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S. L. Malhotra[a]
[a] Département de Génie chimique Faculté des Sciences et de Génie, Université Laval Québec, Qué, Canada

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Polymerization of α-Methylstyrene in Tetrahydrofuran with Potassium as Initiator. V.

NMR Analyses of the Reaction Products

S. L. MALHOTRA

Département de Génie chimique
Faculté des Sciences et de Génie
Université Laval
Québec (Qué.), Canada, G1K 7P4

ABSTRACT

Nuclear magnetic resonance (NMR) studies on poly α-methylstyrene prepared at high temperatures (> 25°C) and having multimodal gel permeation chromatographic (GPC) molecular weight distributions built up of components D + A and B + C showed that their propagation reactions follow 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 polymers prepared at lower temperatures (5 to 25°C) and having unimodal GPC molecular weight distributions also showed the presence of component D + A whose propagation followed Bernoullian statistics but with lower (0.25 to 0.35) P_m value. On further lowering the polymerization temperatures to -25 or -78°C, the reaction continued to yield component D + A; however, the propagation reaction did not correspond to Bernoullian but a first-order Markov statistics. The propagation reaction responsible for the formation of component B + C, on the other hand, always obeyed Bernoullian propagation with P_m of about

0.26. This suggests that the formation of component D + A results from a reaction mechanism which is different from that of B + C.

INTRODUCTION

Gel-permeation chromatographic (GPC) molecular weight distributions of poly-α-methylstyrene initiated with potassium and potassium naphthalene in tetrahydrofuran (THF) [1, 2], p-dioxane [3], and cyclohexane [4] have been reported earlier. It was shown that, irrespective of the solvent used, the polymers prepared at high temperatures (> 25°C) and with high initial living end concentration, $[LE]_0$, yielded multimodal molecular weight distributions made up of components having average degree of polymerization, $\overline{DP}$, 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 denotes a dead polymer, A is the dormant polymer, and B and C denote polymers due to different ion-pair mechanisms. Similar assignments are also reported in the anionic polymerization of methyl methacrylate [5, 6] and styrene [7], as well as cationic polymerization of styrene [8-11] where bimodal GPC molecular weight distributions were observed. These were made on the basis of the C^{13} nuclear magnetic resonance (NMR) studies which showed that the species responsible for the formation of high and low molecular weight fractions were different in nature. Keeping this in mind, poly-α-methylstyrene samples with unimodal and multimodal GPC molecular weight distributions [1, 2] were analyzed by proton NMR spectroscopy and the data thus obtained were compared with those already reported on this polymer in the literature [12-21]. The principal results of these studies form the subject of the present communication.

EXPERIMENTAL

The data on the origin and purification of materials, method of polymerization and the characterization of products have been presented somewhere else [1, 2].

NMR Analyses

Nuclear magnetic resonance spectra of the polymers were recorded with a 220-MHz Varian Associates spectrometer at 25 and 100°C in carbon tetrachloride (CCl_4) and o-dichlorobenzene (o-$C_6H_4Cl_2$) as, solvents, respectively. Tetramethylsilane was used as the internal reference.

IR Analyses

Spectra of the polymers were recorded on KBr pellets with a Beckman-12 infrared spectrophotometer.

RESULTS AND DISCUSSION

Potassium-Initiated High-Temperature Polymerizations

In Fig. 1 are shown the GPC molecular weight distributions of some of the polymers used in the present study. Their analyses in terms of percent proportion of low D + A and high B and C molecular weight components is presented in Table 1 which also carries data for additional polymers whose GPC distributions are presented elsewhere [1, 2]. The results in Table 1 indicate that in order to prepare a polymer rich in component D + A, use of high $[LE]_0$ and high temperatures, which yield low conversions, is necessary.

In Fig. 2 are presented the IR spectra of two polymers, viz., M-14 and L-19, the former being 100% (GPC data in Table 3) and the latter having only 6% of component D + A. The spectra of these two polymers differ as follows: (a) The intensity of the -OH band at 3400 cm^{-1} is more pronounced in the lower molecular weight polymer M-14, which is quite normal, and (b) the make up of methylene, methyl, and benzene resonances between 2900 and 3100 cm^{-1} in the two cases is different. This could, however, very well arise out of the fact that the increase in the number of methylene, methyl and benzene groups (from M-14 to L-19) and the corresponding increase of absorptivity associated with each of the three resonances, do not follow the same scale.

Even if the proportions of methylene, methyl, and benzene groups in the two polymers were to be different, their analyses with IR do not appear to be feasible. Thus it was thought of interest to investigate the structural differences in these polymers with the help of NMR.

In a preliminary study, five samples viz., L-19, 66, 68, 67, and 65-B containing different GPC proportions of D + A, B, and C were selected. In Fig. 3 are shown the benzene protons of these polymers as observed in CCl_4 at 25°C. These appear between 2.7 and 3.5τ. In the case of polymers carrying the B + C component only, benzene

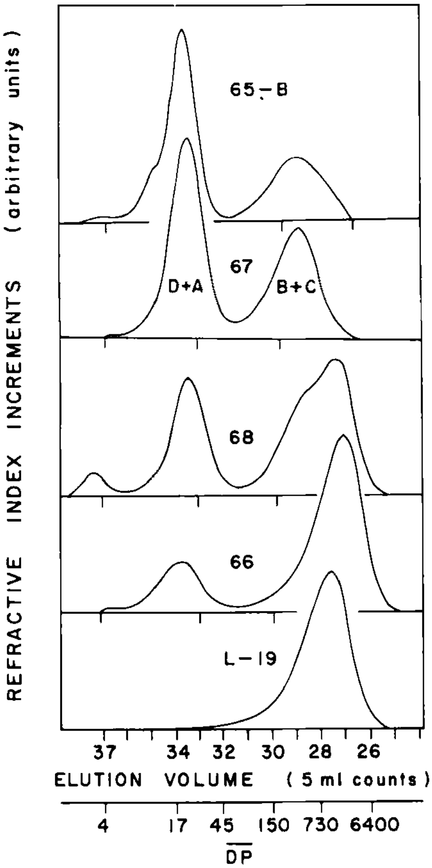

FIG. 1. GPC molecular weight distributions of poly-α-methylstyrene samples 65-B, 67, 68, 66, and L-19 initiated with potassium at 25°C in THF as solvent and polymerized at different temperatures. See Table 1 for other data.

protons appearing between 2.7 and 3.0 may be classified as syndiotactic, between 3.0 and 3.2 as heterotactic, and those between 3.2 and 3.5 as isotactic. In the case of the present polymers, however, where in addition to B + C, there are varying proportions of D + A, the above τ value assignments may not be rigorously true. In Fig. 3 it may be noted that as one moves from L-19 to 65-B the make up of

TABLE 1. GPC Analyses of Poly-α-methylstyrene Prepared at High Temperatures in THF as Solvent with Potassium Metal as Initiator

Sample	$[M]_0$ (mole/ liter)	$[LE]_0$ (mole/ liter)	Time of initiation at 25°C (min)	Temperature of polymerization (°C)	Yield $[P]_e$ (base-mole/ liter)[a]	Proportion (%)			
						D + A	B	B + C	C
62	7.20	0.01	30	60	1.58	6	21		73
63	6.70	0.07	20	60	2.10	19	26		45
64	6.70	0.12	20	60	1.47	45	20		35
67	6.70	0.10	25	55	1.06	59	15		26
68	6.70	0.10	35	55	1.96	39	26		35
66	6.70	0.10	50	55	3.05	18	30		52
53	6.25	0.13	10	55	3.16	37	19		44
60	6.25	0.26	20	55	3.75	54	21		25
65-B	6.25	0.31	30	55	3.85	62	23		15
54	6.40	0.07	15	50	1.72	22	14		64
57	6.44	0.08	15	50	1.88	27	15		58
69	6.45	0.11	15	50	2.00	38	20		42
56	5.82	0.02	10	50	0.63	22	10		68
58	5.85	0.04	10	50	0.78	40	21		39
59	5.80	0.09	10	50	1.31	50	15		35

(continued)

TABLE 1 (continued)

Sample	$[M]_0$ (mole/ liter)	$[LE]_0$ (mole/ liter)	Time of initiation at 25°C (min)	Temperature of polymerization (°C)	Yield $[P]_e$ (base-mole/ liter)[a]	Proportion (%)			
						D + A	B	B + C	C
L-11	4.50	0.23	5	40	2.10	74	4		22
40	4.95	0.15	5	40	1.83	67		33	
L-19	6.00	0.05	10	25	5.10	6	21		73

[a] Reaction was quenched with methanol when it attained a stationary state, thus the yield represents polymer at equilibrium conditions, the time to reach equilibrium varied from reaction to reaction [1, 2].

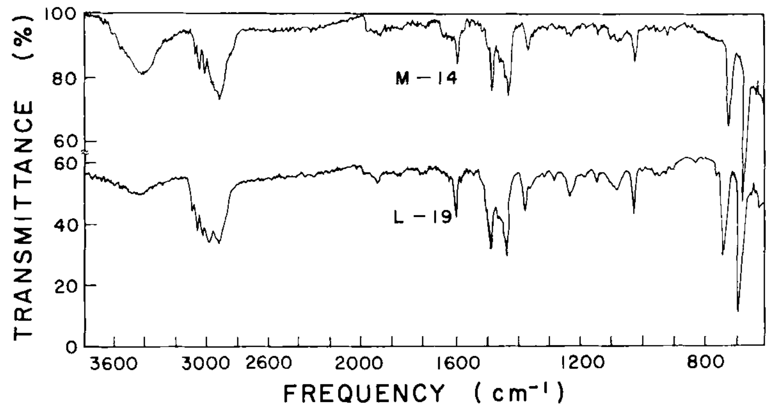

FIG. 2. IR spectra of poly-α-methylstyrene samples M-14 and L-19. See Table 3 and Table 1 for other data.

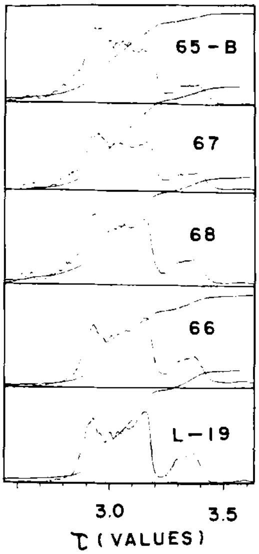

FIG. 3. 220 MHz NMR spectra of the benzene protons of poly-α-methylstyrene samples 65-B, 67, 68, 66, and L-19 observed in CCl_4 at 25°C in the range of 2.7 to 3.5 τ.

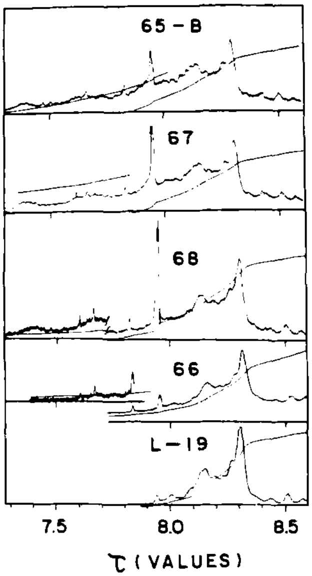

FIG. 4. 220 MHz spectra of the β-methylene protons of poly-α-methylstyrene samples 65-B, 67, 68, 66, and L-19 observed in o-$C_6H_4Cl_2$ at 100°C in the range of 7.3 to 8.6 τ.

benzene protons changes as follows: the relative intensity of protons between 2.7 and 3.0 τ increases whereas intensity values of those appearing between 3.0 and 3.2 τ are lower; and the intensity of protons between 3.2 and 3.5 τ decreases regularly.

Although it is possible that these changes in intensity result from the varying proportions of syndiotactic, heterotactic and isotactic configurations in these polymers, yet these have been assigned to the downfield placement (lower τ values) of benzene protons due to component D + A. The exact assignments of benzene protons corresponding to component D + A is difficult to assess, however.

In Fig. 4 are shown the β-methylene protons of polymers L-19, 66, 68, 67, and 65-B observed in o-$C_6H_4Cl_2$ at 100°C in the range of 7.3 to 8.6 τ. The β-methylene protons in L-19 appear between 7.9 to 8.6 τ, with an important peak at 8.3 τ corresponding to the rrr tetrad. As one moves from L-19 to 65-B, the peak due to the rrr tetrad remains stationary at 8.3 τ although its intensity decreases regularly. Furthermore, in polymers 66, 68, 67, and 65-B other peaks start to appear between 7.2 to 8.0 τ, the most prominent of these being at 7.95 τ. The intensity of this peak varies with the polymer sample. It would appear

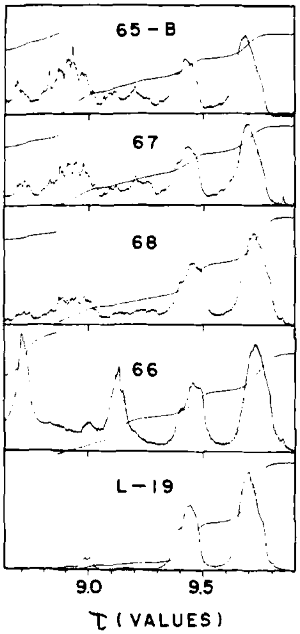

FIG. 5. 220 MHz NMR spectra of the α-methyl protons of poly-α-methylstyrene samples 65-B, 67, 68, 66, and L-19 observed in o-$C_6H_4Cl_2$ at 100°C in the range of 8.6 to 9.8 τ. See Tables 1 and 2 for other data.

that the β-methylene protons associated with component D + A are placed between 7.5 to 8.0 τ (sample 66), 7.3 to 8.0 τ (sample 68) and 7.2 to 8.2 τ (samples 67 and 65-B) depending upon their proportion in the polymer. This makes it difficult to analyze the placement of various tetrads in the β-methylene protons of D + A.

In Fig. 5 are presented the α-methyl protons of polymers L-19, 66, 68, 67, and 65-B observed in o-$C_6H_4Cl_2$ at 100°C in the range of 8.6 to 9.9 τ. The α-methyl protons in L-19 appear between 8.9 and 9.9 τ, with important peaks at 9.0, 9.43, and 9.69 assigned to the triads mm, mr, and rr, respectively [12, 18, 21]. In polymer samples 66, 68, 67, and 65-B, there are numerous other peaks between 8.6 and 9.25 τ. The most prominent of these peaks in the spectra of samples 68, 67, and 65-B are at (8.65, 8.68, 8.71 τ), (8.80, 8.83, 8.86, 8.91, 8.94, 8.97 τ), and 9.06, 9.09, 9.12, 9.20, 9.23, 9.26 τ). These appear to be associated with the different triads due to the methyl groups of the D + A component in the polymer.

The two very prominent peaks in the case of sample 66, however, seem to be of different nature as compared to those in samples 68, 67, and 65-B. These peaks at 8.7 and 9.13 τ may correspond to methylene and methyl protons of yet another component in polymer 66 which is different to those of D + A and B + C in structure. This conclusion was reached from the results of the thermal decomposition of poly-α-methylstyrene samples 66, 67, 68, and 65-B at various temperatures (150-300° C) [22]. The NMR analyses of the 300° C decomposed polymers 67, 68, and 65-B showed the presence of all of the peaks which were present in the undecomposed polymers as well; however on 50 min isothermal decomposition at 250° C of sample 66 the resulting product showed the absence of peaks at 8.7 and 9.13 τ in its NMR spectrum.

In order to assign the peaks between 8.6 and 9.35 τ to the various triads due to α-methyl groups of component D + A, two polymer samples, viz., 65-B and M-14, which yielded well defined spectra were selected. In Fig. 6 are presented the spectra of the methyl protons of component D + A of these two polymers observed in o-$C_6H_4Cl_2$ at 100°C in the range of 8.6 to 9.35 τ. In the spectrum of

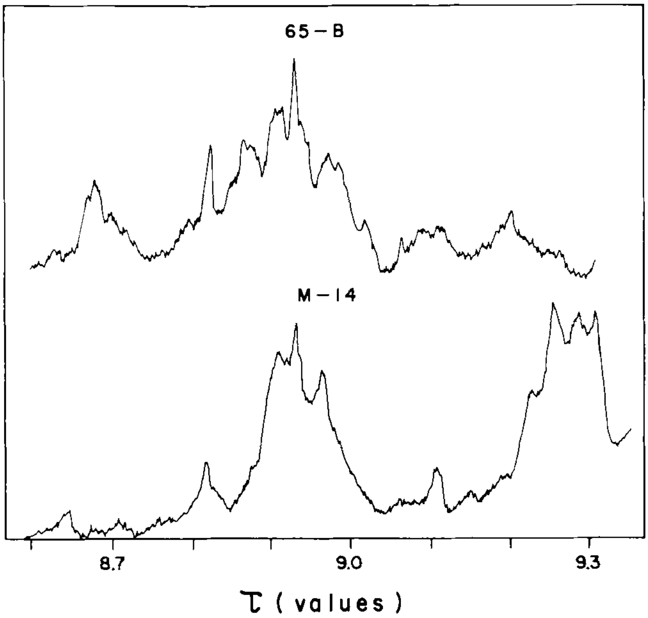

FIG. 6. 220 MHz NMR spectra of the α-methyl protons of the D + A component of poly-α-methylstyrene samples 65-B and M-14 observed in o-$C_6H_4Cl_2$ at 100°C in the range of 8.6 to 9.35 τ. See Tables 2 and 3 for other data.

sample 65-B, the region carrying a major portion of the methyl protons lies between 8.75 and 9.0 τ whereas in the spectrum of sample M-14 the methyl protons are located between 8.75 and 9.05 τ as well as between 9.2 and 9.35 τ. The region between 8.6 and 8.75 τ in both polymers carries a small proportion of the methyl protons, although these are more pronounced in the spectrum of sample 65-B as compared to that of sample M-14. The various regions in the spectra of these two polymers may be assigned to different triads, as follows: Sample 65-B: (a) 8.6-8.75 τ, with peaks at (8.65, 8.68 and 8.71 τ) to mm triads; (b) 8.75-9.05 τ, with peaks at (8.80, 8.83, 8.86 τ) to mr and those at (8.91, 8.94, 8.97 τ) to rm triads; (c) 9.05-9.35 τ, with peaks at (9.06, 9.09, 9.12 τ) as well as (9.20, 9.23, 9.26 τ) to rr triads; Sample M-14: (a) 8.6-8.75 τ, with peaks at (8.65, 8.68, 8.71 τ) to mm triads; (b) 8.75-9.05 τ, with peaks at 8.82 τ to mr and those at (8.90, 8.93, 8.96 τ) to rm triads; (c) 9.05-9.35 τ, with peaks at (9.23, 9.255, 9.286, 9.31 τ) to rr triads.

These assignments of mm, mr + rm, and rr triads to the three regions 8.6-8.75, 8.75-9.05, and 9.05-9.35 τ, respectively, are made exclusively on the basis that similar triads due to the methyl protons of the high molecular weight component B + C have also been shown [12, 18, 21] to follow the ascending order of magnetic field.

By making use of these assignments, the triad analyses for methyl protons associated with the components D + A and B + C were made on all polymers listed in Table 1, and the results of these analyses are presented in Table 2.

It may be added here that the immediate region around 9.0 τ, which carries contribution due to the mm triads of the high molecular weight component B + C, must be taken into account prior to making any calculations for mr or rm triads of component D + A. This has been achieved in two steps assuming that the high molecular weight component B + C in all the polymers studied obey Bernoullian propagation statistics similar to that in polymer L-19 (cf. Table 2).

In the first step the ratio of the integral counts covering the regions 9.7-9.9 τ [$rr = (1 - P_m)^2$] and 9.5-9.7 τ [$mr = 2P_m(1 - P_m)$] is used to compute P_m of component B + C, and consequently the values of mm, mr and rr are known. In the second step, the contribution due to mm integral counts present in the rm or rr region of component D + A is calculated with mr and rr values of component B + C and their integral counts on the NMR spectrum. This mm integral count is added to that of B + C and subtracted from that of component D + A in order to compute the NMR-characterized percent contributions of each of the two components.

The analyses of the results in Tables 1 and 2 reveal two interesting observations. First, the proportions of component D + A calculated by the NMR technique do not agree completely with those

TABLE 2. Intensity of Methyl Protons Associated with Low and High Molecular Weight Part of the Polymers and Their Propagation Statistics as Computed from the NMR Spectra for Poly-α-methylstyrenes Prepared with Potassium at High Temperature[a]

	Methyl protons of component D + A					Methyl protons of component B + C				
	Intensity associated with various configurations					Intensity associated with various configurations[b]				
Sample	8.6 to 8.75 τ mm	8.75 to 9.05 τ mr	9.05 to 9.3 τ rr	Bernoullian statistics $\sim P_m$	Proportion (%)	mm	mr	rr	Bernoullian statistics $\sim P_m$	Proportion (%)
63	0.14	0.44	0.42	0.36	18	0.06	0.37	0.57	0.25	82
64	0.16	0.47	0.37	0.40	37	0.07	0.38	0.55	0.26	63
68	0.15	0.47	0.38	0.38	26	0.07	0.39	0.54	0.26	74
67	0.17	0.47	0.36	0.40	44	0.07	0.39	0.54	0.27	56
53	0.17	0.47	0.36	0.40	23	0.07	0.37	0.56	0.25	77
65-B	0.19	0.51	0.30	0.45	52	0.08	0.40	0.52	0.28	48
57	0.15	0.45	0.40	0.38	20	0.06	0.36	0.58	0.24	80
69	0.16	0.50	0.34	0.40	30	0.06	0.37	0.57	0.25	70
56	0.15	0.44	0.41	0.38	16	0.06	0.37	0.57	0.25	84
58	0.15	0.44	0.41	0.38	26	0.06	0.39	0.55	0.26	74
59	0.16	0.50	0.34	0.40	38	0.07	0.38	0.55	0.26	62

40	0.14	0.43	0.43	0.35	18	0.06	0.38	0.56	0.25	82
L-19	-	-	-	-	2	0.05	0.37	0.58	0.24	98

[a] See Table 1 for other reaction conditions.

[b] By using assignments for mm, mr, and rr triads presented in the literature [12, 18, 21].

obtained from the GPC data presented in Table 1, the values obtained by the former technique being always lower. Secondly, the propagation steps in the formation of components D + A and B + C obey Bernoullian statistics, with P_m values ranging from 0.34 to 45 for the former and 0.26 for the latter component.

This difference in the P_m values of components D + A and B + C formed during the potassium-initiated and high-temperature polymerization of α-methylstyrene leads one to speculate that the reaction steps for their formation may not be the same.

Metal Complex-Initiated High-Temperature Polymerizations

In an earlier study [2], dealing with the GPC molecular weight distributions of poly-α-methylstyrene initiated with potassium and potassium naphthalene in THF as solvent, it was observed that the presence of naphthalene reduced the formation of GPC-characterized D + A component. In order to study the role of complexing agents on the NMR characterized component D + A, solutions of α-methylstyrene were initiated with potassium naphthalene, potassium anthracene, and butyllithium tetramethylethylenediamine (Buli-TMEDA) and polymerized at 50°C.

In Fig. 7 are shown the GPC molecular weight distributions of poly-α-methylstyrene samples M-29, M-26, 56-BB, and M-14 initiated with metal complexes and polymerized at 50°C. One notes that polymers M-29 and M-26 are rich in high molecular weight component B + C, whereas the other two (56-BB and M-14) are rich in component D + A. This is further indicated in the NMR spectra of these polymers presented in Figs. 8 and 9 where are shown their β-methylene and α-methyl protons, respectively. Polymers M-29 and M-26 have a major portion of their β-methylene and α-methyl protons located in the zone assigned to B + C component, while in the case of 56-BB and M-14 these protons are placed in zones assigned to D + A as well as B + C components. The data, based on the GPC molecular weight distributions shown in Fig. 7 and the NMR spectra presented in Figs. 8 and 9, are listed in Table 3. The analyses of the data in Table 3 reveal once again that the proportions of GPC- and NMR-characterized component D + A do not agree, the value obtained by the latter technique being generally lower except in the case of M-29, where the reverse was found true.

A comparison of the data obtained on the GPC- and NMR-characterized polymers prepared with (M-29) and without (sample 57) complexing agent revealed that although the presence of the complexing agent does reduce the GPC proportion from (27% to 9%) of component D + A, the NMR-characterized component D + A reduces very little

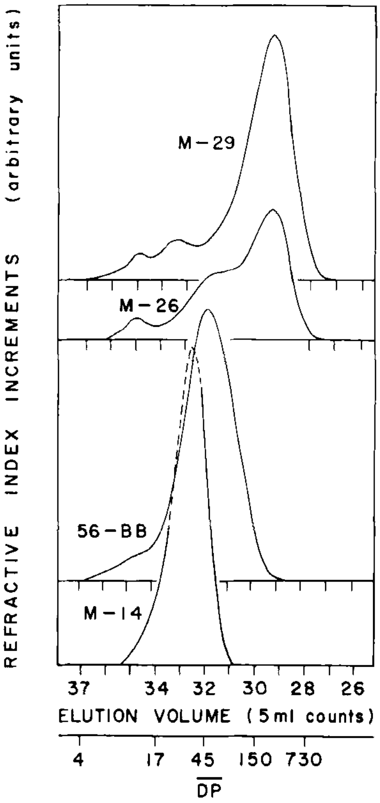

FIG. 7. GPC molecular weight distributions of poly-α-methylstyrene samples M-29, M-26, 56-BB, and M-14 initiated with potassium complexes in THF as well as in bulk at 25°C and polymerized at 50°C. See Table 3 for other data.

(from 20% to 18%). The P_m value of 0.38 in the NMR-characterized D + A (sample 57), however, reduced to 0.30 in M-29. The P_m value of 0.26 associated with component B + C in sample 57 remained the same in the case of M-29 as well.

In the case of Buli-TMEDA-initiated polymerization (samples 56-BB and M-14), it was observed that these 100% GPC-characterized products yielded only 23% and 49%, respectively, of NMR-characterized content in them. The P_m values associated with components D + A of 56-BB and M-14 were 0.30 and 0.29, respectively.

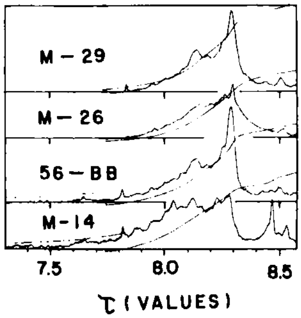

FIG. 8. 220 MHz NMR spectra of the β-methylene protons of poly-α-methylstyrene samples M-29, M-26, 56-BB, and M-14 observed in o-$C_6H_4Cl_2$ at 100° C, in the range of 7.4 to 8.6 τ. See Table 3 for other data.

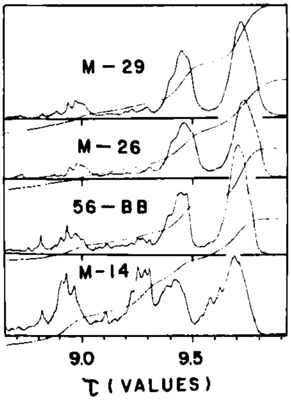

FIG. 9. 220 MHz NMR spectra of the α-methyl protons of poly-α-methylstyrene samples M-29, M-26, 56-BB, and M-14 in o-$C_6H_4Cl_2$ at 100°C in the range of 8.7 to 9.9 τ. See Table 3 for other data.

From these observations it can be concluded that in the presence or absence of complexing agents the NMR-characterized contents of D + A in polymers do not vary by much; however, their presence in general does lower the P_m values. The P_m values of B + C component, on the other hand, remain unaffected irrespective of the presence, absence, or the nature of the complexing agent used.

TABLE 3. GPC and NMR Analyses of Poly-α-methylstyrene Prepared with Metal Complexes in THF and in Bulk at 50°C

Sample	$[M]_0$ (mole/ liter)	Initiator	$[LE]_0$ (mole/ liter)	Yield (base-mole/ liter)	Proportion D + A (%)		Intensity associated with various configurations of D + A				Propagation statistics B + C
					GPC	NMR	mm	mr	rr	P_m	P_m
M-29	6.40	Potassium naphthalene	0.06	2.00	9	18	0.13	0.39	0.49	0.30	0.25
M-26	5.80	Potassium anthracene	0.02	0.44	-	18	0.10	0.40	0.50	0.30	0.26
56-BB	Bulk	BuLi + TMEDA	0.06	3.00	100	23	0.09	0.43	0.48	0.30	0.22
M-14	Bulk	BuLi (excess) + TMEDA	0.08	2.00	100	49	0.08	0.41	0.51	0.29	0.22

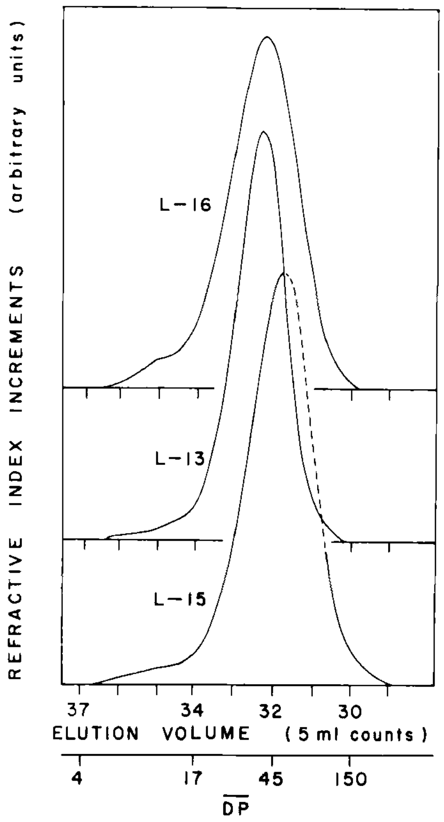

FIG. 10. GPC molecular weight distributions of poly-α-methylstyrene samples L-16, L-13, and L-15 initiated with potassium and its complexes in THF at 25°C and polymerized at different temperatures. See Table 4 for other data.

Potassium-Initiated Low-Temperature Polymerizations

In Fig. 10 are presented the GPC molecular weight distributions of poly-α-methylstyrene samples initiated at 25°C with potassium (L-16, L-13) and potassium naphthalene (L-15) in THF and polymerized at 15, 5, and -78°C respectively. On the basis of the unimodal molecular weight distributions of the polymers, it may be assumed that these correspond to one or the other of components D + A and

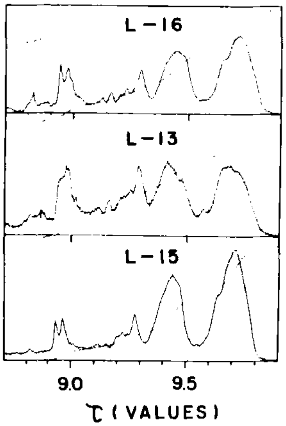

FIG. 11. 220 MHz spectra of the α-methyl protons of poly-α-methylstyrene samples L-16, L-13, and L-15 observed in o-$C_6H_4Cl_2$ at 100°C in the range of 8.7 to 9.9 τ. See Table 4 for other data.

B + C. In the data derived from Fig. 10 and listed in Table 4, these have been assigned arbitrarily to component D + A.

In Fig. 11 are shown the NMR spectra of the methyl protons of poly-α-methylstyrene samples L-16, L-13, and L-15 in the range 8.7 to 9.8 τ. It would appear that, contrary to the GPC assignment of these polymers solely to component D + A, these carry a large proportion of B + C component. The NMR spectra of component D + A in these polymers, however, show them to be more syndiotactic than those prepared under similar conditions but at high temperatures. The NMR data derived from Fig. 11 are also presented in Table 4.

The results of the data analyses in Table 4 again reveal that the GPC- and NMR-characterized proportions of component D + A do not agree, the values computed from the latter technique being lower. The propagation reactions in the polymers prepared at 15 (L-16) and 5°C (L-13) still follow Bernoullian statistics, the P_m value being slightly lower (0.25) than that of the former (0.30). The propagation reaction in the polymer prepared at -78°C, however, did not correspond to Bernoullian, but a first-order Markov statistics with $P_{m/r} = 0.62$ and $P_{r/m} = 0.19$. The propagation reaction for the formation of component B + C was found to obey Bernoullian statistics ($P_m = 0.26$) at all temperatures studied.

Similar observations are reported during the polymerization of 1,6-heptadienes [23, 24] where the propagation reaction occurs by

TABLE 4. GPC and NMR Analyses of Poly-α-methylstyrene Prepared with Potassium and Its Complexes in THF at Low Temperatures

Sample	$[M]_0$ (mole/ liter)	Initiator	$[LE]_0$ (mole/ liter)	Temperature of polymerization (°C)	Yield (base-mole/ liter)	Proportion D + A (%)		Intensity associated with various configurations of D + A				Propagation statistics for B + C
						GPC	NMR	mm	mr	rr	P_m	P_m
L-16	2.10	Potassium	0.04	15	0.65	100	34	0.08	0.42	0.50	0.30	0.26
L-13	1.50	Potassium	0.02	5	0.33	100	41	0.07	0.35	0.58	0.25	0.28
L-15	2.20	Potassium naphthalene	0.10	-78	1.90	100	23	0.09	0.29	0.62	$P_{m/r} = 0.62$ $P_{r/m} = 0.19$	0.26
M-28*	5.80	Potassium anthracene	0.06	25	1.00	70	35	0.11	0.48	0.42	0.35	0.26
M-30*	6.40	Potassium naphthalene	0.06	-25	2.70	100	14	0.11	0.31	0.58	$P_{m/r} = 0.58$ $P_{r/m} = 0.24$	0.26
M-11*	2.50	Potassium anthracene	0.05	-78	3.00	100	19	0.13	0.26	0.61	$P_{m/r} = 0.54$ $P_{r/m} = 0.18$	0.26

[a] Polymerization time: 30 min.

alternating intramolecular and intermolecular steps. In one of these studies [23], it was observed that the propagation reaction for both steps followed Bernoullian statistics and had the same P_m value of 0.31, when the polymerization was carried out at high temperatures (100°C). In polymers prepared at low temperatures (-30 to 55°C) the intramolecular propagation remained Bernoullian while the intermolecular step fitted first-order Markov statistics [24].

If one draws a parallel between the results obtained in the present studies with those reported on the polymerization of 1,6-heptadienes, one would be led to conclude that the reaction steps for the formation of components D + A and B + C at high temperatures are different.

Metal Complex-Initiated Low-Temperature Polymerizations

In Fig. 12 are presented the GPC molecular weight distributions of poly-α-methylstyrene samples initated at 25°C with potassium anthracene (M-28, M-11) and potassium naphthalene (M-30) and polymerized at 25, -78, and -25°C, respectively. The data based on these distributions are listed in Table 4. One notes that these three samples have different proportions of GPC-characterized D + A component. The NMR spectra of these polymers is shown in Fig. 13, and their analyses in terms of NMR-characterized components D + A and P_m values associated with the two components D + A and B + C are also presented in Table 4. It may be remarked that, as usual, the GPC and NMR characterized proportions of component D + A are different. The polymers M-30 (-25°C) and M-11 (-78°C) prepared at low temperatures do not correspond to a Bernoullian propagation but obey a first-order Markov model. Furthermore the deviation from Bernoullian statistics at -78°C is more pronounced ($P_{m/r} = 0.54$, $P_{r/m} = 0.18$) than that at -25°C ($P_{m/r} = 0.58$ and $P_{r/m} = 0.24$). The propagation statistics for component B + C, however, remain Bernoullian at all temperatures, with a P_m of 0.26. These results agree well with those reported on the polymerization of 1,6-heptadienes [24] and further support the concept that the components D + A and B + C must be the products of two different reaction steps.

Nature and $\overline{DP}$ of the NMR-Characterized Low Molecular Weight Polymer

In an earlier study [1] dealing with the polymerization of α-methylstyrene with potassium as initiator and THF as solvent, it was shown that a major part of the component D + A in poly-α-methylstyrene

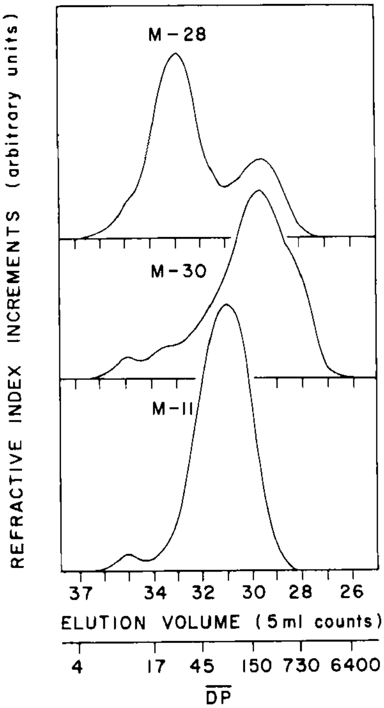

FIG. 12. GPC molecular weight distribution of poly-α-methylstyrene samples M-28, M-30, and M-11 initiated with potassium complexes in THF at 25° C and polymerized at different temperatures. See Table 4 for other data.

sample L-11 was dormant in nature. In order to correlate the GPC results of the earlier study with the NMR data of the present one, the experiment supporting the dormant nature of component D + A has also been retained for the present study. In this experiment a 4.5 M solution of α-methylstyrene was initiated at 40° C and distributed in four ampoules. All of these were polymerized at 40° C. After 24 hr, L-11 was opened at 40° C, whereas the other three were further polymerized at -25° C for periods of 15 (L-12), 30 (L-26), and 60 min (L-27), respectively. The GPC molecular weight distributions of these four polymers are presented in Fig. 14 and their NMR spectra are shown in Fig. 15. The data obtained from the analyses of these two figures are listed in Table 5.

The highlights of the data in Table 5 may be outlined as follows. The species responsible for the propagation reaction at -25° C (L-12, L-26 and L-27) originate from the GPC envelope of component D + A

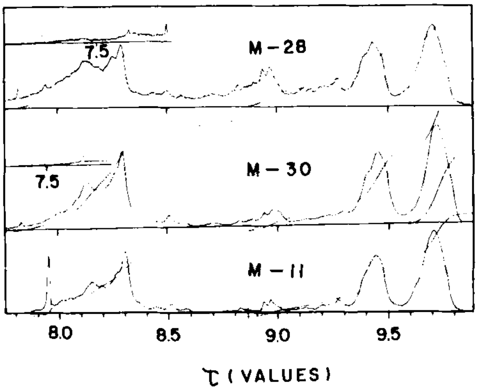

FIG. 13. 220 MHz NMR spectra of the β-methylene and α-methyl protons of poly-α-methylstyrene samples M-28, M-30, and M-11 observed in o-$C_6H_4Cl_2$ at 100°C in the range of 7.2 to 9.8 τ. See Table 4 for other data.

as depicted in Fig. 14. The yield (GPC as well as NMR data) of component D + A remains essentially constant, even after polymerizations at -25°C for different periods, suggesting that a major part of this component is dormant in nature. The P_m value of 0.39 for component D + A in L-11 remains unchanged on further polymerizations at -25°C. The P_m value of 0.27 for component B + C increases to 0.28 in L-26 and to 0.30 in the case of L-27, indicating that the propagating species at -25°C have their origin from a low molecular weight growing polymer with a higher P_m value than that of B + C. This higher P_m value polymer may or may not be part of the NMR-characterized component D + A.

The results of the analyses of the GPC- and NMR-characterized component D + A listed in Tables 2 to 5 have been repeatedly shown to disagree, the latter technique consistently yielding lower values. If one assumes that the dormant part of component D + A is that characterized by the NMR technique, it would mean that under the GPC envelope of D + A there are two different types of polymer, one dormant and one living. Based on the GPC and NMR proportions of component D + A and the total $\overline{DP}$ from $\overline{M}_n$ and $\overline{M}_w$ of the GPC component D + A, an attempt has been made to compute the $\overline{DP}$ of the NMR-characterized component D + A, in some of the polymers, by using Eqs. (1) and (2).

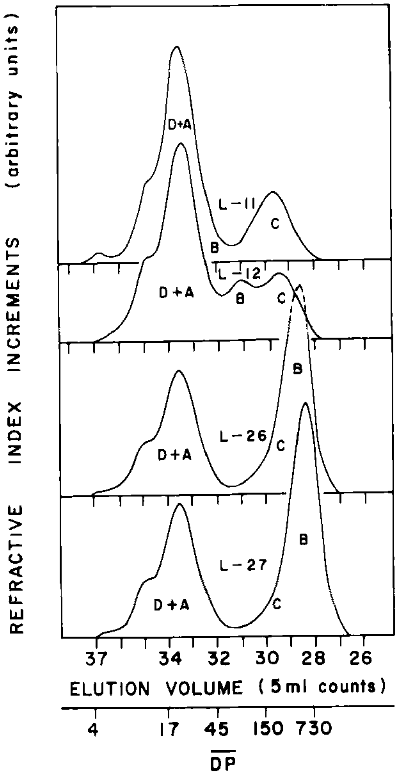

FIG. 14. GPC molecular weight distributions of poly-α-methylstyrene samples L-11, L-12, L-26, and L-27, initiated from a 4.5 M solution with potassium as initiator and THF as solvent, polymerized at 40°C (L-11), and further polymerized at -25°C for 15 min (L-12), 30 min (L-26), and 60 min (L-27). See Table 5 for other data.

$$\%\,(D + A)_{NMR} \times \overline{DP}(D + A)_{NMR} + [\,100 - \%(D + A)_{NMR}]$$

$$\times\, \overline{DP}\,[\,100 - \%(D + A)_{NMR}]$$

$$= 100 \times \overline{DP}\,(D + A)\ (\text{from } \overline{M}_w) \qquad (1)$$

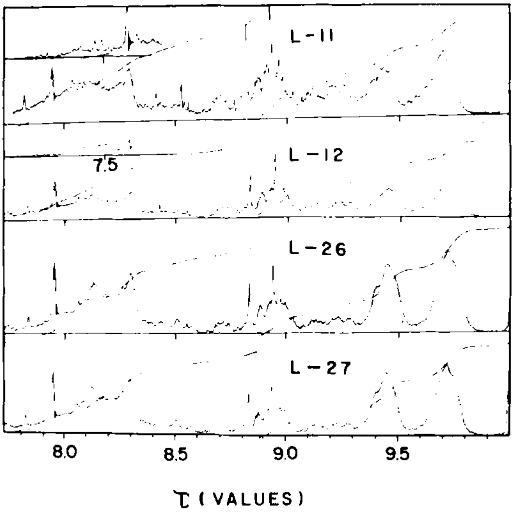

FIG. 15. 220 MHz NMR spectra of the β-methylene and α-methyl protons of poly-α-methylstyrene samples L-11, L-12, L-26, and L-27 observed in o-$C_6H_4Cl_2$ at 100°C in the range of 7.2 to 9.8 τ. See Table 5 for other data.

$$\frac{\%(D + A)_{NMR}}{\overline{DP}(D + A)_{NMR}} + \frac{100 - \%(D + A)_{NMR}}{\overline{DP}[100 - \%(D + A)_{NMR}]} = \frac{100}{\overline{DP}(D + A)\ (\text{from } \overline{M}_n} \tag{2}$$

The values for $\overline{DP}$ (D + A)$_{NMR}$ were selected from 10 to 20 and inserted in Eq. (1) to determine the corresponding values of $\overline{DP}$[100 - % (D + A)$_{NMR}$]. The values of $\overline{DP}$(D + A)$_{NMR}$ and $\overline{DP}$[100 - %(D + A)$_{NMR}$] yielding the best fit in Eqs. (1) and (2) were retained and are listed in Table 6. In the case of samples 65-B and L-11 which were polymerized by using high [LE]$_0$ (> 0.2 mole/liter), the $\overline{DP}$ of the dormant polymer was found to be 14 whereas in polymers prepared at lower [LE]$_0$ (≲ 0.1 mole/liter) this $\overline{DP}$ was 17. The $\overline{DP}$ of the remainder active polymer under the GPC envelope of component D + A was always higher than 40.

The principal conclusions to be drawn from this study may be summarized as follows. Polymerization of α-methylstyrene at high temperatures (> 25°C), initiated with high [LE]$_0$ of metal and metal complexes in THF as solvent, yields bimodal GPC molecular weight

TABLE 5. GPC and NMR Analyses of Poly-α-methylstyrene Prepared from 4.5 M Solution of Monomer with Potassium as Initiator and THF as Solvent, under Different Conditions of Temperature and Time

Sample	$[LE]_0$ (mole/liter)	Time of polymerization (hr)	Temperature of polymerization (°C)	Total yield (base-mole/liter)	Yield D + A (base-mole/liter)		Intensity associated with various configurations of D + A				Propagation statistics B + C
					GPC	NMR	mm	mr	rr	P_m	P_m
L-11	0.23	24	40	2.10	1.55	1.16	0.14	0.51	0.35	0.39	0.27
L-12	0.28	24 0.25	40 -25	2.70	1.73	1.43	0.14	0.53	0.33	0.39	0.27
L-26	0.25	24 0.5	40 -25	3.00	1.68	1.05	0.15	0.51	0.34	0.39	0.28
L-27	0.24	24 1.0	40 -25	3.43	1.52	1.13	0.14	0.50	0.36	0.39	0.30

TABLE 6. Computation of the Average Degree of Polymerization $\overline{DP}$ for the NMR-Characterized Low Molecular Weight Component on the Basis on $\overline{M}_n$, $\overline{M}_w$, and GPC Data for D + A

	$\overline{DP}$ (D + A) GPC		% (D + A)		NMR-characterized data on $\overline{DP}$	
Sample	From $\overline{M}_n$	From $\overline{M}_w$	GPC	NMR	$\overline{DP}$ $(D + A)_{NMR}$	$\overline{DP}$ $[100 - \%(D + A)_{NMR}]$
65-B	16	19	63	52	14	40
L-11	18	21	77	55	14	77
67	20	24	58	44	17	51
M-14	25	31	100	49	17	46
L-13	27	34	100	41	17	48
L-16	31	40	100	34	17	50
L-15	40	52	100	23	17	62

distributions built up of components D + A, B and C. The propagation reactions responsible for the formation of components D + A and B + C at high temperatures follow Bernoullian statistics, the P_m value in the former being higher (0.34 to 0.45) than that in the latter component (0.26). This suggests that the propagation step for component D + A is different than that for B + C. On lowering the temperature of polymerization to -25 or -78° C the propagation step in D + A does not correspond to Bernoullian statistics but obeys a first-order Markov model. The propagation reaction for B + C, however, follows Bernoullian statistics at all temperatures. A major portion of component D + A is dormant in nature and has a $\overline{DP}$ in the range of 14 to 17.

Further studies on the NMR analyses of poly-α-methylstyrene samples prepared in p-dioxane and cyclohexane are in progress, and these will be reported in due course.

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