different structures than those of the high molecular weight counterparts.

Analysis of Polystyrene Standards

With a view to affirm that indeed the downfield displacement of protons is not a function of the molecular weight of a polymer, standard polystyrene samples of varying molecular weights were analyzed by NMR and IR. In Fig. 5 are shown 220 MHz NMR spectra of the benzene protons of four polystyrene standards with \bar{M}_w ranging from 600 to 10300, observed in CCl₄ at 75°C in the range of 2.5 to 4.0 τ . The NMR spectra of PS-10300, PS-4000, and PS-2030 are identical. In the NMR spectrum of PS-600, however, protons appearing at 3.5 τ have moved downfield, whereas those at 3.0 τ are not affected. It

TABLE 2. NMR Assignments for Various Protons Associated with Oligomers as well as High Molecular Weight Components in P α MeS-685 and P α MeS-960

Component	\overline{DP}	Type of the proton	τ values	Literature τ values
L	2	$\left\{ \begin{array}{l} \text{CH}_2 \\ \text{CH}_3 \end{array} \right.$	8.43: Singlet	8.56 [31]
			8.37, 8.46, 8.51: Triplet	8.87 [31]
M	4	$\left\{ \begin{array}{l} \text{CH}_2 \\ \text{CH}_3 \end{array} \right.$	8.64, 8.67, 8.70: Triplet	8.2 [31]
			8.770, 8.864, 8.961: Triplet	8.2 [31]
$\left\{ \begin{array}{l} \text{N} \\ \text{O} \end{array} \right.$	$\left\{ \begin{array}{l} 6 \\ 9 \end{array} \right.$	$\left\{ \begin{array}{l} \text{CH}_2 \\ \text{CH}_3 \end{array} \right.$	7.3 to 8.3: Broad multiplet	7.3 to 8.3 [6, 7]
			8.6 to 9.3: Broad multiplet	8.6 to 9.3 [6, 7]
$\left\{ \begin{array}{l} \text{Q} \\ \text{R} \end{array} \right.$	$\left\{ \begin{array}{l} 29 \\ 75 \end{array} \right.$	$\left\{ \begin{array}{l} \text{CH}_2 \\ \text{CH}_3 \end{array} \right.$	7.9 to 8.5: Broad multiplet	7.9 to 8.5 [7, 26, 29, 33]
			9.0 (mm), 9.43 (mr), 9.69 (rr) with P_m = 0.16: Triplet	9.0, 9.43, 9.69 [26, 29, 35]
S	330	CH ₃		

appears that only protons in a specific configuration (isotactic) move downfield.

In Fig. 6 are shown 220 MHz NMR spectra of the methine, methylene, and methyl protons of PS-10300, PS-4000, PS-2030, and PS-600 observed in CCl₄ in the range of 7.4 to 9.5 τ . The NMR spectra of PS-10300, PS-4000, and PS-2030 are identical with the exception that the protons corresponding to peaks at 8.9 and 9.2 τ increase with decreasing \overline{M}_w of the PS standard. In the NMR spectrum of PS-600 the proportion of protons corresponding to 8.9 and 9.2 τ is maximum. Furthermore, the methine as well as the methylene protons move downfield. Assigning the peaks at 8.9 and 9.2 τ to endgroup methyl protons and with the assumption that the total integral covering the aromatic region represents five protons, an analysis of PS standards with \overline{M}_w ranging from 51,000 to 600 was made and the results are

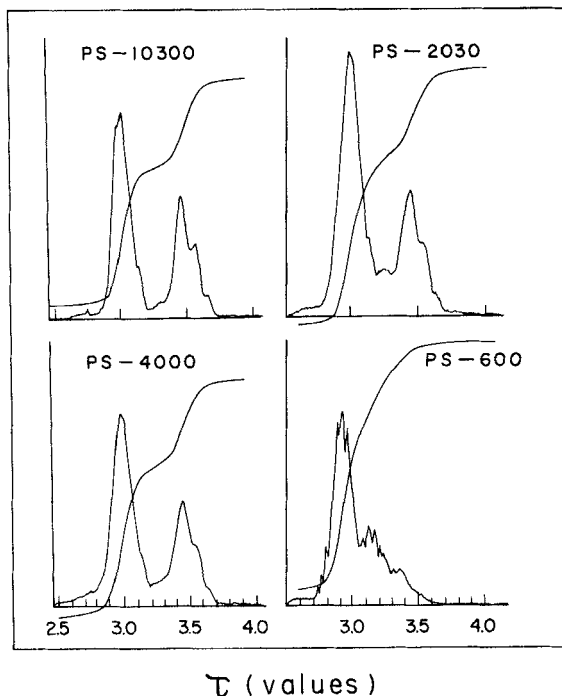


FIG. 5. 220 MHz NMR spectra of the benzene protons of four polystyrene standards with \bar{M}_w ranging from 600 to 10,300, observed in CCl_4 at 75°C in the range of 2.5 to 4.0 τ .

presented in Table 3. The visual analysis of Fig. 6 shows that in PS-600 only the methine and methylene protons which have specific environmental differences with the rest of the protons move downfield. The analysis of the results in Table 3 show that as the molecular weight of the PS standard decreases, the endgroup methyls become very significant.

In Fig. 7 are shown the IR spectra of polystyrene standards PS-10300, PS-2030, and PS-600. One notes that these spectra are identical, indicating that there are no major structural differences in the high and the low molecular weight PS standards.

Based on the analyses of Figs. 5, 6, and 7, it may be said that in PS standards of similar structures the observed downfield movement of some of the aromatic, methine, and methylene protons in PS-600 arise due to their different environment rather than to the low molecular weight of the polymer.

If one applies these conclusions to the NMR analyses of P α MeS-685

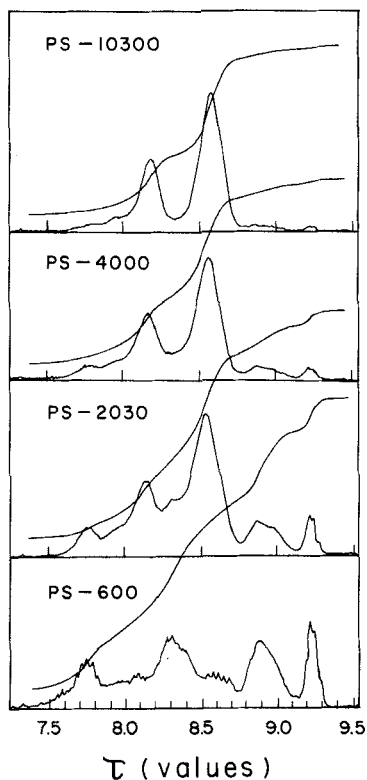


FIG. 6. 220 MHz NMR spectra of the methine, methylene, and methyl protons of four polystyrene standards with \overline{M}_w ranging from 600 to 10,300, observed in CCl_4 at 75°C in the range of 7.4 to 9.5 τ .

and P α MeS-960 samples, it would mean that the low molecular weight oligomers represented by the components L, M, N, O, and P differ in their structure or environment from those of high molecular weight polymers represented by components Q, R, and S.

The concept that two sets of protons (e.g., $-\text{CH}_3$) from the same parent polymer, one representing the low molecular weight fraction and the other the high molecular weight fraction, appearing at different τ values are the result of their having environmental or structural differences may be helpful in explaining the bimodal or even multimodal GPC molecular weight distributions observed in anionic poly- α -methylstyrene [1-7]. Retaining the possibility that these multimodal GPC molecular weight distributions may be the result of two different types of tetramers growing simultaneously but at different rates, each responding to its own individual thermodynamic equilibrium,

TABLE 3. NMR Proportions of Methine, Methylene, and Methyl Protons in Polystyrene Standards^a

Molecular weight, \bar{M}_w	Methine, 7.5-8.4 τ	Methylene, 8.4-8.7 τ	Methyl, 8.7-9.3 τ
51,000	1.07	2.00	-
19,800	1.13	1.83	0.17
10,300	1.10	1.87	0.24
4,000	1.33	1.77	0.33
2,030	1.39	1.67	0.70
600	1.74	1.60	1.78

^aThe analysis is based on the assumption that the total integral counts of the aromatic region correspond to five protons.

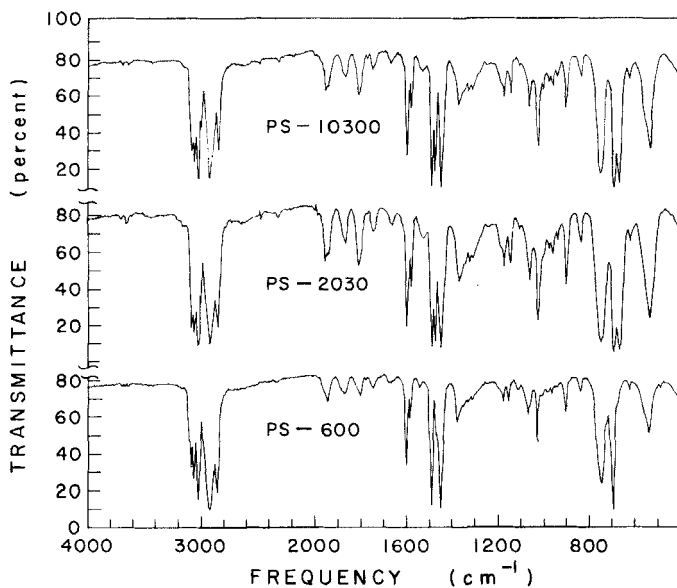
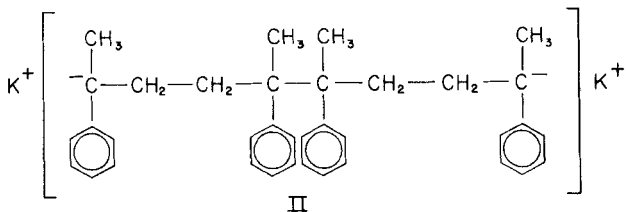
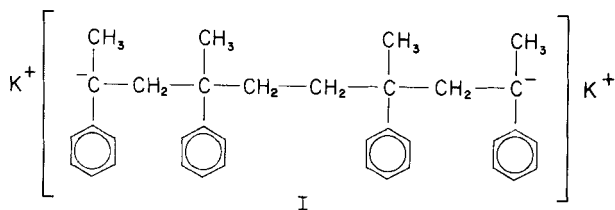


FIG. 7. IR spectra of polystyrene standards PS-10,300, PS-2030, and PS-600.

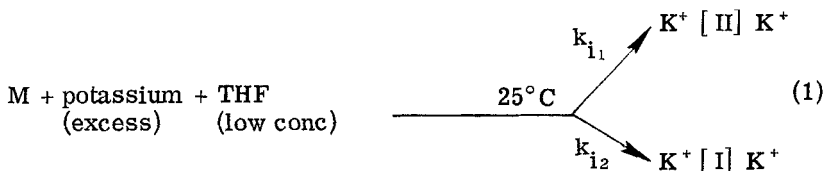
the results of earlier work on the anionic polymerization of α -methylstyrene [1-7] have been reinvestigated. The hypothesis that bimodal or multimodal GPC molecular weight distributions arise solely out of different reaction steps or different ion-pair mechanisms being involved has been modified.

It is proposed that the reaction of α -methylstyrene with excess potassium ($[LE]_0 > 10^{-2}$ mol/L) would yield the conventional tetramer (Structure I) [23, 24] as well as a living isomeric tetramer (Structure II) similar to the one formed during the reaction of sodium with α -methylstyrene [24, 25]. Both tetramers grow at different rates.

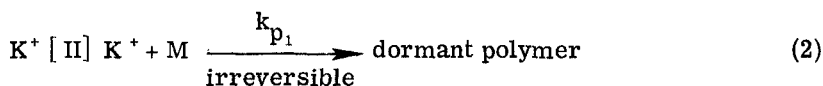


Reaction Scheme for the Initiation (at 25°C) and Propagation (at 25°C and Higher) of α -Methylstyrene with Potassium [2, 3, 6]

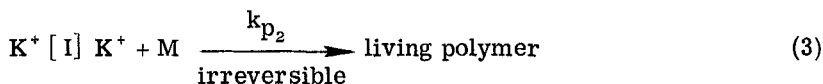
The reaction of α -methylstyrene (M) solution in THF with excess potassium at 25°C yields two initiating species:



where $[k_{i_1} \gg k_{i_2}]$



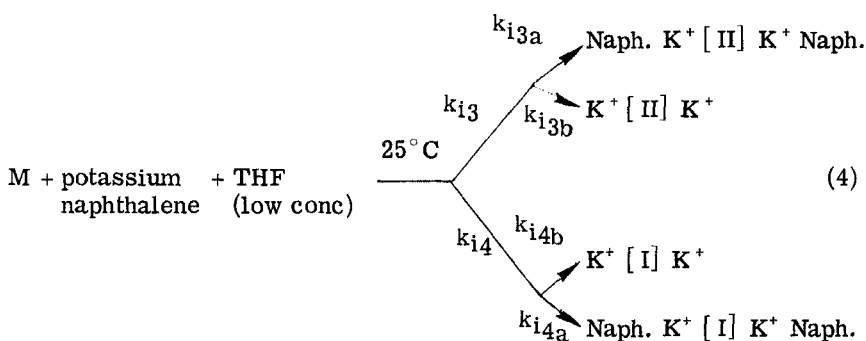
The propagation reaction in Eq. (2) follows Bernoullian statistics with $P_m > 0.35$.



The propagation reaction in Eq. (3) also follows Bernoullian statistics but with $P_m = 0.26$. The propagation constant k_{p_2} is equal to or greater than k_{p_1} . The $\text{K}^+ \text{C}^-$ ion-pair in structures $\text{K}^+ [\text{II}] \text{K}^+$ and $\text{K}^+ [\text{I}] \text{K}^+$ correspond to contact ion-pairs [18].

Reaction Scheme for the Initiation (at 25°C) and Propagation (at 25°C and Higher) of α -Methylstyrene with Potassium Naphthalene [3, 6]

The reaction of α -methylstyrene (M) solution in THF with excess potassium naphthalene at 25°C yields four initiating species:

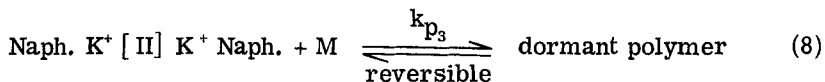


$$k_{i_3} = k_{i_{3a}} + k_{i_{3b}} \quad (\text{where } k_{i_{3a}} \gg k_{i_{3b}}) \quad (5)$$

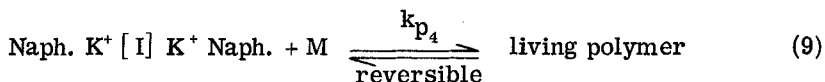
$$k_{i_4} = k_{i_{4a}} + k_{i_{4b}} \quad (\text{where } k_{i_{4a}} \gg k_{i_{4b}}) \quad (6)$$

and

$$k_{i3} \gg k_{i4} \quad (7)$$



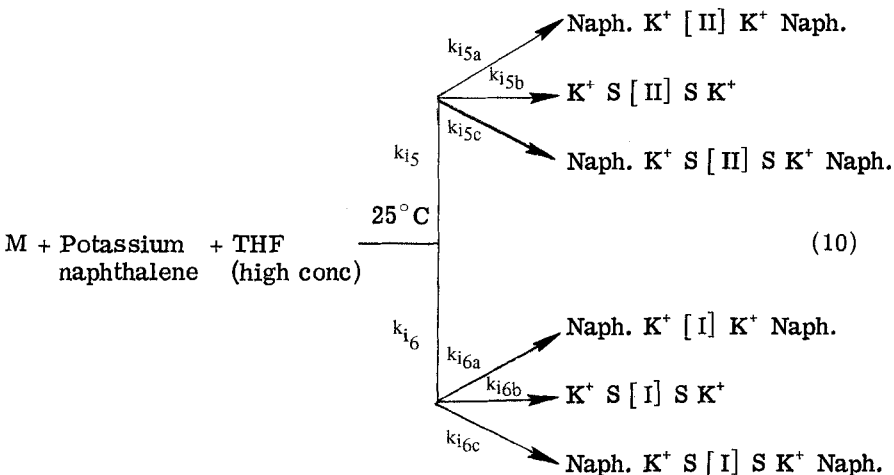
The propagation reaction in Eq. (8) follows Bernoullian statistics with $P_m = 0.30$.



The propagation reaction in Eq. (9) follows Bernoullian statistics with $P_m = 0.26$. The propagation constant k_{p4} is equal to or greater than k_{p3} . The $\text{Naph. K}^+ \text{ C}^-$ ion-pair in structures $\text{Naph. K}^+ [\text{II}] \text{ K}^+ \text{ Naph.}$ and $\text{Naph. K}^+ [\text{I}] \text{ K}^+ \text{ Naph.}$ correspond to naphthalene coordinated contact ion-pairs similar to those proposed by Korotkov et al. [19-22]. These yield reversible propagation.

Reaction Scheme for the Initiation (at 25°C) and Propagation ($\leq 25^\circ\text{C}$) of α -Methylstyrene (M) with Potassium Naphthalene or Anthracene [3, 6]

The reaction of α -methylstyrene (low concentration) solution in THF with excess potassium naphthalene yields six initiating species:

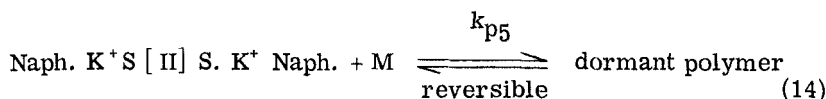


$$k_{i_5} = k_{i_{5a}} + k_{i_{5b}} + k_{i_{5c}} \quad (\text{where } k_{i_{5a}} \equiv k_{i_{5b}} \equiv k_{i_{5c}}) \quad (11)$$

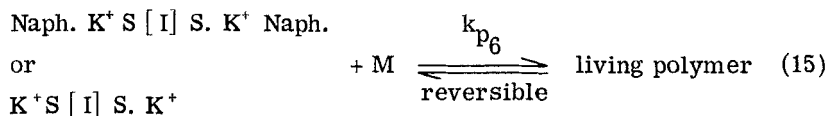
$$k_{i_6} = k_{i_{6a}} + k_{i_{6b}} + k_{i_{6c}} \quad (\text{where } k_{i_{6a}} \equiv k_{i_{6b}} \equiv k_{i_{6c}}) \quad (12)$$

and

$$k_{i_5} > k_{i_6} \quad (13)$$



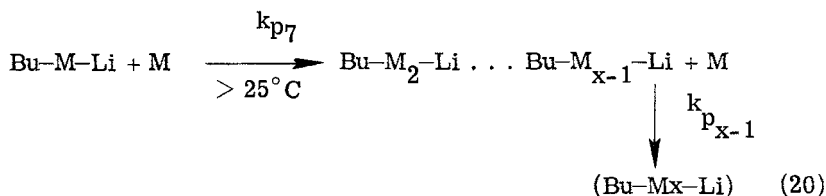
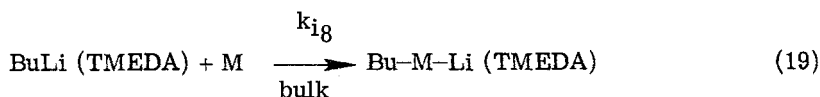
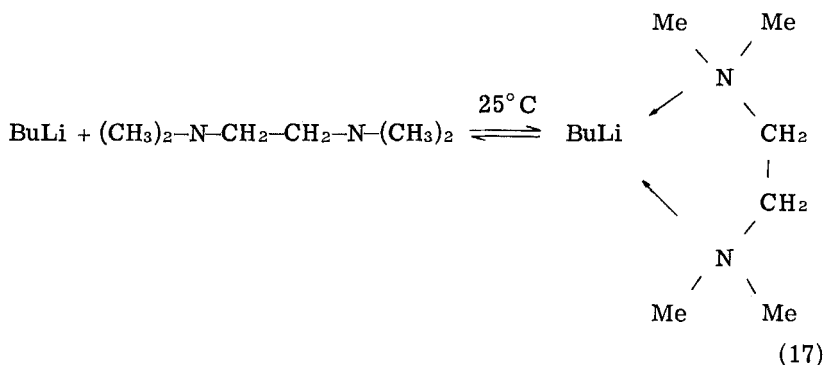
The propagation in Eq. (14) follows Markovian statistics with $P_{m/r} = 0.58$ and $P_{r/m} = 0.24$.



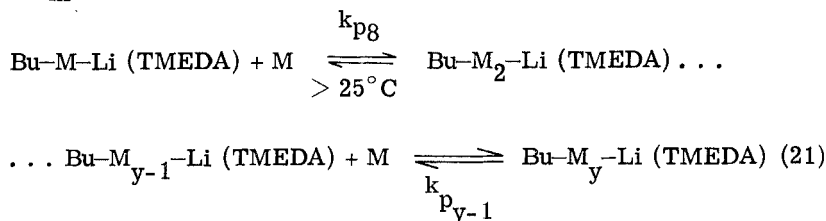
The propagation reaction in Eq. (15) follows Bernoullian statistics with $P_m = 0.26$. The propagation constant k_{p6} is equal to or greater than k_{p5} . The $\text{K}^+ \text{S}^- \text{C}^-$ ion-pair in structures $\text{K}^+ \text{S [I] S K}^+$ and $\text{K}^+ \text{S [II] S K}^+$ corresponds to the solvent separated ion-pairs [18], and $\text{Naph. K}^+ \text{S}^- \text{C}^-$ in $\text{Naph. K}^+ \text{S [I] S K}^+ \text{Naph.}$ and $\text{Naph. K}^+ \text{S [II] S K}^+ \text{Naph.}$ correspond to naphthalene coordinated solvent separated ion-pairs. These naphthalene coordinated $\text{Naph. K}^+ \text{ [II] K}^+ \text{Naph.}$ and solvent separated $\text{K}^+ \text{S [II] S K}^+$ ion-pairs yield reversible propagations and show identical behavior in initiation as well. However, it is believed that these differ in their structure and that is why naphthalene coordinated structures are not shown here as $\text{K}^+ \text{Naph. [II] Naph. K}^+$ which is identical in structure to $\text{K}^+ \text{S [II] S K}^+$. Reaction schemes for the polymerization of α -methylstyrene in THF at 25°C or higher are also applicable to other systems which use p-dioxane [4, 7] and cyclohexane [5, 7] as solvents.

Reaction Scheme for the Polymerization of α -Methylstyrene in Bulk Initiated with BuLi or BuLi-TMEDA at 25°C and Polymerized at Temperatures Higher than 25°C [6]





The propagation reaction in Eq. (20) follows Bernoullian statistics with $P_m = 0.30$.



The propagation reaction in Eq. (21) also follows Bernoullian statistics but with $P_m = 0.22$. Although the propagation of α -methylstyrene with BuLi alone yields irreversible propagation [41], the BuLi-TMEDA complexed polymerizations are reversible in nature.

The principal conclusions to be drawn from this study may be summarized as follows: The concept that two sets of protons (one

representing the low molecular weight and the other the high molecular weight fraction) from the same polymer appearing at different values may be the result of their having environmental or structural differences has been used to explain multimodal GPC molecular weight distributions in poly- α -methylstyrene. It has been postulated that multimodal GPC distributions in poly- α -methylstyrene initiated with potassium at 25°C and polymerized at 25°C or higher in THF [2, 3, 6], p-dioxane [1, 4, 7], and cyclohexane [5, 7] as solvents result from a combination of different reaction steps and different ion-pair mechanisms being involved. The reaction of α -methylstyrene with potassium at 25°C is thought to yield two different types of tetramers, viz., K^+ [I] K^+ (living polymer) and K^+ [II] K^+ (dormant polymer), which do not grow at the same rate. The $K^+ \cdots C \sim$ ion-pair in the two tetramers correspond to contact ion-pair structures [18]. Replacing potassium with potassium naphthalene as the initiator, naphthalene-coordinated [19-22] species, viz., Naph. K^+ [I] K^+ Naph. and Naph. K^+ [II] K^+ Naph., which yield reversible propagation are formed. In the presence of excess solvent and at low temperatures ($< 25^\circ C$), $K^+ S [I] S K^+$ and $K^+ S [II] S K^+$ species [18] are formed where $K^+ S \cdots C \sim$ ion-pair are solvent separated and yield reversible propagation. These solvent-separated species are not identical in structure to naphthalene-coordinated (Naph. K^+ [I] K^+ Naph. or Naph. K^+ [II] K^+ Naph.) species. Naphthalene-coordinated solvent-separated species, i.e., Naph. $K^+ S [I] S K^+$ Naph. and Naph. $K^+ S [II] S K^+$ Naph. are also present at low temperature polymerizations with potassium naphthalene as initiator and yield reversible propagation. Although the propagation of α -methylstyrene with BuLi alone yields irreversible propagation [41], the BuLi-TMEDA complex polymerizations are reversible in nature. This shows the effect of coordinating agents like naphthalene, anthracene, or TMEDA to convert irreversible propagations into reversible ones.

Further studies on the ^{13}C analyses of poly- α -methylstyrene samples prepared in THF, p-dioxane, and cyclohexane are in progress and will be reported in due course.

ACKNOWLEDGMENTS

The author gratefully acknowledges the financial assistance received from the Natural Sciences and Engineering Research Council of Canada, the Department of Education of the Government of Quebec, and Laval University. The work described in this paper forms part of the general research program by the Groupe de Recherches en Sciences Macromoléculaires at this University.

REFERENCES

- [1] J. Léonard and S. L. Malhotra, J. Polym. Sci., Part A-1, **9**, 1983 (1971).

- [2] J. Léonard and S. L. Malhotra, J. Macromol. Sci.-Chem., A10, 1279 (1976).
- [3] J. Léonard and S. L. Malhotra, Ibid., A11, 1867 (1977).
- [4] S. L. Malhotra and J. Leonard, Ibid., A11, 1907 (1977).
- [5] S. L. Malhotra, J. Leonard, and M. Thomas, Ibid., A11, 2213 (1977).
- [6] S. L. Malhotra, Ibid., A12, 73 (1978).
- [7] S. L. Malhotra, Ibid., A12, 883 (1978).
- [8] S. L. Malhotra, C. Baillet, and L. P. Blanchard, Ibid., A12, 909 (1978).
- [9] S. L. Malhotra, L. Minh, and L. P. Blanchard, Ibid., A13, 51 (1979).
- [10] D. L. Glusker, I. Lysloff, and E. Stiles, J. Polym. Sci., 49, 315 (1961).
- [11] V. Warzelhan and G. V. Schulz, Makromol. Chem., 177, 2185 (1976).
- [12] B. J. Schmitt and G. V. Schulz, Ibid., 175, 3261 (1974).
- [13] T. Higashimura, O. Kishiro, K. Matsuzaki, and T. Uryu, J. Polym. Sci., Polym. Chem. Ed., 13, 1393 (1975).
- [14] T. Masuda, M. Sawamoto, and T. Higashimura, Makromol. Chem., 177, 2981 (1976).
- [15] M. Sawamoto, T. Masuda, and T. Higashimura, Ibid., 177, 2995 (1976).
- [16] M. Shmelir, N. Cardona, and G. V. Schulz, Ibid., 178, 169 (1977).
- [17] Y. Yamamoto, M. Irie, and K. Hayashi, Polym. J., 8, 437 (1976).
- [18] M. Szwarc, Carbanions, Living Polymers and Electron Transfer Processes, Wiley-Interscience, 1968, New York, p. 212.
- [19] A. F. Podolsky and A. A. Korotkov, J. Polym. Sci., Part C, 16, 3667 (1968).
- [20] A. A. Korotkov, Paper Presented at IUPAC International Symposium on Macromolecular Chemistry, Prague, 1957, Paper 66.
- [21] A. A. Korotkov and G. Rakova, Vysokomol. Soedin., 10, 1462 (1961).
- [22] A. A. Korotkov, S. P. Mitsengendler, and V. N. Krasulina, J. Polym. Sci., 53, 217 (1961).
- [23] M. Szwarc, Makromol. Chem., 35, 132 (1960).
- [24] A. Vrancken, J. Smid, and M. Szwarc, Trans. Faraday Soc., 58, 2036 (1962).
- [25] A. Vrancken, J. Smid, and M. Szwarc, J. Am. Chem. Soc., 83, 2772 (1961).
- [26] S. Brownstein, S. Bywater, and D. J. Worsfold, Makromol. Chem., 48, 127 (1961).
- [27] Y. Sakurada, M. Matsumoto, K. Imai, A. Nishioka, and Y. Kato, J. Polym. Sci., Part B, 1, 633 (1963).
- [28] Y. Ohsumi, T. Higashimura, and S. Okamura, J. Polym. Sci., Part A, 3, 3729 (1965).
- [29] K. C. Ramey and G. L. Statton, Makromol. Chem., 85, 287 (1965).
- [30] M. N. Berger, J. J. K. Boulton, B. W. Brooks, and M. J. Evan, Chem. Commun., p. 8 (1967).

- [31] R. L. Williams and D. H. Richards, Ibid., p. 414 (1967).
- [32] K. Fujii, D. J. Worsfold, and S. Bywater, Makromol. Chem., 117, 275 (1968).
- [33] K. C. Ramey, G. L. Statton, and W. C. Jankowsky, J. Polym. Sci., Part B, 7, 693 (1969).
- [34] Y. Okamoto, H. Takano, and H. Yuji, Polym. J., 1, 403 (1970).
- [35] F. Heatley, S. Bywater, and D. J. Worsfold, Paper Presented to Division of Organic Coatings and Plastics Chemistry, Joint American Chemical Society-Canadian Institute of Chemistry Meeting, Toronto, May 1970.
- [36] Y. Matsuguma and T. Kunitake, Polym. J., 2, 353 (1971).
- [37] Y. Inoue, A. Nishioka, and R. Chūjō, Makromol. Chem., 156, 207 (1972).
- [38] T. Kunitake, J. Macromol. Sci.-Chem., A9, 797 (1975).
- [39] R. W. Lenz, Ibid., A9, 945 (1975).
- [40] T. Kunitake and S. Tsugawa, Macromolecules, 8, 709 (1975).
- [41] I. Mita and H. Okuyama, J. Polym. Sci., Part A-1, 9, 3137 (1971).

Accepted by editor September 13, 1979

Received for publication November 13, 1979