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Polymerization of α-Methylstyrene in p-Dioxane and Cyclohexane with Potassium as Initiator.
VI. NMR Analyses of the Reaction Products

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ABSTRACT

Nuclear magnetic resonance (NMR) analyses of poly-α-methylstyrene samples prepared in p-dioxane and cyclohexane at high initial living end concentration [LE] and showing multimodal gel-permeation chromatographic (GPC) molecular weight distributions built up of components D + A, B and C, have been carried out. Methylene and methyl protons associated with the low molecular weight component D + A have similar τ values to those noted for the same component but prepared in tetrahydrofuran (THF) in all polymers studied. The proportions of component D + A as determined by GPC are higher than those found by NMR. Triad analyses showed that both low and high molecular weight components follow Bernoullian propagation statistics, the P_m value being higher for component D + A, suggesting that the reaction step responsible for formation of component D + A is the same in cyclohexane, p-dioxane, and THF. In reactions involving p-dioxane as solvent, where there was noticeable killing of active chain ends in the beginning of the reaction, there was very little component D + A, contrary to expectation. Parts of the component D + A prepared in p-dioxane and cyclohexane have also been noted to be dormant in nature. Reactions in p-dioxane as solvent and initiated with metal complexes or metal alone did not show any difference in NMR analyses, although GPC results had shown polymers to be poorer in D + A content when the initiation was carried out in the presence of a complexing agent. Comparison of the proportion of D + A in polymers prepared in three different solvents showed that under identical reaction conditions cyclohexane yields the least of the NMR characterized low molecular weight products. THF and p-dioxane showed similar magnitudes of D + A component yields.

INTRODUCTION

In an earlier study [1] related to nuclear magnetic resonance (NMR) spectroscopy of poly-α-methylstyrene it was pointed out that the methylene and methyl protons associated with the low and the high molecular weight component of a polymer having multimodal molecular weight distributions appear at different τ values. The proportion of low molecular weight component as determined by gel-permeation chromatography (GPC) was higher than that provided by the NMR analyses.

The triad analyses of the methyl region of low as well as high molecular weight components had shown that all polymers prepared in THF [2, 3] in the temperature range of 25-60°C obeyed Bernoullian propagation statistics [1], the P_m value being higher for the lower molecular weight component. On lowering the temperature of the reaction to 5°C it was observed that the P_m value of D + A decreased, and on further lowering the temperature to -25 and -78°C the propagation statistics of this component changed from Bernoullian to first-order Markov. Component B + C, on the other hand, always obeyed Bernoullian statistics.

Based on these results it was concluded that the reaction step responsible for component D + A is not the same as that for component B + C, whose formation has been associated with ion-pair mechanisms. These studies were carried out in THF as solvent having a high dielectric constant, a property which controls the nature of the ion-pair, e. g., free ions, solvent-separated ion-pair, or contact ion-pair. In solvents of low dielectric constants (p-dioxane, cyclohexane), the nature of the ion-pair responsible for the formation of component B + C is known to be different than that in THF; however, it is not known as to what role the dielectric constant of the medium plays during the formation of component D + A. Thus it was thought of interest to analyze poly-α-methylstyrene samples prepared in p-dioxane and cyclohexane with the help of GPC and NMR techniques. The results of these studies form the subject of the present communication.

EXPERIMENTAL

The data on the origin and purification of materials, mode of initiation, and procedure of polymerization, and the characterization of the products have been presented elsewhere [2-5] in detail; however some relevant points concerning the GPC and NMR techniques are discussed briefly.

Molecular weight distributions were studied with a Waters Associates Model 200 gel-permeation chromatograph equipped with five Styrogel columns having maximum rated porosities of 1.0×10^6, 1.5×10^5, 3.0×10^3, 250, and 60 Å, respectively. The calibration of the instrument was performed with narrowly dispersed poly-α-methylstyrene samples, and the values of $\overline{M}_w$ and $\overline{M}_n$ were computed by using the summation method [6].

NMR spectra of the 15% (w/v) polymer solutions were recorded with a 200 MHz Varian Associates spectrometer at 100°C in $o\text{-}C_6H_4Cl_2$ as solvent and with TMS as the internal standard.

RESULTS AND DISCUSSION

Polymerizations in p-Dioxane as Solvent

In Fig. 1 are shown the GPC molecular weight distributions of poly-α-methylstyrene samples L-6 and B initiated with potassium at 25°C in p-dioxane as solvent and polymerized at 40 and 25°C, respectively. Their GPC analyses in terms of percent proportion of D + A presented in Table 1 show that these two polymers have 83% (in sample L-6) and 100% (in sample B) of this type of component.

In Fig. 2 are shown the α-methyl protons of polymer samples L-6 and B, observed in $o\text{-}C_6H_4Cl_2$ at 100°C in the range of 8.6 to 10.0 τ. One notes that besides the well known peaks at 9.0, 9.43, and 9.69 τ, assigned respectively to mm, mr, and rr triads of the methyl groups in high molecular weight poly-α-methylstyrene [7-9] similar to component B + C, there are numerous other peaks between 8.6 and 9.3 τ. The most prominent of these peaks in the spectrum of sample L-6 are at (8.64, 8.66, 8.68 τ), (8.77 τ), (8.82, 8.83, 8.85, 8.86, 8.88, 8.89, 8.91, 8.92, 8.94, 8.97, 8.99, 9.02 τ) and (9.07, 9.10, 9.13, 9.20, 9.23, 9.26 τ). In the spectrum of sample B there are fewer peaks,

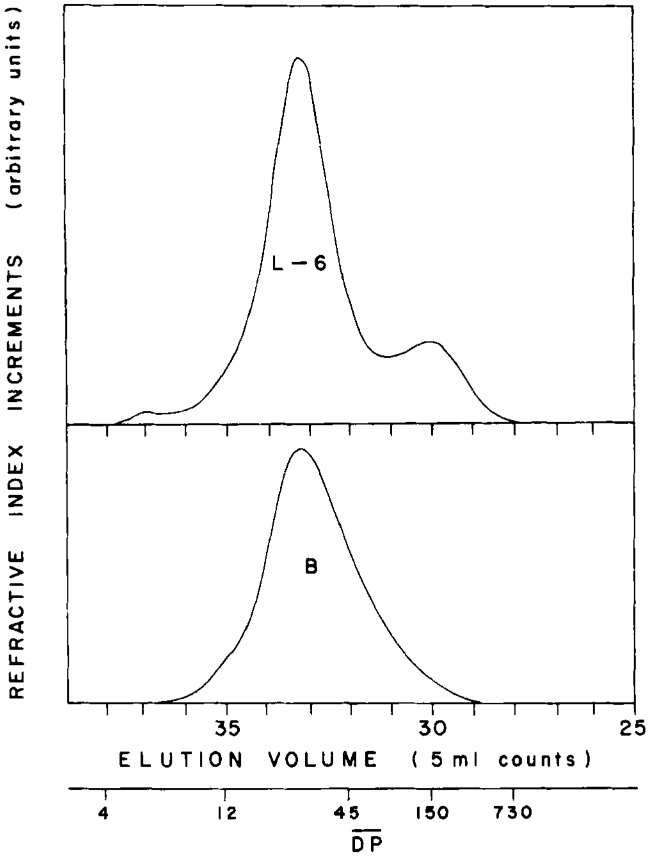

FIG. 1. GPC molecular weight distributions of poly-α-methylstyrene samples L-6 and B initiated with potassium at 25°C in p-dioxane as solvent and polymerized at different temperatures. (See Table 1 for other data.)

and these are located at (8.67 τ), (8.82 τ), (8.91, 8.94, 8.97 τ) and (9.13, 9.16, 9.19, 9.23, 9.26, 9.29 τ). Similar peaks were also observed in the spectra of poly-α-methylstyrene samples prepared in THF with potassium and potassium complexes as well as in bulk with butyllithium-tetramethylethylenediamine and were attributed to the methyl groups of the low molecular weight component D + A present in the polymers [1]. On the basis of the triad analyses of the methyl groups present in component D + A made in the earlier study [1], the various peaks in the spectra of samples L-6 and B may be assigned as follows.

TABLE 1. GPC and NMR Analyses of Poly-α-methylstyrene Prepared with Potassium Metal in p-Dioxane at Different Temperatures[a]

No.	$[M]_0$ (mole/liter)	[LE] (mole/liter)	Temperature of polymerization (°C)	Yield (base-mole/liter)	Proportion D + A (%)		Intensity associated with various configurations of D + A[b]				Propagation statistics of B + C
					GPC	NMR	mm	mr	rr	P_m	P_m
L-11[c]	4.50	0.23	40	2.10	77	55	0.14	0.51	0.35	0.39	0.27
L-6	4.20	0.10	40	1.00	83	53	0.13	0.51	0.36	0.38	0.27
L-19[c]	6.00	0.05	25	5.10	6	2	-	-	-	-	0.26
35	3.54	0.06	25	2.22	23	10	0.10	0.36	0.54	0.30	0.25
19	3.54	0.05	25	2.11	23	9	0.11	0.39	0.50	0.33	0.23
L-7	3.00	0.09	25	1.80	54	24	0.12	0.42	0.46	0.33	0.24
L-3	2.75	0.05	25	0.84	82	33	0.12	0.43	0.45	0.34	0.25
L-1[d]	2.75	0.05	25	0.90	67	30	0.16	0.46	0.38	0.40	0.21
L-5[c]	2.75	0.04	25	0.90	60	24	0.11	0.40	0.49	0.33	0.25
16	2.60	0.05	25	0.90	48	15	0.13	0.35	0.52	0.34	0.24
B	1.60	0.08	25	0.80	100	47	0.11	0.46	0.43	0.34	0.26
L-17	2.20	0.04	15	1.00	100	16	0.08	0.37	0.55	0.26	0.24
L-4	2.75	0.05	5	1.74	26	13	0.12	0.38	0.50	0.34	0.24
L-8	3.00	0.09	5	2.75	40	19	0.11	0.46	0.43	0.34	0.25

[a] Data of Malhotra and Léonard [4].
[b] By using assignments for mm, mr, and rr triads presented in the literature [1, 7-9].
[c] Solvent THF.
[d] Initiator potassium naphthalene.

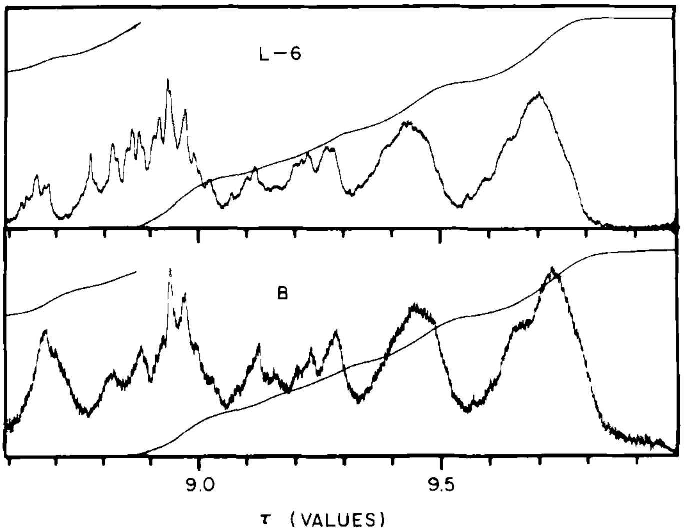

FIG. 2. 220 MHz NMR spectra of the α-methyl protons of poly-α-methylstyrene sample L-6 and B observed in $o\text{-}C_6H_4Cl_2$ at 100°C in the range of 8.6-10.0 τ. (See Table 1 for other data.)

For sample L-6, the peak at 8.6-8.7 τ, with peaks at (8.64, 8.66, 8.68 τ), is assigned to mm triads; that at 8.7-9.00, with doublets as (8.82, 8.85) and (8.83, 8.86) τ to mr, and doublet as (8.88, 8.91), (8.89, 8.92) (8.94, 8.97) and (8.99, 9.02) τ to rm triads; that at 9.05-9.26, with peaks at (9.07, 9.10, 9.13) and (9.20, 9.23, 9.26) τ, to rr triads.

For sample B, the peak at 8.6-8.75 τ, with a broad peak at 8.67 τ, is assigned to mm triads; that at 8.75-9.05 τ, with broad peaks at 8.82 and 8.86 τ to mr, and 8.94, 8.97 τ, to rm triads; that at 9.05-9.30 τ, with peaks at (9.13, 9.16, 9.19) and (9.23, 9.26, 9.29) τ, to rr triads.

It may be mentioned here that these assignments of mm, mr + rm, and rr triads to the three regions, viz., 8.6-8.75 τ, 8.75-9.05 τ, and 9.05-9.3 τ, respectively, are made exclusively on the basis that similar triads, in the case of the high molecular weight poly-α-methylstyrene, have been shown to follow the ascending order of magnetic field [7-9].

Prior to making any analyses of the mr + rm triads of component D + A (8.75-9.05 τ), the contribution due to the mm triad of the component B + C which is located at 9.0 τ must be taken into account. This was achieved with the ratio of the integral counts between the regions 9.7 to 9.9 τ $[rr = (1 - P_m)^2]$ and 9.5 to 9.7 τ $[mr = 2 P_m (1 - P_m)]$, which yielded the propagation probability value P_m, and consequently the intensity values for the triads mm, mr, and rr are easy to calculate. From the knowledge of the intensity data for mr and rr and their integral counts on the NMR spectrum, a corresponding number of integral counts for the triad mm is calculated and added to that of component B + C and subtracted from that of component D + A in order to compute the percent NMR characterized contributions of each component. This also serves to compute the mm, mr, and rr triad intensity associated with methyl protons of component D + A.

In Fig. 3 are shown the NMR spectra of the β-methylene protons of poly-α-methylstyrene samples L-6 and B observed in o-$C_6H_4Cl_2$ at 100°C in the range of 7.3 and 8.5 τ. These spectra are different from that of the high molecular weight poly-α-methylstyrene sample L-19 (see Fig. 4) prepared in THF at 25°C whose β-methylene protons appear between 7.9 to 8.6 τ with an important peak at 8.31 τ attributed to the rrr triad [8]. In the spectra of polymer samples L-6 and B, these rrr triads are placed at lower τ values of 8.25 and 8.28, respectively. The other point of difference between the spectrum of sample L-6 with that of sample B lies in the presence of an important peak at 7.9 τ in the former. It may be added here that most of the polymers prepared in THF at high temperatures [1] also carried this peak at about 7.95 τ; however, its assignment is difficult to make.

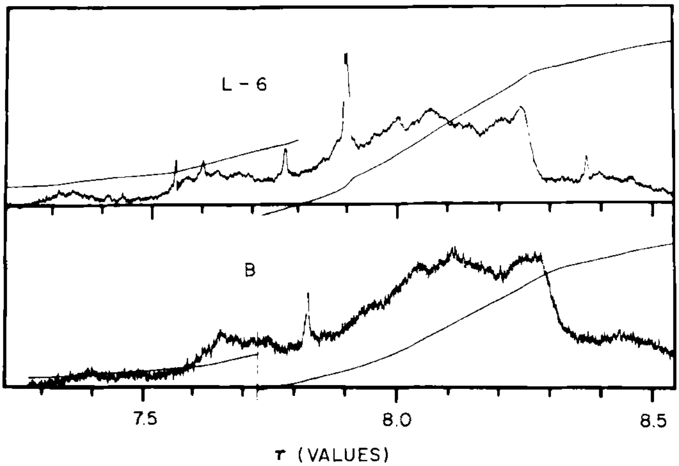

FIG. 3. 220 MHz NMR spectra of the β-methylene protons of poly-α-methylstyrene samples L-6 and B observed in o-$C_6H_4Cl_2$ at 100°C in the range of 7.3-8.5 τ.

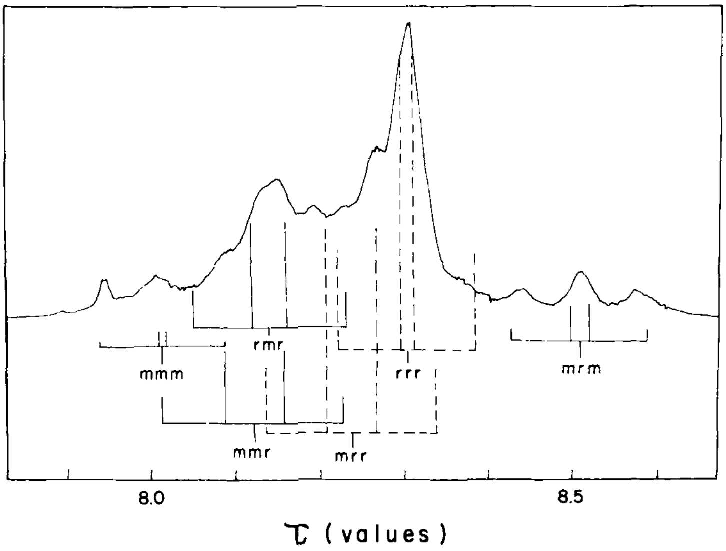

FIG. 4. 220 MHz NMR spectrum of the β-methylene protons of poly-α-methylstyrene sample L-19 showing the placement of six tetrads (See Table 2 for other data.)

The spectra presented in Fig. 3 resemble those of poly-α-methylstyrene samples prepared in THF carrying mixtures of components D + A and B + C [1] and confirms the presence of the former component in polymers prepared in p-dioxane as solvent. In the earlier paper [1], it was noted that the make up of β-methylene protons between 7.3 and 8.5 τ depended on the relative proportion of components D + A and B + C, which made it difficult to assign the absolute chemical shifts for the six tetrads due to the methylene groups of the former. It may be mentioned here that the values of the chemical shifts for the six tetrads due to the methylene groups of components similar to B + C have already been reported in the literature [8]. By making use of τ values for some of the tetrads of component B + C it was thought of interest to analyze the spectrum of the β-methylene protons of component D + A in terms of tetrads. Prior to discussing the results of the present analyses of β-methylene it was thought necessary to evaluate the reported assignments for the same protons but belonging to high molecular weight poly-α-methylstyrene.

With a view to verify the earlier assignments [8], poly-α-methylstyrene sample L-19 [2% (D + A) and 98% (B + C)] prepared in THF at 25°C was subjected to NMR analyses. In Fig. 4 is shown the β-methylene region of sample L-19 observed in o-$C_6H_4Cl_2$ at 100°C. The triad analyses of this polymer had shown it to follow Bernoullian propagation [1] with $P_m = 0.26$. The intensity of three triads mm, mr, and rr was 0.07, 0.38, and 0.55, respectively. By making use of the P_m value of 0.26 and the equations established for Bernoullian propagation [10], the intensity of the six tetrads, viz., mmm, mmr, rmr, mrr, mrm and rrr were computed. These are presented in Table 2, which also includes data for intensity of various important peaks calculated from the area measurements as well as on the basis of the tetrad placement.

In the spectrum of sample L-19 the intensity calculated under the peak at 8.31 τ attributed to rrr tetrad [8] is 0.29, whereas the intensity of the same rrr tetrad based on a P_m value of 0.26 is 0.40. This would suggest that in the case of sample L-19 the rrr tetrad does not appear as a singlet located at 8.32 τ [8] but must be in the form of a quartet, with its center placed at 8.31 τ. The mmm tetrad, on the other hand, has been placed at 8.01 as well as at 8.55 τ [8]. In the present case the intensity of 0.06 based on area measurements in the vicinity of these τ values is nearly three times that (0.02) calculated from a P_m value of 0.26. This indicated that the assignments made on the poly-α-methylstyrene sample used by Ramey et al. [8] may not be applicable to the polymers of the present study. This necessitated an independent tetrad analyses of the β-methylene protons of sample L-19.

By making use of the J_{AB} value of 15 Hz [8] in combination with the calculated intensity of the six tetrads on the basis of $P_m = 0.26$, quartets bearing peak ratios of 1:3:3:1 (stick spectra) were arranged to simulate the spectrum of the β-methylene protons of sample L-19. If the tetrads mmm, mmr, rmr, mrr, rrr, and mrm are placed at τ values of 8.015, 8.12, 8.14, 8.23, 8.31, and 8.51, the intensity values based on area measurements and based on tetrad placement agree quite well as shown in Table 2. These assignments are only slightly different than those made by Ramey et al. [8], except in the case of mrm tetrad.

After having established the average chemical shifts for the six tetrads due to the methylene groups of B + C type component in poly-α-methylstyrene, the next step is to find the chemical shifts for the six tetrads of the component D + A. This was achieved in the case of sample B in the following manner: (a) The total surface area between 7.3 to 8.6 τ was measured and distributed between components D + A (47% by NMR) and B + C (53% by NMR). (b) On the basis of area assigned to component B + C, intensity of the important peaks between 8.0 and 8.6 were computed. (c) By making use of

TABLE 2. Assignment of Chemical Shifts on the Basis of the Triad Population for the Six Tetrads: Case of Poly-α-methylstyrene L-19 Carrying 98% Component B + C (NMR Data)

	Important Peaks			Configuration placement				
				Sequence			Center τ values	
Nature of protons	τ values	Intensity based on area	Intensity based on tetrad placement	Triads	Tetrads	Intensity based on P_m = 0.26	Present study	Ramey et al. [8]
Methyl								
$\underline{CH_3}$ $\vert$ $-C-CH_2-$		0.07		mm			9.00	
		0.38		mr			9.45	
		0.55		rr			9.69	
			Bernoullian propagation P_m = 0.26					
Methylene								
CH_3 $\vert$ $-C-\underline{CH_2}$	8.01	0.04	0.03		mmm	0.02	8.015	8.01 8.55
	8.05	0.02	0.02					
	8.09	0.05	0.04					
	8.12	0.10	0.09		mmr	0.10	8.12	8.06 8.48
	8.16	0.09	0.09					
	8.20	0.10	0.10		rmr	0.14	8.14	8.14 8.35

8.23	0.07	0.07	mrr	0.28	8.23	8.21 8.31
8.27	0.12	0.11				
8.31	0.29	0.30	rrr	0.40	8.31	8.32
8.37	0.03	0.05				
8.44	0.02	0.03				
8.51	0.03	0.03	mrm	0.05	8.51	8.14
8.57	0.02	0.02			J_{AB} = 15 Hz	

TABLE 3. Assignment of Chemical Shifts on the Basis of the Triad Population for the Six Tetrads: Case of Poly-α-methylstyrene Sample B Carrying 53% of Component B + C and 47% Component D + A (NMR Data)

		Important peaks			Configuration placement			
					Sequence			
Component	Nature of protons	τ values	Intensity based on area	Intensity based on tetrad placement	Triads	Tetrads	Intensity based on P_m value	τ values
(B + C)	Methyl							
	$\underline{CH_3}$		0.07		mm			9.00
	–C–CH$_2$–		0.38		mr			9.45
			0.55		rr			9.72
		Bernoullian propagation with $P_m = 0.26$						
	Methylene							
	CH$_3$	8.005	0.105	0.02		mmm	0.02	8.01
	–C–$\underline{CH_2}$–	8.015	0.15	0.02				
		8.045		0.02				
		8.084	0.13	0.04				
		8.114	0.10	0.09		mmr	0.10	8.11
		8.145	0.085	0.095		rmr	0.14	8.13
		8.184	0.18	0.105				
		8.205		0.05				
		8.215		0.03		mrr	0.28	8.21

		8.234	0.095	0.105				
		8.275	0.24	0.15		rrr	0.40	8.28
		8.290		0.15				
		8.304		0.05				
		8.360		0.05				
		8.430	0.19	0.01		mrm	0.05	8.43
		8.443		0.03				
		8.510		0.01			J_{AB} = 15 Hz	
(D + A)	Methyl							
	C$\underline{H_3}$ $\vert$ —C—CH$_2$—		0.11		mm			8.6- 8.75
			0.46		mr			8.75- 9.00
			0.43		rr			9.05- 9.30
		Bernoullian propagation with P_m = 0.34						
	Methylene							
	CH$_3$ $\vert$ —C—C$\underline{H_2}$—	7.584	0.02	0.02				
		7.610		0.015				
			0.04	0.015		mmm	0.04	7.62
		7.630						

(continued)

TABLE 3 (continued)

Component	Nature of protons	Important peaks: τ values	Important peaks: Intensity based on area	Important peaks: Intensity based on tetrad placement	Configuration placement: Sequence: Triads	Configuration placement: Sequence: Tetrads	Configuration placement: Intensity based on P_m value	Configuration placement: τ values
		7.655	0.07	0.075				
		7.700	0.05	0.055		mmr	0.15	7.68
		7.734	0.05	0.055				
		7.770	0.03	0.02		rmr	0.15	7.77
		7.802	0.04	0.055				
		7.822	0.05	0.04				
		7.868	0.02	0.02				
		7.900	0.09	0.12				
						mrr	0.30	7.91
		7.927	0.095	0.11				
		7.98	0.08	0.11				
						mrm	0.08	8.01
		8.045	0.15	0.135				
		8.084	0.13	0.105				
		8.114	0.10	0.01		rrr	0.29	8.065
		8.155	-	0.04			$J_{AB} = 15$ Hz	

J_{AB} = 15 Hz in combination with the calculated intensity of the six tetrads from a P_m value of 0.26, quartets bearing peak ratios of 1:3:3:1 were arranged according to the assignments made in Table 2. (d) The remainder area belonging to component D + A was transformed into intensities. (e) By making use of J_{AB} = 15 Hz in combination with the calculated intensity of the six tetrads from a P_m value of 0.34, quartets bearing peak ratios of 1:3:3:1 were arranged to match the intensity based on area measurements.

The results of the analyses are presented in Table 3. It would appear that if one places the quartets corresponding to the six tetrads viz mmm, mmr, rmr, mrr, mrm and rrr of component D + A at τ values of 7.62 (7.54, 7.61, 7.63, 7.70), 7.68 (7.584, 7.655, 7.70, 7.768), 7.77 (7.66, 7.734, 7.802, 7.868), 7.91 (7.822, 7.893, 7.927, 7.98), 8.015 (7.90, 7.975, 8.045, 8.114), 8.065 (7.975, 8.045, 8.084, 8.155) and those of component B + C at τ values of 8.01 (7.935, 8.005, 8.015, 8.084), 8.114 (8.015, 8.084, 8.145, 8.215), 8.13 (8.045, 8.114, 8.145, 8.215), 8.21 (8.114, 8.184, 8.234, 8.304), 8.435 (8.36, 8.43, 8.443, 8.51), 8.28 (8.205, 8.275, 8.290, 8.36) one can get an approximate match between the experimental and calculated spectra of the β-methylene protons in sample L-19.

A comparison of the τ values for various tetrads due to methylene protons of the two components reveal that tetrads belonging to component D + A are placed at an average of 0.4 τ in the downfield as compared to those for B + C. The triad analyses of the methyl groups (Table 3) also yield similar conclusions and in the same direction, adding to the validity of the tetrad placement for component D + A.

As mentioned earlier, the data in Table 1 carries some other results pertaining to GPC analyses and a comparison of these results with those obtained with NMR may also yield other relevant information. In Table 1 results are also listed (for comparison purposes) on polymer samples prepared in THF as solvent. The highlights of the data in Table 1 may be outlined as follows. Polymerizations of α-methylstyrene initiated with high [LE] of potassium initiator in p-dioxane as solvent also yield the component D + A. The percent proportion of component D + A computed from the GPC and NMR analyses do not agree, the values obtained from the latter technique being lower. The propagation reactions responsible for the formation of components D + A and B + C, both, follow Bernoullian statistics, the P_m value (0.34 - 0.39) of the former being higher than that (~0.26) of the latter component, suggesting the possibility of two different reaction steps being involved. Poly α-methylstyrene samples prepared under identical conditions of $[M]_0$, initiator, and temperature of polymerization but in p-dioxane (L-6) and THF (L-11) as solvents yield similar results when analyzed with the NMR technique. The values of P_m for components D + A and B + C in both solvents were found to be 0.39 and 0.27 respectively.

Based on the comparison of the NMR data of samples L-6 and L-11 it would appear that the dielectric constant of the medium has no visible effect on the propagation statistics of component D + A. Like the propagation reactions responsible for the formation of component B + C between the temperature range of 60 to -78°C in THF as solvent, the reaction for the formation of this component in p-dioxane yield a P_m value (0.27) which is close to 0.26.

Mode of Formation of Component D + A

Although the presence of low molecular weight component D + A along with that of the high molecular weight component B + C has been attributed to different reaction mechanisms [1-5], there are others [11, 12] who believe that the killing of the bifunctional initiators would also yield similar results. Brower and McCormick [12] had indeed suggested that if the killing of the bifunctional initiator could be achieved in the early stages of the reaction then the polymer should have trimodal distributions: (1) due to a dead polymer, (2) due to monofunctional initiator, and (3) due to a bifunctional initiator. The molecular weight of polymer (2) should be one half of that in (3).

In order to verify the above hypothesis, a 2.6 M solution of α-methylstyrene was initiated and polymerized at 25°C with potassium as initiator. It was observed that in the first 15 min the intensity of the red color diminished throughout the solution, indicating that there were some impurities present in the monomer or the solvent. The polymerization reaction, however, continued till it attained a steady state. This reaction (sample 16) yielded 0.90 base-mole/liter of polymer and thus satisfied the thermodynamic requirements. The GPC chromatogram of sample 16 is shown in Fig. 5 and compared with that of another polymer (sample L-3) prepared from a 2.75 M solution in the same solvent and exhibiting unimodal molecular weight distribution. In this latter polymer there was no killing of living ends as was the case in sample 16.

The analyses of the GPC chromatograms in Fig. 5 reveal that although killing of the bifunctional initiator in sample 16 has produced a bimodal distribution, the molecular weights of polymers eluting at 33 and 28.5 do not bear a ratio of 1:2. In an earlier study [4], it was clearly established that this bimodal distribution in sample 16 may not be solely attributed to killing of living ends but also to the presence of different reaction steps. Polymer fraction appearing under the elution count of 33 (low molecular weight) was termed as component D + A and the remainder fraction as component B + C. In a recent study [1], it was shown that the NMR spectra of the low

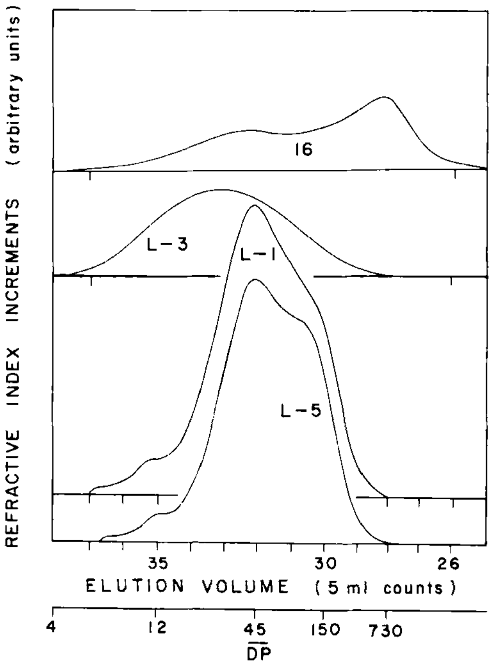

FIG. 5. GPC molecular weight distributions of poly-α-methylstyrene samples initiated with potassium (16, L-3, and L-5) and potassium naphthalene (L-1) at 25°C in p-dioxane and polymerized at 25°C. (See Table 1 for other data.)

(D + A) and high (B + C) molecular weight components were different, the latter polymer yielding lower P_m values. Furthermore it was shown that, irrespective of the distribution, whether unimodal or multimodal, the NMR-characterized component D + A was always present.

With a view to verify the proportions of component D + A in polymers 16 and L-3, their NMR spectra were observed in o-$C_6H_4Cl_2$ at 100°C in the range of 7.5 to 10.0 τ (Fig. 6). The data based on GPC and NMR analyses of Figs. 5 and 6 are listed in Table 1. It may be noted that polymer L-3, where there was no visible killing of living ends, has more of the component D + A than sample 16, where killing was observed in the very beginning of the reaction. The evidence that the components D + A in the two polymers are identical, comes from the same P_m value of 0.34 in the two cases. The remainder

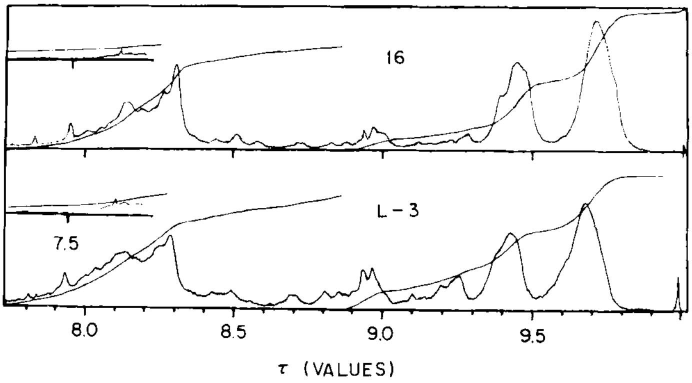

FIG. 6. 220 MHz NMR spectra of the β-methylene and α-methyl protons of poly-α-methylstyrene samples 16 and L-3 initiated with potassium at 25°C in p-dioxane as solvent and polymerized at 25°C. Polymer 16: killing of living ends in the very beginning of polymerization; L-3: no visible killing prior to or during polymerization. (See Table 1 for other data.)

components B + C, too, had identical P_m values. This experiment shows that the killing phenomenon actually reduces the proportion of component D + A.

Dormant Nature of Component D + A

In an earlier study [1], it was shown that component D + A in poly-α-methylstyrene sample prepared in THF was dormant in nature. In order to verify the nature of this component, in the present case, poly-α-methylstyrene samples prepared in p-dioxane were subjected to polymerization and further polymerization approach [2]. A 2.75 M solution of α-methylstyrene in p-dioxane was initiated with potassium ([LE] = 0.05 mole/liter) at 25°C and divided in two parts. Both of these were polymerized at 25°C. One of these (L-3) was opened at 25°C, and it yielded 0.84 base-mole/liter of polymer. The other (L-4) was further polymerized at 5°C and yielded 1.74 base-mole/liter of polymer. The normalized GPC chromatograms of these two polymers are shown in Fig. 7 and their analyses in terms of proportion of D + A in each are listed in Table 1.

In yet another experiment, a 2.75 M solution of α-methylstyrene in p-dioxane was initiated with potassium ([LE] = 0.09 mole/liter) and divided in two parts. Both of these were polymerized at 25°C. One of these (L-7) was opened at 25°C and yielded 1.80 base-mole/

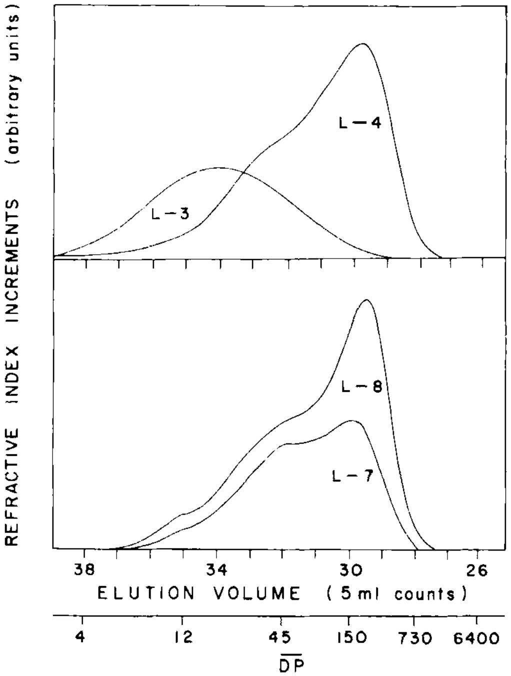

FIG. 7. GPC molecular weight distributions of two pairs of poly-α-methylstyrene samples (L-3, L-4 and L-7, L-8) initiated with potassium at 25°C in p-dioxane as solvent. L-3 and L-7 were polymerized at 25°C, whereas L-4 and L-8 were polymerized at 25°C and further polymerized at 5°C. (See Table 1 for other data.)

liter of polymer. The other (L-8) was further polymerized at 5°C, and it yielded 2.75 base-mole/liter of polymer. The GPC chromatograms of L-7 and L-8 are presented in Fig. 7 and their analyses in terms of proportions of component D + A are listed in Table 1.

A close examination of the GPC results of these two sets of experiments shows that in the pair (L-3, L-4) the propagation contribution in L-4 at 5°C originates under the envelope of low molecular weight component of L-3; in the pair (L-7, L-8) the propagation contribution in L-8 at 5°C may originate from the low as well as high molecular weight component of L-7.

In Fig. 8 are shown the NMR spectra of poly-α-methylstyrene samples L-7 and L-8 observed in o-$C_6H_4Cl_2$ at 100°C. The results of the analyses of Fig. 8 in terms of the proportion of components D + A and B + C as well as the P_m values associated with each of

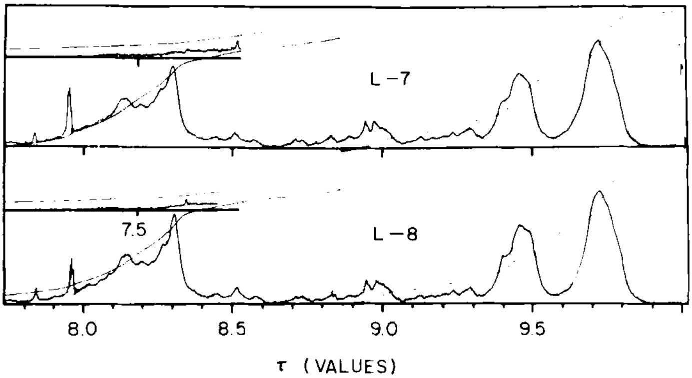

FIG. 8. 220 MHz NMR spectra of the β-methylene and α-methyl protons of poly-α-methylstyrene samples L-7 and L-8 observed in o-$C_6H_4Cl_2$ at 100°C in the range of 7.5-10.0 τ. (See Table 1 for other data.)

these are listed in Table 1. It may be noted that although the proportion of D + A in L-3 and L-4 as well as L-7 and L-8 are different by NMR (lower values for L-4 and L-8) the absolute values in terms of base-mole/liter of component D + A in each pair (L-3 = 0.28, L-4 = 0.23), (L-7 = 0.43, L-8 = 0.52) at 25 and 5°C do not vary by much. This shows that part of component D + A, in polymers prepared in p-dioxane, is also dormant in nature.

Influence of Initiator Type and the Solvent

In earlier studies [2-4], the role of naphthalene in the polymerization of α-methylstyrene in THF as well as in p-dioxane was discussed. It was shown [4] that in the presence of naphthalene, p-dioxane behaved like THF as far as the GPC molecular weight distributions were concerned. The results of these experiments are also retained for the present study so that a comparison of the GPC and NMR data be made.

In Fig. 5 are shown the GPC chromatograms of poly-α-methylstyrene samples L-3, L-1, and L-5 initiated with potassium in p-dioxane, potassium-naphthalene in p-dioxane, and potassium in THF, respectively, and polymerized at 25°C. It is noteworthy that the addition of naphthalene in p-dioxane renders the GPC molecular weight distribution of polymer L-1 identical to that of L-5 prepared with potassium but in THF as solvent.

In order to compute the proportions of D + A in these polymers

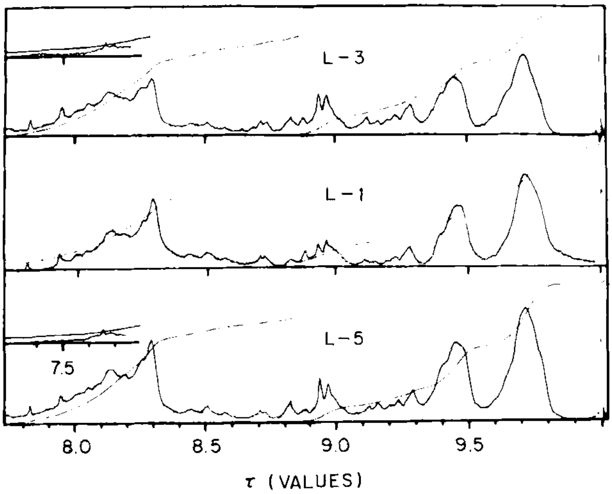

FIG. 9. 220 MHz NMR spectra of the β-methylene and α-methyl protons of poly-α-methylstyrene samples L-3, L-1, and L-5 observed in o-$C_6H_4Cl_2$ at 100°C in the range of 7.5-10.0 τ. (See Table 1 for other data.)

their NMR spectra were observed in o-$C_6H_4Cl_2$ at 100°C, and these are shown in Fig. 9. The analyses of the spectra in terms of the proportion of component D + A and B + C as well as the values of P_m associated with each of the two components are presented in Table 1. It may be noted that, although the GPC proportions of component D + A in L-3 (potassium alone in p-dioxane) and L-1 (potassium-naphthalene in p-dioxane) are different, the NMR proportions are nearly the same. It would mean that the addition of naphthalene does not affect the NMR characterized component D + A. The NMR-characterized component in L-5 (potassium alone in THF) however, is lower than that in p-dioxane (L-1). It may be mentioned here that polymers prepared in THF (L-11) and in p-dioxane (L-6) but at 40°C had shown that under similar polymerization conditions the percentage of NMR-characterized component D + A in the two solvents was of similar magnitude. The only conclusion that can be drawn from the results of polymerization at 25°C (L-3, L-1) is, that in a solvent of lower dielectric constant there is a higher proportion of the dormant polymer in the D + A component.

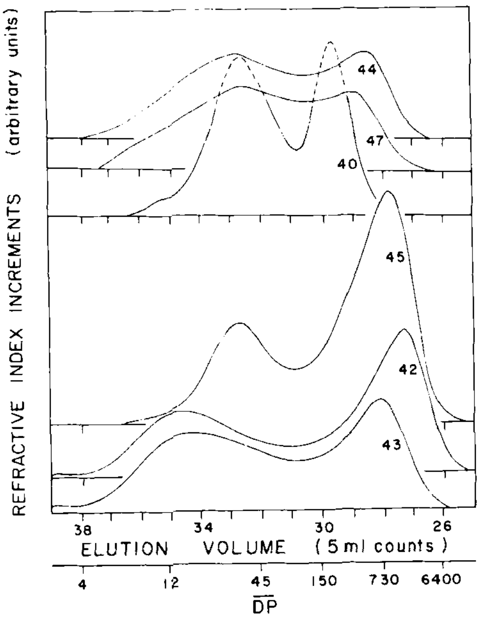

FIG. 10. GPC molecular weight distributions of poly-α-methylstyrene samples 44, 47, 45, 42, and 43 initiated at 25°C with potassium in cyclohexane (sample 40 in THF) and polymerized at 40°C. (See Table 4 for other data.)

Polymerizations in Cyclohexane as Solvent

In an earlier publication from this laboratory [5], results on the thermodynamics and GPC molecular weight distribution of poly-α-methylstyrene samples prepared in cyclohexane at 40°C, were reported. The polymerization reaction in cyclohexane took two months to reach a stationary state; however, even after such a long time, there was no visible sign of killing of living ends. The GPC molecular weight distributions of all polymers were bi- or trimodal, split into components D + A, B, and C as in the other [2-4] studies.

In order to verify the influence of the dielectric constant of the medium on the proportion of component D + A, these polymer samples prepared in cyclohexane were subjected to GPC and NMR analyses. In Fig. 10 are shown the GPC molecular weight distributions of poly-α-methylstyrene samples 43, 42, 45, 47, and 44 prepared in cyclohexane and sample 40 prepared in THF. These samples have bimodal distributions and carry different proportions of component

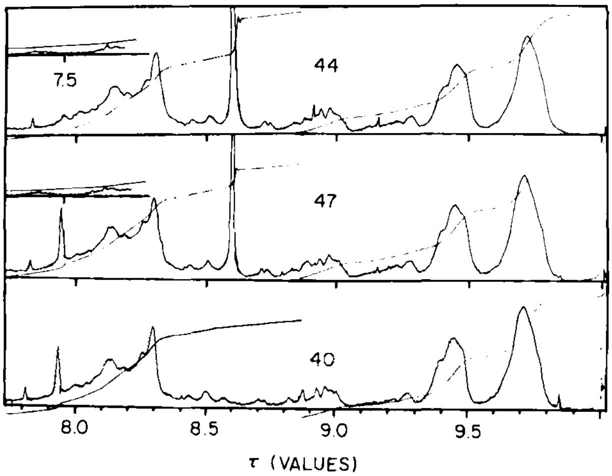

FIG. 11. 220 MHz NMR spectra of the β-methylene and α-methyl protons of poly-α-methylstyrene samples 44, 47, and 40 observed in o-$C_6H_4Cl_2$ at 100°C in the range of 7.5-10.0 τ. (See Table 4 for other data.)

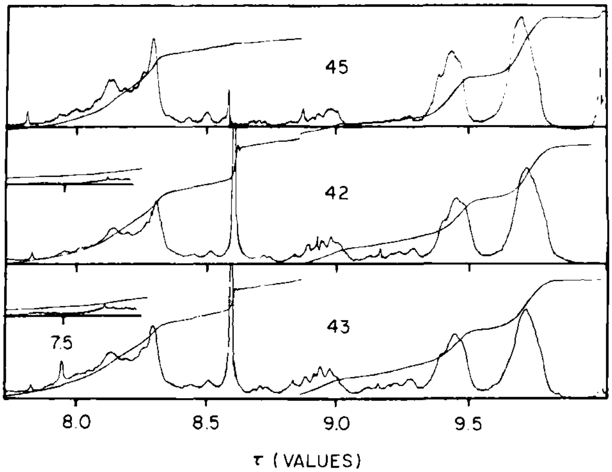

FIG. 12. 220 MHz NMR spectra of the β-methylene and α-methyl protons of poly-α-methylstyrene samples 45, 42, and 43 observed in o-$C_6H_4Cl_2$ at 100°C in the range of 7.5-10.0 τ. (See Table 4 for other data.)

TABLE 4. GPC and NMR Analyses of Poly-α-methylstyrene Prepared with Potassium Metal at 40°C in Cyclohexane Containing Traces of THF[a]

No.	$[M]_0$ (mole/liter)	[LE] (mole/liter)	Yield (base-mole/liter)	Proportion D + A (%)		Intensity associated with various configurations				Propagation statistics of B + C
				GPC	NMR	mm	mr	rr	P_m	P_m
45	6.35	0.17	5.42	30	12	0.14	0.45	0.41	0.37	0.25
42	5.85	0.29	5.20	63	23	0.10	0.47	0.43	0.33	0.24
43	5.80	0.22	3.20	63	27	0.11	0.46	0.43	0.33	0.25
44	5.17	0.11	2.15	60	21	0.10	0.44	0.46	0.33	0.25
47	5.17	0.12	1.92	60	22	0.10	0.45	0.45	0.33	0.26
40[b]	4.95	0.15	1.83	72	18	0.14	0.43	0.43	0.35	0.25

[a] Data of Malhotra et al. [5].

[b] Solvent THF.

D + A. The NMR spectra of these polymers, (44, 47, 40) and (45, 42, 43), are shown in Figs. 11 and 12, respectively. The analyses of Figs. 10, 11, and 12, in terms of different proportions of components D + A and B + C as well as the P_m values ascribed to these two components, are presented in Table 4.

The important observations from these results may be summed up as follows. The proportion of component D + A calculated by the NMR technique are farther apart than those obtained from the GPC data, the values computed from the latter technique being lower. The propagation steps in the formation of components D + A and B + C obey Bernoullian statistics with a P_m value of 0.33 for the former and 0.25 for the latter component, suggesting the possibility of two different reaction steps being involved. The proportion of component D + A in poly-α-methylstyrene samples prepared in cyclohexane is not pronounced, considering the high [LE] used in the present work. Because of the low dielectric constant of cyclohexane, one would have normally expected to see more dormant polymer than that computed from the NMR spectra. This would suggest that factors other than the dielectric constant of medium control the proportion of component D + A.

The principal conclusions to be drawn from this work, keeping in mind the results obtained in the previous studies [1-5], may be outlined as follows. Potassium-initiated polymerizations of α-methylstyrene in THF, p-dioxane, and cyclohexane as solvents yield multimodal GPC molecular weight distributions built up of low D + A and high B + C molecular weight components. The propagation reactions responsible for the formation of components D + A and B + C both follow Bernoullian statistics, the P_m value of the former being higher than that of the latter component, suggesting the possibility of two different reaction steps being involved. A part of component D + A, present in all poly-α-methylstyrene samples prepared with high [LE] in THF, in p-dioxane, and in cyclohexane as solvents, is dormant in nature. Under identical polymerization conditions, the proportion of this component in the polymer seems to be independent of the dielectric constant of the medium.

Further studies on the thermal decomposition and glass transition temperatures on polymers carrying excess component D + A are in progress, and the results will be published shortly.

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