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Polymerization of α -Methylstyrene in p-Dioxane with Potassium as Initiator. III. Gel-Permeation Chromatographic Analyses of Polymers

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ABSTRACT

Gel-permeation chromatographic studies on poly- α -methylstyrene initiated with potassium and potassium-naphthalene in p-dioxane as solvent and polymerized at 5, 15, 25, and 40°C, have been carried out. Bimodal and trimodal distributions are observed in these polymers. It has been shown that these multimodal distributions do not arise because of the monofunctional and bifunctional living ends produced by the reaction of solvent dioxane with the living polymer. These, on the other hand, may be related to the presence of different ion-pairs which contribute to the reaction but to different extents. Contrary to the belief that only contact ion-pairs are responsible for propagation in p-dioxane because of its low dielectric constant, the presence of solvent-separated ion-pairs yielding reversible propagation has been speculated. The different components (D + A), B, and C, similar to the ones present in the α -methylstyrene-potassium tetrahydrofuran system, have been found in the present study also and are attributed to the dead and a dormant polymer, solvent-separated ion-pair polymer, and that due to a contact pair, respectively. The extent of the formation

of component (D + A) has been linked directly to the concentration of living ends. In reactions where naphthalene was used along with potassium for initiation purposes, a unique component yielding reversible propagation was observed. This has been attributed to the presence of polymer due to potassium-naphthalene complex which is different in character to a contact ion-pair but may resemble a solvent-separated ion-pair.

INTRODUCTION

Thermodynamic studies on the polymerization of α -methylstyrene initiated with potassium in p-dioxane as solvent were reported earlier from this laboratory [1]. The variation of the concentration of monomer at equilibrium $[M]_e$ with the concentration of polymer at equilibrium $[P]_e$ was linear at all temperatures studied. Most of the experimental points obeyed the linear curves of $[M]_e$ versus $[P]_e$, and this was considered normal in view of the fact that the living end concentrations $[LE]$ used in these experiments were generally low and were of the order of 3.0×10^{-3} mole/liter. These $[LE]$ values were calculated from the viscosity-average molecular weight, \overline{M}_v . In recent studies [2], it was found that the $[LE]$ based on \overline{M}_n calculated from gel-permeation chromatography (GPC) and \overline{M}_v were very much different.

In order to find the values of $[LE]$ from \overline{M}_n , GPC molecular weight distributions were studied on all polymers prepared in p-dioxane as solvent. Most of these exhibited bimodal or trimodal distributions which could be split into three major components, and the $[LE]$ values based on \overline{M}_n were very much different than those calculated from \overline{M}_v . Multimodal distributions in living polymers growing simultaneously from both ends in a medium containing terminating impurities was discussed by Figini [3] as well as by Orofino and Wenger [4]. These authors assumed that the terminating agents attack the growing ends indiscriminately and hence the reaction produces three types of polymers: dead polymers, polymers having only one growing end, and polymers possessing two growing ends. Brower and McCormick [5], who initiated the polymerization of styrene in p-dioxane by adding an electron-transfer initiator (sodium-naphthalene) to the monomer, found that the distribution of molecular weight of the polymer formed were indeed bimodal in character, the lower molecular weight component having half the average

molecular weight \overline{M}_n of the higher molecular weight component. In the present studies, the molecular weights of different components in the bimodal distributions of any polymer did not necessarily correspond to a 1:2 ratio.

Recently Schmitt and Schulz [6] have shown that the polymerization of styrene in 3-methyltetrahydrofuran initiated with oligomers of α -methylstyrene, yielding bimodal GPC distributions were due to two different ion-pairs responsible for the polymerization. Furthermore in an earlier work from this laboratory on the polymerization of α -methylstyrene in tetrahydrofuran [7] initiated with potassium and potassium-naphthalene, bimodal distributions were related to different ion-pairs. Keeping this in mind, the GPC chromatograms showing bimodal or trimodal distributions were separated into different components, and the values of [LE] associated with each of them were calculated. The principal results of this study form the subject of this publication.

EXPERIMENTAL

The purification of materials used and the experimental procedure employed in the present study have already been presented in an earlier publication [1] and need not be discussed again. However some relevant points concerning the GPC distribution analyses need clarification and hence shall be dealt with here. In the present studies, three different set of columns were used to characterize the polymers with GPC. In the first set (a), two 3-ft long columns with maximum rated porosity of 1.0×10^6 and 1.5×10^5 Å were connected in series with two 4-ft long columns of porosity 3×10^3 and 250 Å. In the second set (b), only three columns, each 4 ft long, were used in series; these had the maximum rated porosity of 1.0×10^6 , 1.5×10^5 , and 3×10^3 Å, respectively. The third set of column arrangements (c), consisted of four 4-ft long columns with maximum rated porosity of 1.0×10^6 , 1.5×10^5 , 3.0×10^3 , and 250 Å, respectively.

RESULTS AND DISCUSSION

In Tables 1-4 are presented the results of the analyses of GPC chromatograms obtained on polymers prepared in p-dioxane. These results shall be discussed in the light of the studies carried out in THF as solvent [2, 7] as well as the results presented by Brower and McCormick [5].

TABLE 1. GPC Analysis Showing $[P]_e$ and $[LE]$ Associated with Different Components in Poly- α -methylstyrene Prepared at 5°C with Potassium as Initiator and p-Dioxane as Solvent

No.	$[M]_0$ (mole/ liter)	$[P]_e$ (base-mole/liter) (by GPC)			$[LE]$ (mole/liter) (by GPC)			$[LE]$ (by \bar{M}_v) (mole/ liter)		
		(D+A)	B	(B+C) C	Total $[P]_e$ (D+A)	B	(B + C) C		Total $[LE]$	
1	1.21	0.02		0.40	0.42	0.002	0.001	0.003	0.001	
2	1.62	0.07		1.07	1.14	0.011	0.007	0.018	0.003	
L-114	2.00	0.15	0.55		0.72	1.42	0.020	0.004	0.002	0.026
3	2.27	0.10		1.72	1.82	0.003	0.004	0.007	0.002	
5	2.65	0.15		2.38	2.53	0.005	0.004	0.009	0.004	
L-4	2.75	0.46	1.13		0.15	1.74	0.033	0.016	0.004	0.053
L-112	3.00	0.13	1.93		1.24	3.30	0.025	0.023	0.004	0.052
L-109 ^a	3.00	0.26	1.26 + 0.67 Kn		0.65	2.84	0.032	0.002 + 0.011 Kn	0.004	0.049

^a Potassium-naphthalene as initiator.

TABLE 2. GPC Analysis Showing $[P]_e$ and $[LE]$ Associated with Different Components in Poly- α -methylstyrene Prepared at 15°C with Potassium as Initiator and p-Dioxane as Solvent

No.	$[M]_0$ (mole/ liter)	$[P]_e$ base-mole/liter (by GPC)			$[LE]$ mole/liter (by GPC)			Total $[LE]$ (mole/ liter)
		(D + A) + B)	B	(B + C) C	Total $[P]_e$ (D + A) + B)	(D + A) + B)	B	
8	2.11	0.25	0.33	0.61	0.86	0.007	0.002	0.009 0.004
28	2.23	0.11	0.33	0.54	0.98	0.004	0.002	0.007 0.002
9	2.37	0.31	0.99	1.30	1.30	0.009	0.003	0.012 0.004
10	2.75	0.46	1.50	1.96	1.96	0.015	0.005	0.020 0.007
12	2.77	0.66	1.42	2.08	2.08	0.035	0.005	0.040 0.009
11	2.82	0.41	1.63	2.04	2.04	0.019	0.004	0.023 0.004
13	3.04	0.36	1.94	2.30	2.30	0.008	0.004	0.012 0.005
14	3.31	0.57	2.39	2.96	2.96	0.009	0.006	0.015 0.006
32	4.41	0.47	1.02	2.93	4.42	0.038	0.006	0.047 0.005

TABLE 3. GPC Analysis Showing $[P]_e$ and $[LE]$ Associated with Different Components in Poly- α -methylstyrene Prepared at 25°C with Potassium as Initiator and p-Dioxane as Solvent

No.	$[M]_0$ (mole/ liter)	$[P]_e$ (base-mole/liter) (by GPC)				$[LE]$ (mole/liter) (by GPC)				$[LE]$ (by M_w) (mole/ liter)	
		(D+A)	(D+A+B)	B	C	Total $[P]_e$	(D+A)	(D+A+B)	B		C
L-115	2.00	0.17	0.15	0.68	1.00	0.020	0.002	0.002	0.002	0.024	-
B	2.00		0.59	0.21	0.80	0.070			0.009	0.079	-
16	2.60	0.08	0.35	0.47	0.90	0.026	0.020	0.005	0.005	0.051	0.007
L-1	2.75		0.60	0.30	0.90	0.045			0.006	0.051	-
L-3	2.75		0.69	0.15	0.84	0.053			0.004	0.057	-
17a	2.86	0.14	0.39	0.61	1.14	0.008	0.006	0.002	0.002	0.016	0.004
17b	2.86		0.46	0.68	1.14	0.016			0.002	0.018	0.004
L-7	3.00	0.27	0.71	0.82	1.80	0.047	0.036	0.012	0.007	0.095	-
L-108a	3.00		0.76	0.77	1.53	0.056			0.007	0.063	-
L-107a	3.00	0.26	0.42	1.39	2.07	0.034	0.007	0.005	0.005	0.046	-
L-111	3.00		0.43	0.52	0.95	0.022			0.004	0.026	-
L-110	3.00	0.13	0.46	1.21	1.80	0.027	0.011	0.004	0.004	0.042	-
29	3.10	0.12	0.37	0.84	1.33	0.006	0.004	0.003	0.003	0.013	0.005
35	3.54	0.51	0.43	1.28	2.22	0.046	0.007	0.004	0.004	0.057	0.013
19	3.54	0.49	0.52	1.10	2.11	0.038	0.005	0.003	0.003	0.046	0.008
18	3.57	0.18	0.51	0.98	1.67	0.007	0.004	0.002	0.002	0.013	0.005

21	3.62	0.40	0.78	1.64	2.82	0.011	0.004	0.002	0.017	0.005
20	3.74	0.42	0.61	1.56	2.60	0.017	0.005	0.003	0.025	0.006
31	3.88	0.29	0.78	1.60	2.68	0.010	0.005	0.003	0.018	0.006
34	4.23	0.57	0.94	1.72	3.23	0.041	0.005	0.003	0.049	0.008
33	5.16	0.71	1.53	2.36	4.60	0.056	0.008	0.003	0.067	0.007

^aInitiated with potassium naphthalene.

TABLE 4. GPC Analysis Showing $[P]_e$ and $[LE]$ Associated with Different Components in Poly- α -methylstyrene Prepared at 40°C with Potassium as Initiator and p-Dioxane as Solvent

No.	$[M]$ (mole/ liter)	$[P]_e$ (base-mole/liter) (by GPC)			$[LE]$ (mole/liter) (by GPC)			$[LE]$ (by M_w) (mole/ liter)		
		(D+A) + B)	B	(B+C) C	Total $[P]_e$ (D+A) + B)	(D + A (D + A) + B)	B		(B + C) C	Total $[LE]$ (mole/ liter)
23a	4.20	0.43	0.43	0.43	0.86	0.014	0.003	0.017	0.007	
23c	4.20	0.43	0.43	0.43	0.86	0.015	0.002	0.017	0.007	
L-6	4.20	0.82	0.18	0.18	1.00	0.095	0.003	0.098	-	
24	4.69	0.21	0.28	1.11	1.60	0.021	0.003	0.002	0.026	0.004
25	4.72	0.15	0.39	1.15	1.69	0.010	0.003	0.002	0.015	0.003
26	5.55	1.03	1.77	2.80	2.80	0.068	0.008	0.076	0.013	
27	6.60	0.64	0.99	2.70	4.33	0.027	0.005	0.003	0.035	0.006

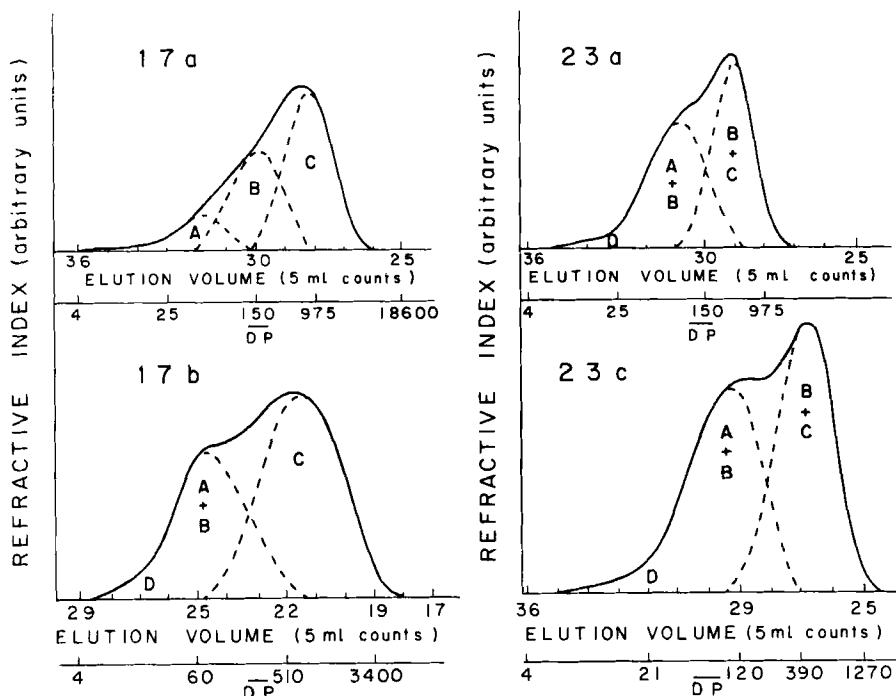


FIG. 1. GPC molecular weight distributions of poly- α -methylstyrene samples 17 and 23 eluting from three different column arrangements: (a) set of four columns, two of them having maximum rated porosity of 1.0×10^6 and 1.5×10^5 Å and 3 ft each in length, the other two having porosity of 3×10^3 and 250 Å and 4 ft each in length; (b) set of three 4 ft columns having maximum rated porosity of 1.0×10^6 , 1.5×10^5 , and 3.0×10^3 Å; (c) set of four 4-ft columns having maximum rated porosity of 1.0×10^6 , 1.5×10^5 , 3.0×10^3 and 250 Å. See Tables 3 and 4 for other data.

Effect of Column Arrangement on the GPC Chromatograms

In order to compare the analysis of GPC chromatograms obtained by using different column arrangements, two samples of poly- α -methylstyrene (17 and 23) were run through various set of columns. In Fig. 1 are shown the GPC chromatograms of polymer 17 observed in the set of columns (a) and (b) as well as those of polymer 23 observed in column arrangements (a) and (c). Polymer 17, when

passed through column set (a), may be split into three parts (D + A), B, and C, whereas through arrangement (b), the contribution of components A, B, and C is difficult to separate. Polymer 23, on the other hand, elutes the same way in the column sets (a) and (c), the splitting being better in the latter arrangement. The values of $[P]_e$ and $[LE]$ associated with each component as calculated from the chromatograms of polymer 17 are presented in Table 3 and those for polymer 23 in Table 4. The values of $[P]_e$ associated with components (D + A), B, and C for polymer 17 through set (a) are 0.14, 0.39, and 0.61 base-mole/liter, respectively, whereas through column (b) the contribution of (D + A + B) is 0.46 instead of 0.53 base-mole/liter and that with (c) is 0.68 base-mole/liter. The distribution of $[LE]$ for components (D + A), B, and C for polymer 17 through set (a), are 0.008, 0.006, and 0.002 mole/liter, yielding a total $[LE]$ of 0.016 mole/liter. The same distribution as seen through column arrangement (b), for components (D + A + B) and C are 0.016 and 0.002 mole/liter, thereby yielding a total $[LE]$ of 0.018 mole/liter. It may be noted that the value of 0.002 mole/liter for $[LE]$ in the component C with both set of columns is the same.

For polymer 23, the values of $[P]_e$ associated with components (D + A + B) and (B + C) are 0.43 and 0.43 base-mole/liter, irrespective of the column set used. The values of $[LE]$ associated with component D + A + B and C through column set (a), however, are 0.014 and 0.03 mole/liter, whereas through column set (c), these are 0.015 and 0.002 mole/liter, yielding the same $[LE]$ value in both set of columns. These results show the margin of error to be expected in the results of the present study.

Reproducibility of the GPC Chromatograms under Identical Conditions

As has been mentioned earlier, Brower and McCormick [5] found bimodal distributions in polystyrene prepared through initiation with potassium-naphthalene in p-dioxane as solvent. These bimodal distributions were explained on the basis of the killing of the initiator thereby yielding polymer mixtures due to monofunctional and bifunctional initiators along with some dead polymer. The killing of living ends in their studies was presumed to be indiscriminate, which arouses the curiosity whether the distribution of molecular weights in two polymers prepared under identical conditions would be the same or different. With a view to explore this aspect, GPC analyses were carried out on two pairs of polymers, one prepared from a 3.54 M solution of α -methylstyrene with $[LE]$ of 0.008 (polymer 19) and 0.013 mole/liter (polymer 35) as calculated on the basis of their

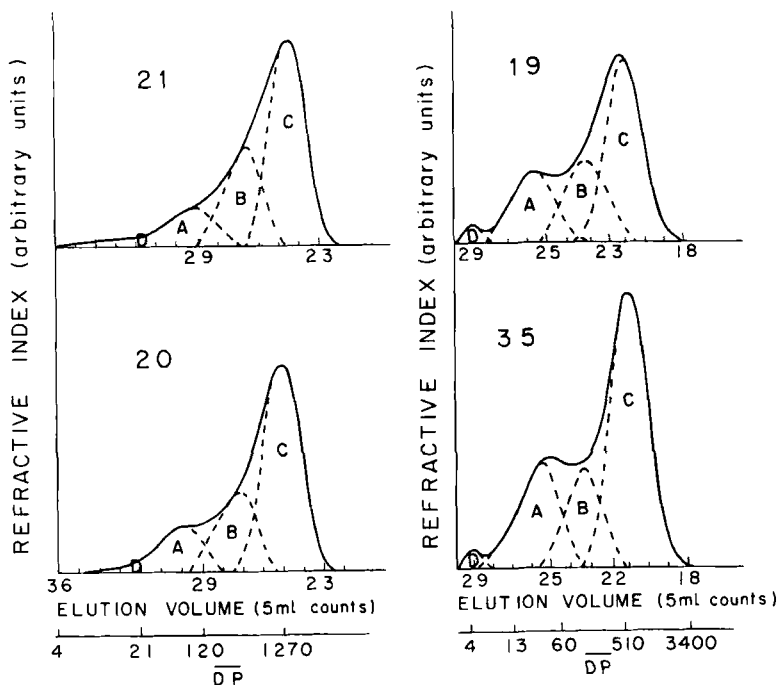


FIG. 2. GPC molecular weight distributions of two pairs of poly- α -methylstyrene samples 21, 20 and 19, 35 prepared with potassium at 25°C using low and high [LE], respectively. See Table 3 for other data.

viscosity average molecular weights \overline{M}_v and the other prepared from 3.6 (polymer 21) and 3.74 (polymer 20) molar solutions with [LE] of about 0.006 mole/liter.

In Fig. 2 are shown the GPC chromatograms of polymers from pairs 21 and 20 as well as 19 and 35. The analyses of these chromatograms are shown in Table 3. It may be noted that the [LE] values in polymers 19 and 35 are 0.046 mole/liter and 0.057 mole/liter, respectively, as computed on the basis of their number-average molecular weights \overline{M}_n (GPC) and not 0.013 and 0.008 mole/liter given by \overline{M}_v . Furthermore, for identical [LE], the GPC distribution of molecular weight in polymers 19 and 35 are identical. The values of $[P]_e$ and [LE] associated with components (D + A), B and C are

also reasonably close (cf. Table 3). In polymers 21 and 20, where the $[LE]$ values from \overline{M}_v were of the order of 0.006, these were found to be 0.017 mole/liter for polymer 21 and 0.025 mole/liter for polymer 20. The shape of the GPC chromatograms, once again, is similar in the two cases. The values of $[P]_e$ and $[LE]$ associated with different components also have similar magnitudes (cf. Table 3). Based on these results it may be said that in polymers where the distribution of molecular weights is not unimodal one should not use the values of \overline{M}_v for the calculation of $[LE]$, as these invariably project a false image.

It may also be said that the reaction of the solvent with the growing polymer may not be the sole reason for the bimodal or trimodal molecular weight distributions observed in the GPC analyses of the polymers. If the killing phenomenon is so methodical as to yield reproducible distributions, it may be termed as a mechanism rather than a side reaction.

Effect of $[LE]$ on the GPC Molecular Weight Distribution

In the earlier experiments it has been shown that the polymers prepared from the same $[M]_0$ and $[LE]$ yield identical distributions. It should be interesting therefore to study the effect of $[LE]$ on the GPC distributions of polymers prepared from the same initial monomer concentration, $[M]_0$. In Fig. 3 are shown the GPC distributions of two pairs of polymers, one (polymers 11, 12) prepared at 15°C from 2.80 M solution and the other (polymers 24, 25) at 40°C from 4.70 M solution. The results of their component analyses in terms of $[P]_e$ and $[LE]$ are presented in Tables 2 and 4, respectively. In the presence of 0.023 mole/liter total $[LE]$, the $[P]_e$ associated with component D + A + B is 0.41 base-mole/liter (polymer 11) and carries 0.019 mole/liter of $[LE]$ with it. In polymer 12, where the total $[LE]$ is 0.04 mole/liter, the $[P]_e$ associated with the same component viz., D + A + B is 0.66 base-mole/liter and carries 0.035 mole/liter of $[LE]$. The remainder $[LE]$ are associated with component (B + C). It is quite likely that the contribution due to component (B + C) as shown here may in reality be that due to component C alone. However the possibility of the polymers due to B and C eluting together is also quite high at 15°C, as shall be shown a little later.

The results of the component analyses of polymers 24 and 25 are shown in Table 4. It may be seen that for different $[LE]$ the total $[P]_e$ in the two experiments are nearly identical. The $[P]_e$ contribution due to component C in the two cases is about the same. In

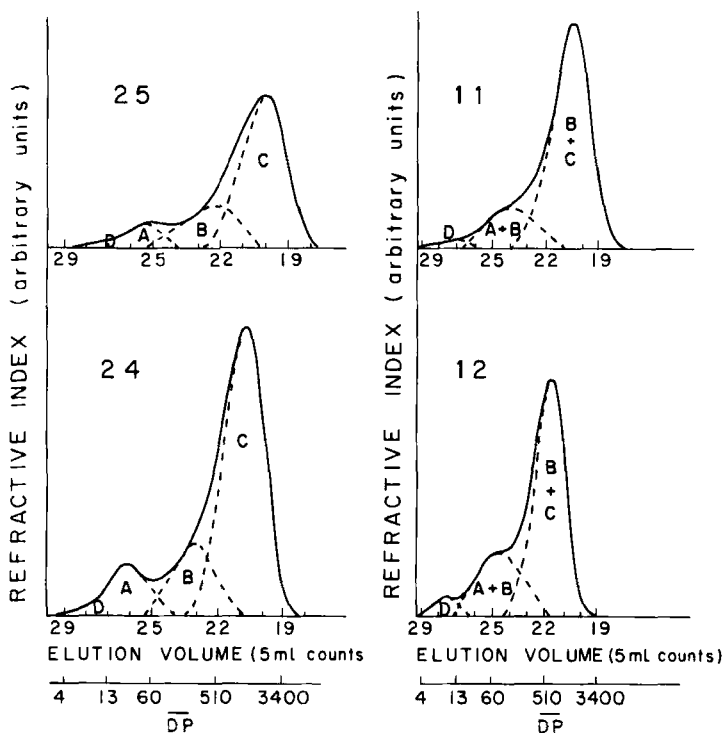


FIG. 3. GPC molecular weight distributions of two pairs of poly- α -methylstyrene samples 24, 25 and 11, 12, the former pair polymerized at 40°C and the latter at 15°C . Potassium was used as the initiator. The $[\text{LE}]$ values in the two pairs of polymers were different. See Tables 2 and 4 for other data.

polymer 24, where $[\text{LE}]$ of 0.026 mole/liter was used, the $[\text{P}]_e$ contribution due to component (D + A), however, is 0.21 base-mole/liter as compared to 0.15 base-mole/liter when the $[\text{LE}]$ was 0.015 mole/liter. The contribution due to component B is higher (0.39 base-mole/liter in the case of lower $[\text{LE}]$) as compared to that of 0.28 base-mole/liter when higher $[\text{LE}]$ was used. As for the distribution of $[\text{LE}]$ in these components is concerned, it is observed that in both experiments components B and C have same $[\text{LE}]$ of 0.003 and 0.002 mole/liter, respectively associated with them, whereas it is component (D + A) which carries the major part of the excessive $[\text{LE}]$. Out of a total $[\text{LE}]$ of 0.026 mole/liter in polymer 24, component (D + A) has 0.021 mole/liter; when the $[\text{LE}]$ value was 0.015 (polymer 25),

the same component has 0.01 mole/liter $[LE]$ attached to it. Based on these experiments it may be seen that the effect of $[LE]$ is predominantly on the lower molecular weight components D + A and B. It may be remarked that this effect is methodical and not haphazard which one would expect if the bimodal distributions had their origin from killing of the bifunctional initiator.

Splitting of Components in the GPC Distributions of Polymers Obtained from Identical Solutions at Different Temperatures

It has been shown earlier that sometimes the $[P]_e$ contribution of two components may elute at the same count in GPC, and hence their analyses in terms of their individual contributions is not possible. However, it has also been seen that the same solution, when polymerized at another temperature, yields polymer that may be split into its three components, viz., D + A, B, and C. This way it is possible to get an idea about the distribution of the total $[LE]$ in different components. In Fig. 4 are shown the GPC chromatograms of two pairs of polymers each having been prepared from solutions with the same $[M]_0$ and $[LE]$ but at different temperatures. In the first pair of polymers (3 and 28), these were prepared from about 2.25 M solutions of the monomer and 0.007 mole/liter of $[LE]$, the former being carried out at 5°C whereas the latter at 15°C.

Because of the lower $[P]_e$ in polymer 28, the contribution due to the three components is possible to separate, whereas in polymer 3 the $[P]_e$ contribution of B and C is difficult to separate. Based on the analyses of polymer 28 (cf. Table 2) it may be said that in a 2.25 M solution of α -methylstyrene in p-dioxane for a $[LE]$ of 0.007 mole/liter the distribution of $[LE]$ in different components (D + A), B, and C is 0.004, 0.002, and 0.001 mole/liter, respectively.

In the second pair of polymers, viz., 13 and 29, these were prepared from 3.04 and 3.10 M solutions of the monomer and with $[LE]$ of 0.012 and 0.013 mole/liter, respectively, the former having been polymerized at 15°C and the latter at 25°C. The splitting of components at 15°C is not possible; however, at 25°C these can be easily separated. Thus for a 3.10 M solution of α -methylstyrene in p-dioxane the distribution of the total $[LE]$ of 0.013 mole/liter with different components (D + A), B, and C is 0.006, 0.004, and 0.003 mole/liter.

In these two set of experiments, the splitting of $[LE]$ could be achieved by increasing the temperature; however, in some other cases one may have to lower the temperature to achieve the same goal, as is shown in Fig. 5. Two polymer samples, 23 and 26 (cf. Table 4) prepared at 40°C from 4.20 and 5.55 M solutions, respectively,

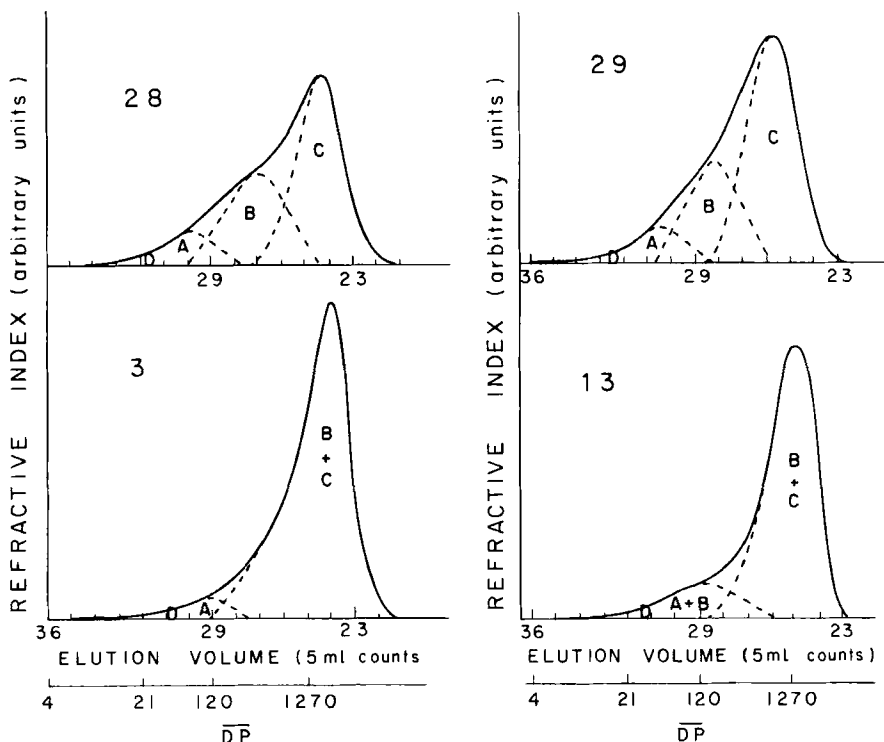


FIG. 4. GPC molecular weight distributions of two pairs of poly- α -methylstyrene samples 3, 28 and 13, 29. Each pair was prepared with potassium from identical solutions but at different temperatures and shows different degree of splitting of components. See Tables 1, 2, and 3 for other data.

showed bimodal distributions; the splitting of components (D + A) and B was not possible. However when similar solutions were polymerized at 25°C (cf. Table 3), their splitting into their components posed no problem. In this case, polymers 31 and 33 were initiated from 3.9 and 5.16 M solutions with [LE] of 0.018 and 0.067 mole/liter, respectively. The [LE] of their counterparts (23 and 26) at 40°C was 0.017 and 0.062 mole/liter, respectively. From these two sets of experiments, one may say that in about 4.0 M solutions with [LE] of 0.018 mole/liter, the [LE] distribution with different components (D + A), B, and C are 0.010, 0.005, and 0.003 mole/liter and in solutions with molarity of about 5.25 mole/liter with total [LE] of 0.067 these are 0.056, 0.008, and 0.003 mole/liter, respectively.

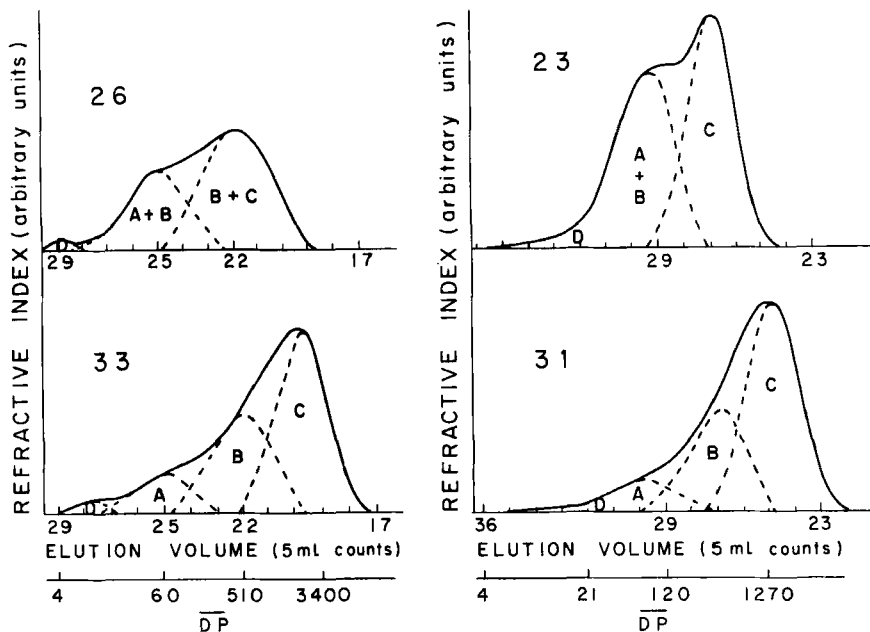


FIG. 5. GPC molecular weight distributions of two pairs of poly- α -methylstyrene samples 26, 33 and 23, 31. Each pair was prepared with potassium from identical solutions but at different temperatures and shows different degree of splitting of components. See Tables 3 and 4 for other data.

From the GPC chromatograms of polymers (Figs. 4 and 5) it may be seen how the splitting into individual components is achieved in order to obtain information about the living end distributions in a given solution. However, the distribution of [LE] in identical solutions but different temperatures may not necessarily be the same. In Fig. 6 are shown the GPC chromatograms of two polymers; one (polymer 34) was prepared at 25°C from 4.23 M solution with a [LE] of 0.049 mole/liter and the other (polymer 32) polymerized at 15°C from a 4.41 M solution with [LE] of 0.047 mole/liter. These GPC chromatograms are split into three components each, and [LE] associated with them are presented in Tables 3 and 2, respectively. It may be noted that the components (D + A), B, and C of polymer 34 at 25°C have values of [LE] associated with them of 0.041, 0.005, and 0.003 mole/liter, whereas in polymer 32 at 15°C these read at 0.038, 0.006, and 0.003 mole/liter, indicating that the margin of error is not too large.

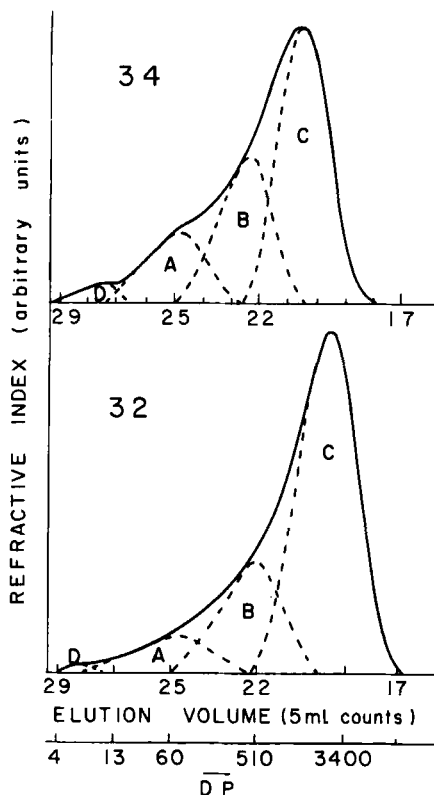


FIG. 6. GPC molecular weight distributions of a pair of poly- α -methylstyrene samples 34 and 32. Each was prepared with potassium from identical solution but at different temperatures and shows similarities in the degree of splitting of the components. See Tables 2 and 3 for other data.

Species Responsible for Polymerizations at 25°C and 5°C

Earlier in the text all of GPC chromatograms were separated into three components (D + A), B, and C. A similar analysis of the GPC chromatograms was also carried out in the polymerization of α -methylstyrene in tetrahydrofuran [7]. The question now arises, is the nature of the species responsible for the components (D + A), B, and C in the two solvents, the same or different? In most of the GPC distributions

in polymers prepared at 25°C or higher, the highest molecular weight component and the most reactive one because of the maximum $[P]_e$ associated with it, has been labeled as C and represents a contact-pair mechanism polymer. This inference has been based on the reported literature [8, 9] that the contact-pair is the only mechanism possible in p-dioxane as solvent, because of its low bulk dielectric constant. Furthermore, the $[LE]$ associated with these high molecular weight components traced in p-dioxane as well as in tetrahydrofuran are of the same order of magnitude. Of the other two components, (D + A and B), establishing the nature of species responsible for component B is more difficult, because if it is the same species which gives rise to component B in p-dioxane and tetrahydrofuran, in that case the presence of solvent-separated ion-pair mechanism in p-dioxane as well is indicated, an inference which has been ruled out in the literature. The presence of dead and dormant polymer (D + A) in p-dioxane may be accepted without much argument because it is known that p-dioxane reacts with the polymer, thereby yielding a dead polymer, and in a solvent of low dielectric constant, association of low molecular weight polymers yielding a dormant polymer can exist.

In order to establish that the species responsible for the formation of component B in p-dioxane as well as in THF are the same, an approach similar to the one used in the earlier study was tried. A 2.75 M solution of α -methylstyrene in p-dioxane was initiated at 25°C with potassium and divided into two parts. Both of these were polymerized at 25°C. One of these (L-3) was opened at 25°C and 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 polymer. The GPC chromatograms of these two polymers are shown in Fig. 7, and their analyses in terms of $[P]_e$ and $[LE]$ associated with different components are presented in Tables 1 and 3.

In polymer L-3, out of the total $[P]_e$ of 0.84 base-mole/liter 0.69 base-mole/liter is associated with component (D + A + B) and only 0.15 base-mole/liter with component C. On further polymerization at 25°C (L-4), it appears that a part of component (D + A + B) polymerizes and has a maximum at the elution count of 29.5. The $[P]_e$ associated with the component (D + A + C) in L-4 is 0.61 base-mole/liter, whereas that associated with B is 1.13 base-mole/liter. In this calculation it has been assumed that out of the component D + A + B, it is the component B which further polymerizes.

In order to eliminate any doubt about the growth of B at lower temperatures, another approach similar to the one used in the analysis of polymerized and depolymerized samples of polystyrene [10, 11] or poly- α -methylstyrene [7] was used. From the GPC chromatograms of the samples L-3 and L-4, base-mole/liter associated with various

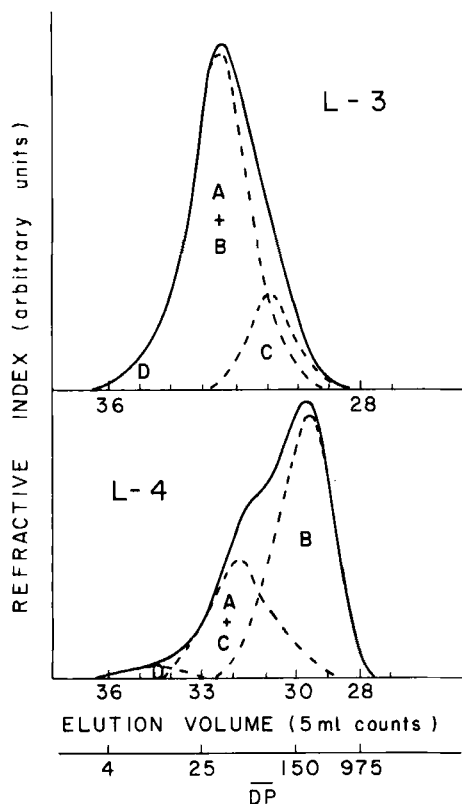


FIG. 7. GPC molecular weight distributions of two samples of poly- α -methylstyrene prepared with potassium from 2.75 M solution. L-3 was polymerized at 25°C; L-4 was polymerized at 25°C and further polymerized at 5°C. See Tables 1 and 3 for other data.

elution counts were calculated, and based on these data, weight-normalized GPC chromatograms of L-3 and L-4 were traced and superimposed as shown in Fig. 8. One notes that on further polymerization at 5°C an area (-), marked with vertical hash lines, disappears and appears at lower elution counts where it is marked with horizontal hash lines, (+). This area has been transformed into distributions of molecular weight which meet at the elution count of 32. In reality these could have been superimposed in a way that the tail of (+) distribution and the head of (-) distribution falls at the same elution count as shown by the dotted lines. The tracing of these broken

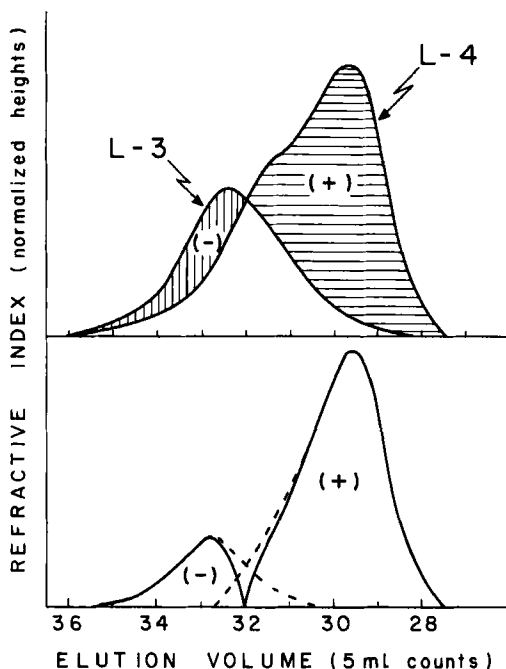


FIG. 8. Graphical method of analysis by which the GPC curves are broken down into their components for poly- α -methylstyrene samples L-3 and L-4. See Tables 1 and 3 for other data.

lines is based essentially on the overall shape of the curves be they broad, gaussian or other in distribution; but they are at best only a first approximation of the true situation.

The base-mole/liter due to (-) distribution were calculated to be 0.25 and had 0.019 mole/liter of [LE] associated with it. On the other hand, (+) distribution carried 1.17 base-mole/liter of polymer and had 0.017 mole/liter of [LE] attached to it. This can explain the difference in $[P]_e$ of 0.9 base-mole/liter between the polymer at 25°C (L-3) and polymer at 5°C (L-4). Furthermore, it shows that the excess polymer is really a product of the 0.25 mole/liter component in L-3, because of the similar [LE] values of 0.017 and 0.019 mole/liter in them. This component may take its origin either from component B or component (D + A) in L-3. In an earlier publication [2], it was shown that in the polymerization of α -methylstyrene at lower temperatures the contribution towards polymerization comes

out of component B. On making use of this parallel, it may be said that this component B is also present in the p-dioxane- α -methylstyrene system.

Reversible Propagation in Polymerization at 5°C

It has been reported in the literature [8, 9] that in solvents of low bulk dielectric constant, such as p-dioxane, the propagation is primarily controlled by the contact ion-pair mechanism. This would mean that in such cases the propagation process is irreversible in nature. In order to verify this point, a 3.0 M solution of α -methylstyrene in p-dioxane as solvent was initiated with potassium metal at 25°C. This solution was divided into two parts, and both were polymerized at 5°C. One of these (L-112) was opened at 5°C and yielded 3.30 base-mole/liter of polymer. The other (L-110) was depolymerized at 25°C and yielded 1.80 base-mole/liter, indicating the presence of reversible propagation. However if a 3.0 M solution with a [LE] of 0.04 mole/liter is polymerized directly at 25°C, it should yield about 1.4 base-mole/liter polymer. Higher [P]_e on depropagation (L-110) would mean that there are not enough reversible-propagation yielding species in solution.

From the raw GPC curves of these polymers, base-mole/liter of polymer at various elution counts were calculated, and these are presented in Table 5. Based on these data, normalized GPC curves of the two polymers L-112 and L-110 were traced and superimposed (Fig. 9) in order to see the changes in the GPC chromatogram after depropagation [10, 11]. It may be noted from Fig. 9 that the area marked with horizontal hash lines has disappeared on depropagation at 25°C. This area under the hash lines has been transformed into molecular weight distributions as shown with the dotted lines in Fig. 9. This distribution is missing from the overall distribution of the polymer at 5°C. This would mean that if the concept of reversibility associable solely to the solvent-separated ion-pair mechanism [7] is true, then in p-dioxane solvent there is a strong possibility of the existence of this mechanism.

In Fig. 10 are shown the GPC chromatograms of samples polymerized at 5°C (L-112) and depolymerized at 25°C (L-110). The left-hand side distribution of component C in L-110 may be traced on the basis of its right-hand side distribution. Keeping in mind that the total area under the GPC envelope is the same as that of the combined area of components (D + A), B, and C, their distribution in L-110 is easily traced. On adding to the distribution of B in L-110, the distribution of the depropagated polymer from Fig. 9, one may trace the original component B in L-112. Once the distribution of B in L-112 is known, those of others like C or (D + A) can be easily traced. The

TABLE 5. GPC Analyzed Concentration of Poly- α -methylstyrene at Various Elution Counts and Concentration of Polymer Associated with Each Component

Elution counts	L-112 (base-mole/liter) ^a	L-110 (base-mole/liter) ^b	(L-112) - (L-110) (base-mole/liter)	L-112 components (base-mole/liter)			L-110 components (base-mole/liter)		
				(D + A)	B	C	(D + A)	B	C
26	0.01	0.00	-0.01	-	0.01	0.00	-	-	-
26.5	0.05	0.03	-0.02	-	0.02	0.03	-	-	0.03
27	0.23	0.12	-0.11	-	0.04	0.19	-	-	0.12
27.5	0.45	0.28	-0.17	-	0.09	0.36	-	-	0.28
28	0.57	0.33	-0.24	-	0.13	0.44	-	-	0.33
28.5	0.49	0.26	-0.23	-	0.18	0.31	-	-	0.26
29	0.37	0.18	-0.19	-	0.23	0.14	-	0.04	0.14
29.5	0.28	0.12	-0.16	-	0.25	0.03	-	0.08	0.04
30	0.22	0.09	-0.13	-	0.22	-	-	0.08	0.01
30.5	0.16	0.07	-0.09	-	0.16	-	-	0.07	-
31	0.12	0.05	-0.07	-	0.12	-	-	0.06	-
31.5	0.09	0.04	-0.05	0.01	0.08	-	-	0.05	-
32	0.06	0.04	-0.02	0.02	0.04	-	-	0.03	-
32.5	0.05	0.05	-0.00	0.03	0.02	-	0.02	0.02	-
33	0.04	0.03	-0.01	0.04	-	-	0.01	0.02	-
33.5	0.03	0.03	-	0.03	-	-	0.02	0.01	-

34	0.03	0.03	-	0.03	-	0.02	-	-
34.5	0.02	0.02	-	0.02	-	0.02	-	-
35	0.02	0.02	-	0.02	-	0.02	-	-
35.5	0.01	0.01	-	0.01	-	0.02	-	-
$\Sigma [P]_e$	3.30	1.80	-1.50	0.21	1.59	0.13	0.46	1.21

^aL-112: initiated with potassium at 25°C and polymerized at 5°C.

^bL-110: polymerized at 5°C and depolymerized at 25°C.

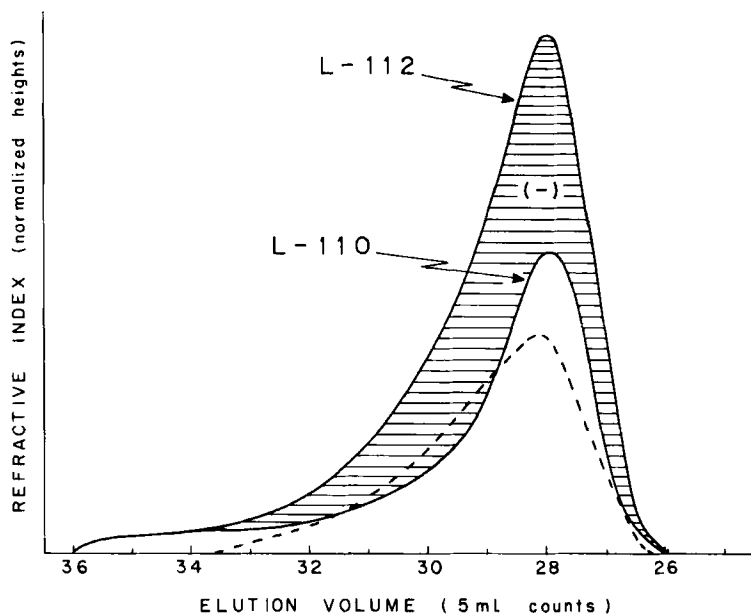


FIG. 9. Graphical method of analysis by which the GPC curves are broken down into their components for poly- α -methylstyrene samples L-112 and L-110. L-112 was polymerized at 5°C; L-110 was polymerized at 5°C but depolymerized at 25°C. See Tables 1, 3 and 5 for other data.

GPC analyses of these chromatograms in terms of $[P]_e$ and $[LE]$ is presented in Tables 1, 3, and 5. It appears that, of 1.93 base-mole/liter of polymer associated with component B in L-112, 1.47 base-mole/liter has disappeared on depropagation at 25°C. Of 0.023 mole/liter of $[LE]$ associated with component B in L-112, now there remains only 0.011 mole/liter in L-110. This experiment clearly shows the presence of reversible propagation.

In yet another experiment, a 2.0 M solution of α -methylstyrene in *p*-dioxane was initiated with potassium at 25°C and divided into two parts. Both of these were polymerized at 5°C. One of these (L-114) was opened at 5°C, and the other was depolymerized at 25°C (L-115). The base-mole/liter of polymer in the polymerized and depolymerized samples at different elution counts is shown in Table 6. Based on these data the presence of different component were traced by using the method of superimposition of the weight normalized GPC chromatograms as shown earlier in Fig. 7. These components were fitted in

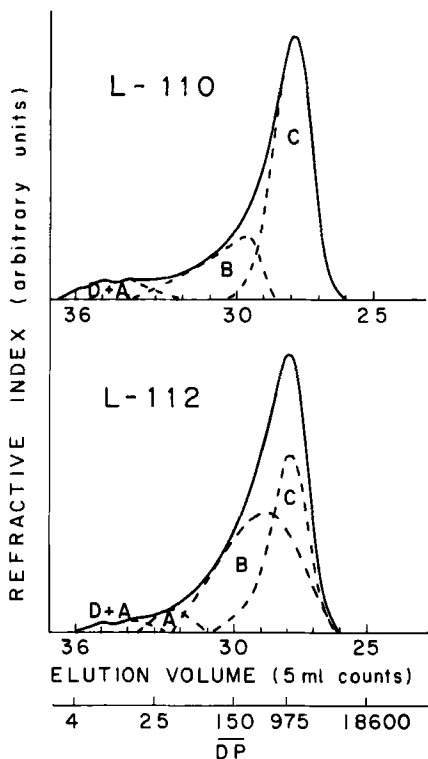


FIG. 10. GPC molecular weight distributions of poly- α -methylstyrene L-112 and L-110 in terms of various components traced on the basis of Fig. 9. L-112 was polymerized from a 3.0 M solution at 5°C; L-110 was polymerized at 5°C but depolymerized at 25°C. See Tables 1 and 3 for other data.

the original GPC curves of L-114 and L-115 as shown in Fig. 11. The GPC analyses of these samples in terms of $[P]_e$ and $[LE]$ are presented in Tables 1 and 3 and the weight distribution of the components, polymerized and depolymerized, are shown in Table 6. Once again it can be remarked that 0.55 base-mole/liter of polymer associated with component B in L-114 prepared at 5°C has been reduced to 0.15 base-mole/liter on depropagation at 25°C. The $[LE]$ of 0.004 mole/liter associated with the component B in L-114 is reduced to 0.002 mole/liter on depropagation in L-115. These experiments clearly show the presence of reversible propagation due to the solvent separated ion-pair mechanism in *p*-dioxane as solvent. It is possible that the

TABLE 6. GPC Analyzed Concentration of Poly- α -methylstyrene at Various Elution Counts and Concentration of Polymer Associated with Each Component

Elution counts	L-114 (base-mole/liter) ^a	L-115 (base-mole/liter) ^b	(L-114) - (L-115) (base-mole/liter)	L-114 components (base-mole/liter)			L-115 components (base-mole/liter)			
				(D + A)	B	C	(D + A)	B	C	
26.5	0.01	0.00	-0.01	-	0.01	-	-	-	-	-
27	0.07	0.03	-0.04	-	0.04	0.03	-	-	-	0.03
27.5	0.21	0.12	-0.09	-	0.07	0.14	-	-	-	0.12
28	0.38	0.24	-0.14	-	0.09	0.29	-	-	-	0.24
28.5	0.29	0.20	-0.09	-	0.09	0.20	-	-	0.01	0.19
29	0.14	0.11	-0.03	-	0.08	0.06	-	-	0.03	0.08
29.5	0.07	0.06	-0.01	-	0.06	0.01	-	-	0.04	0.02
30	0.05	0.04	-0.01	-	0.05	-	-	-	0.03	0.01
30.5	0.03	0.03	-	-	0.03	-	-	-	0.03	-
31	0.03	0.03	-	-	0.01	0.02	-	0.01	0.02	-
31.5	0.02	0.02	-	-	0.01	0.01	-	0.02	-	-
32	0.02	0.02	-	-	0.02	-	-	0.02	-	-
32.5	0.02	0.02	-	-	0.02	-	-	0.02	-	-
33	0.02	0.02	-	-	0.02	-	-	0.02	-	-
33.5	0.02	0.02	-	-	0.02	-	-	0.02	-	-
34	0.01	0.01	-	-	0.01	-	-	0.01	-	-

34.5	0.01	0.01	-	0.01	-	-	0.01	-	-
35	0.01	0.01	-	0.01	-	-	0.01	-	-
35.5	0.01	0.01	-	0.01	-	-	0.01	-	-
$\Sigma [P]_e$	1.42	1.00	0.42	0.14	0.55	0.73	0.15	0.16	0.69

^aL-114: initiated with potassium at 25° C and polymerized at 5° C.

^bL-115: polymerized at 5° C and depolymerized at 25° C.

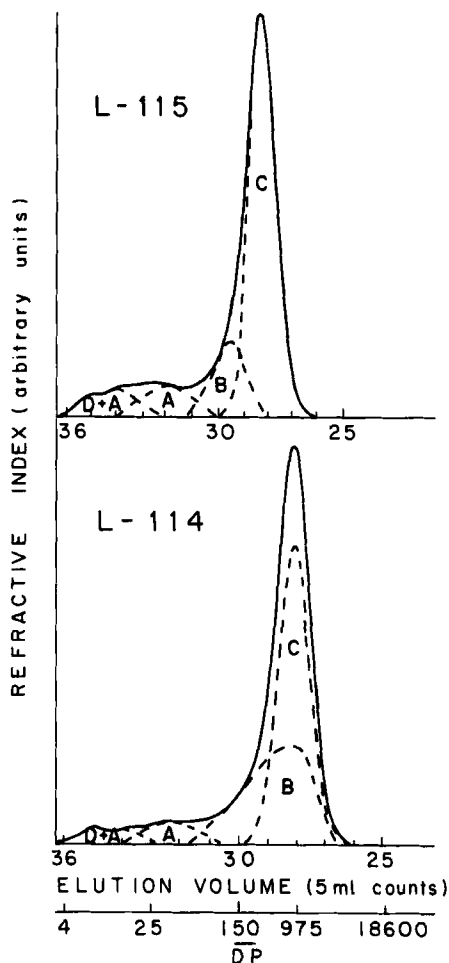


FIG. 11. GPC molecular weight distributions of poly- α -methylstyrene (in terms of its components) prepared with potassium from a 2.0 M solution of α -methylstyrene in *p*-dioxane. L-114 was polymerized at 5°C; L-115 was polymerized at 5°C but depolymerized at 25°C. See Tables 1, 3, and 6 for other data.

dielectric constant of the solution in the vicinity of the ion-pair [9] plays a greater role in determining the mode of propagation as compared to the bulk dielectric constant of the medium.

Comparison of GPC Molecular Weight Distributions of Poly- α -methylstyrene Prepared in THF and in p-Dioxane

Earlier in the text it was speculated that the bulk dielectric constant of the medium used may not be that important in controlling the distribution of molecular weight of polymer. This possibility was examined experimentally by making a comparison of molecular weight distributions of poly- α -methylstyrenes prepared in tetrahydrofuran and in p-dioxane. In Fig. 12 are shown GPC chromatograms of two polymers (37 and 27) prepared at 40°C. One of these (polymer 37) was prepared from a 6.5 M solution of α -methylstyrene in THF with 0.033 mole/liter of initiator. It yielded 4.13 base-mole/liter of polymer, which, when analyzed in terms of components (D + A), B, and C gave $[P]_e$ values of 0.55, 1.21, and 2.37 base-mole/liter, respectively. The distribution of [LE] attached with these components was 0.022, 0.009 and 0.002 mole/liter respectively. The other polymer, polymer 27, was prepared from a 6.6 M solution of α -methylstyrene but in p-dioxane as solvent with 0.035 mole/liter of initiator potassium (cf. Table 4). This experiment yielded 4.33 base-mole/liter of polymer, which when analyzed in terms of components (D + A), B, and C gave values of 0.64, 0.99, and 2.7 base-mole/liter, respectively. The distribution of [LE] attached with these components was 0.027, 0.005, and 0.003 mole/liter.

It may be noted that under identical conditions there are more living ends of type B (solvent-separated ion-pair) in THF as solvent as compared to that in p-dioxane. Furthermore the contribution of contact ion-pair mechanism in the form of component C is more when p-dioxane is the solvent as compared to that in THF. The overall results lead one to believe that in this particular experiment the effect of the bulk dielectric constant of THF does not have that significant effect as for as the molecular weight distributions of the two polymers are concerned.

It may be argued that solutions with molarity of 6.5 and 6.6 are very much near the bulk conditions and there is not much of solvent present in these cases in any case to affect the distributions of molecular weight. In order to circumvent this objection, a 2.75 M solution of α -methylstyrene in THF was polymerized at 25°C with 0.049 mole/liter of [LE] with potassium as initiator (L-5). This experiment yielded 0.90 base-mole/liter of polymer which, when analyzed in terms of the components (D + A), B, and C gave values of 0.56 base-mole/liter with component (D + A + B) and 0.34 base-mole/liter with component (B + C). In this case the higher molecular weight component has been attributed to (B + C) in place of C alone, as it is thought that there may be contribution due to B hidden under component C. It is quite possible that this component marked as

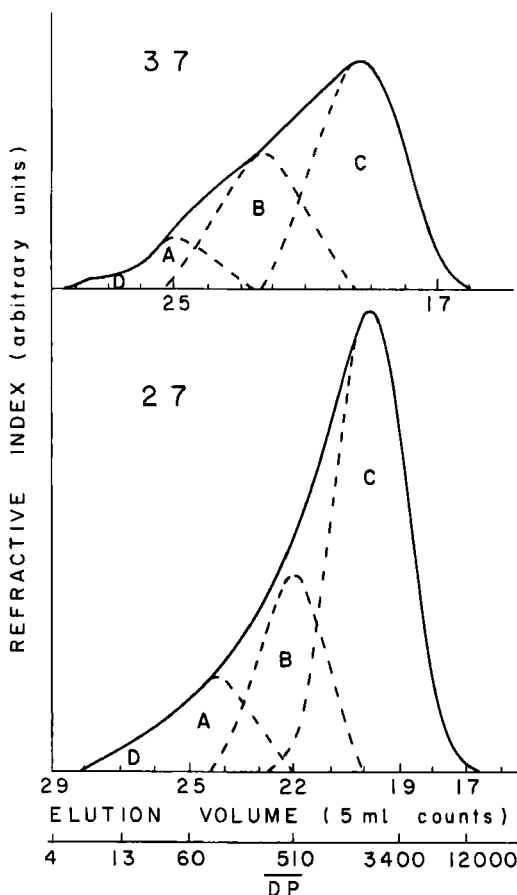


FIG. 12. Comparison of GPC molecular weight distributions in poly- α -methylstyrene prepared with potassium at 40°C. Polymer 37 was polymerized from 6.5 M solution in THF with 0.033 mole/liter in initiator and polymer 27 was polymerized from a 6.6 M solution in *p*-dioxane with 0.035 mole/liter of initiator.

(B + C) is in reality component C all alone. Out of a total $[LE]$ of 0.049 mole/liter, 0.043 mole/liter are associated with component (D + A + B) and 0.006 mole/liter with either component (B + C) or C alone. These results may be compared to those obtained in the case of polymer L-3 which had been prepared from a 2.75 M solution of α -methylstyrene at 25°C with 0.057 mole/liter $[LE]$ with

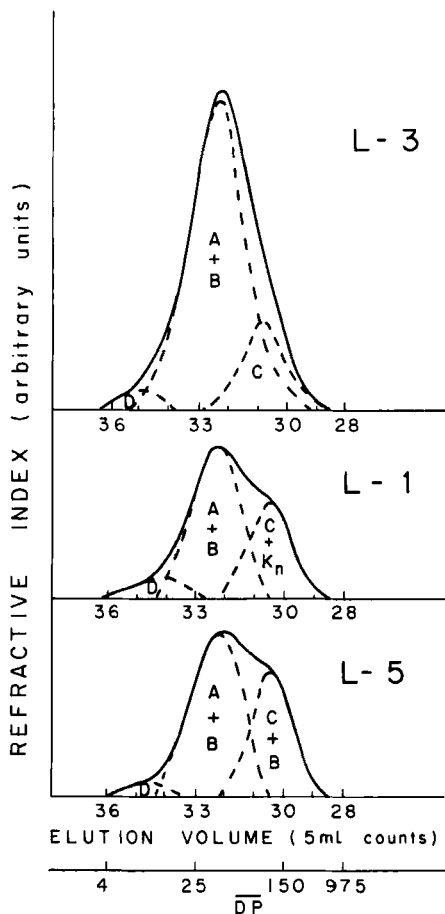


FIG. 13. Comparison of GPC molecular weight distributions in poly- α -methylstyrene prepared from 2.75 M solutions at 25°C. L-3 prepared with potassium as initiator, $[LE] = 0.057$ mole/liter, and p-dioxane as solvent; L-1 prepared with potassium-naphthalene as initiator, $[LE] = 0.051$ mole/liter in p-dioxane; L-5 prepared with potassium as initiator, $[LE] = 0.053$ mole/liter in THF. See Table 3 for other data.

potassium as initiator. This experiment had yielded 0.84 base-mole/liter of polymer which, when analyzed in terms of components (D + A), B, and C (see Fig. 13) gave 0.69 base-mole/liter with the component

(D + A + B) and 0.15 base-mole/liter with C. The distribution of [LE] attached to these components read at 0.053 mole/liter for the total component (D + A + B) and 0.004 mole/liter for component C. These two experiments clearly show that the distribution of molecular weight as seen through GPC are slightly different for polymers prepared from lower $[M]_0$ values in THF and in p-dioxane, thus pointing the magnitude of the role of the dielectric constant of the medium in controlling the nature of the active species.

Role of Naphthalene in p-Dioxane- α -Methylstyrene Potassium-Naphthalene System

In an earlier study [7], the role of naphthalene in the polymerization of α -methylstyrene in THF initiated with potassium-naphthalene was discussed. It was suggested that the presence of naphthalene during the initiation process gives reactive species yielding reversible propagation which was not possible in its absence. Korotkov et al. [12] have postulated that the propagation by naphthylsodium is due to a coordinative catalytic mechanism. These authors are of the opinion that both the coordinate complex and the step wise mechanism operate in polymerizations initiated by naphthylsodium. Based on the earlier GPC studies [7], it could not be said whether or not the concept of a coordinate complex mechanism is a valid one. However it was clearly seen that the introduction of naphthalene did result in additional species besides the contact pair, solvent-separated pairs and free ions as suggested by Szwarc [9]. In the present study the role of naphthalene was again evaluated.

In order to do that, a 2.75 M solution (polymer L-1) of α -methylstyrene in p-dioxane was initiated with 0.051 mole/liter of potassium-naphthalene complex. This experiment yielded 0.90 base-mole/liter of polymer. The GPC chromatogram of sample L-1 is shown in Fig. 13, which also carries the GPC chromatograms of polymers L-3 and L-5 prepared from 2.75 M solutions of α -methylstyrene in p-dioxane and in THF as solvents, respectively, initiation in both cases having been carried out with potassium alone. One notes that the distribution of poly- α -methylstyrene L-3 prepared in p-dioxane is different from that of L-5, prepared in THF. Due to the presence of naphthalene in p-dioxane solution, however, the polymer-formed L-1, has the same distribution as that of L-5. The analysis of L-1, in terms of $[P]_e$ and [LE] associated with different components (D + A), B, and C is presented in Table 3. Out of a total $[P]_e$ of 0.9 base-mole/liter, 0.60 base-mole/liter are attached with the component (D + A + B) and 0.30 with component (C + Kn). In the case of L-5 the values of $[P]_e$ with component (D + A + B) was 0.56 and that

with component (C + B) it was 0.34 base-mole/liter. Out of a total [LE] of 0.051 mole/liter used in L-1, 0.045 mole/liter are attached with the component (D + A + B) whereas the other component C + Kn has 0.006 mole/liter. In the case of L-5, the component C + B has 0.006 mole/liter associated with it. These experiments clearly show that in the presence of naphthalene, p-dioxane behaves like THF as far as the GPC molecular weight distributions are concerned.

In these calculations it has been assumed that on the addition of naphthalene the species formed are different from those due to (D + A), B, or C and have been termed as species due to potassium-naphthalene complex, Kn. In order to show the origin of these species, the GPC chromatograms of samples L-3 (potassium alone) and L-1 (potassium-naphthalene) were weight-normalized and superimposed as shown in Fig. 14. It may be noted that between the elution counts of 36 and 32, an area marked with vertical hash lines (-) has disappeared from L-3 and appeared between the elution counts of 32 and 28, marked with the horizontal hash lines (+). These areas have

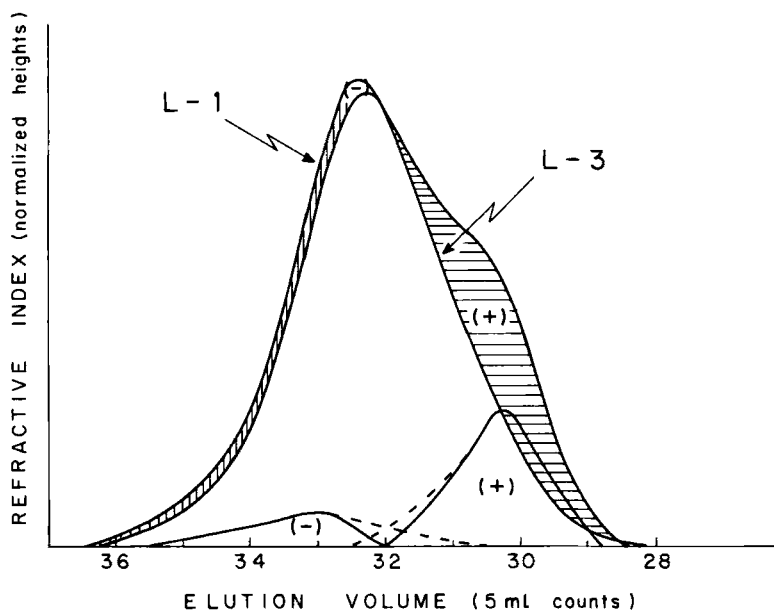


FIG. 14. Graphical method of analysis by which the GPC curves are broken down into components: The case of poly- α -methylstyrene samples, L-1 and L-3 prepared at 25°C in p-dioxane with and without naphthalene in combination with potassium as initiator.

been transformed into their respective distributions (-) and (+). It may be noted that (-) distribution which grows to yield (+) has its origin from the component $D + A + B$.

The only positive observation one may make is that K_n does not have its origin from component C, though the presence of naphthalene may reduce the contribution of C to start with. The observation clearly suggest that the role of naphthalene in propagation of the reaction needs a careful study. Could it be that the presence of naphthalene somehow increases the dielectric constant of the solution or that it creates additional species like the coordinate complex one, besides the contact pairs, solvent-separated pairs, or free ions in the solution?

Reversible Propagation in α -Methylstyrene-p-Dioxane Potassium-Naphthalene System

Earlier in this paper it was shown that depolymerization at 25°C of poly- α -methylstyrene prepared at 5°C yielded reversible propagation, indicating the possibility of solvent-separated ion-pairs being present in solution even in p-dioxane. As a complement to this experiment it was decided to conduct a reversibility test in polymers prepared at 5°C but initiated with potassium-naphthalene instead of potassium alone.

A 3.0 M solution of α -methylstyrene in p-dioxane was initiated at 25°C with 0.049 mole/liter of potassium-naphthalene and divided into two parts. Both of these were polymerized at 5°C. One of them (L-109) was taken out of the bath at 5°C and opened in air to stop the reaction. The dried product gave 2.86 base-mole/liter of polymer. The other (L-107) was depolymerized at 25°C and yielded 2.07 base-mole/liter. The expected value of $[P]_e$ at 25°C is about 1.45 base-mole/liter, suggesting that propagation is reversible but only partially so.

From the GPC distributions of polymers L-109 and L-107 base-mole/liter of polymer associated with different elution counts were computed, and these are presented in Table 7. Based on these data the weight normalized curves for the two polymers were traced and superimposed (Fig. 15). It may be noted that the area (-) between the elution counts of 26 and 32.8 and marked with horizontal hash lines, has disappeared from the polymer prepared at 5°C and re-appeared as (+) after depolymerization between the elution counts of 32.8 and 36.0, marked with vertical hash lines. These areas may be converted into their respective distributions. The area representing the depropagated polymer when translated in terms of molecular weight distribution seems to have been built from two distinct distributions, one (B) appearing between the elution counts of 26 and 29

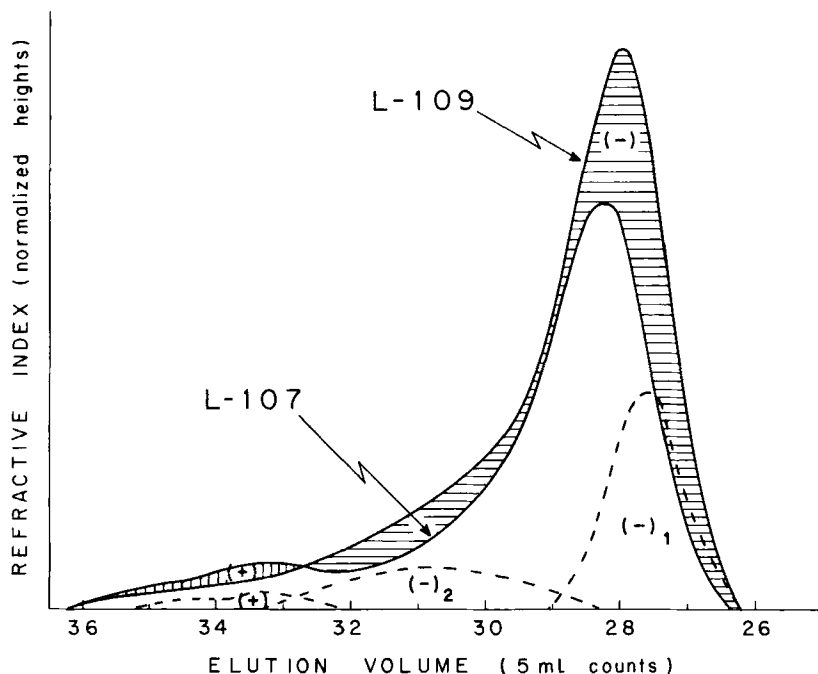


FIG. 15. Graphical method of analysis by which the GPC curves are broken down into components for poly- α -methylstyrene samples prepared from 3.0 M solutions with potassium-naphthalene as initiator. L-109 was polymerized at 5°C; L-107 was polymerized at 5°C but depolymerized at 25°C. See Tables 1, 3 and 7 for other data.

and the other between 28.5 and 33.0. This is little different from the earlier results of depropagation obtained in poly- α -methylstyrene in *p*-dioxane, where initiation was carried out with potassium alone. The depropagated polymer with potassium alone as initiator appeared to be made up of distribution out of a single species B. This once again confirms the formation of potassium-naphthalene complex species Kn, which is different in nature from a solvent-separated ion-pair B as well as the contact ion-pair C.

In order to get a better picture of the make up of distributions of L-109 and L-107 (see Fig. 16) one may proceed as follows. In the GPC distribution of sample L-107, the tracing of the distribution C may be carried out by drawing a mirror image of its right hand side distribution. Now on keeping in mind that the sum total area due to

TABLE 7. GPC Analyzed Concentration of Poly- α -methylstyrene at Various Elution Counts and Concentration of Polymer Associated with Each Component

Elution counts	L-109 (base-mole/liter) ^a	L-107 (base-mole/liter) ^b	(L-109) - (L-107) (base-mole/liter)	L-109 components (base-mole/liter)			L-107 components (base-mole/liter)					
				(D + A)	B	Kn	C	C	(D + A + B)	Kn	C	
26.5	0.04	0.01	-0.03	-	0.01	-	0.03	-	0.01	-	0.01	-
27	0.19	0.08	-0.11	-	0.08	-	0.11	-	0.08	-	0.08	-
27.5	0.42	0.21	-0.21	-	0.21	-	0.21	-	0.21	-	0.21	-
28	0.55	0.38	-0.17	-	0.36	-	0.19	-	0.36	-	0.38	-
28.5	0.44	0.38	-0.06	-	0.32	0.04	0.09	-	0.32	0.04	0.38	-
29	0.29	0.27	-0.02	-	0.19	0.08	0.02	-	0.19	0.08	0.22	0.05
29.5	0.19	0.17	-0.02	-	0.08	0.11	-	-	0.08	0.11	0.09	0.08
30	0.15	0.12	-0.03	-	0.01	0.14	-	-	0.01	0.14	0.10	0.02
30.5	0.12	0.08	-0.04	-	-	0.12	-	-	-	0.12	0.08	-
31	0.10	0.06	-0.04	-	0.01	0.09	-	-	0.01	0.09	0.06	-
31.5	0.08	0.05	-0.03	-	0.02	0.06	-	0.01	0.02	0.06	0.04	-
32	0.06	0.04	-0.02	-	0.03	0.03	-	0.03	0.03	0.03	0.01	-
32.5	0.05	0.04	-0.01	-	0.05	-	-	0.04	-	-	-	-
33	0.04	0.04	0.00	-	0.04	-	-	0.04	-	-	-	-
33.5	0.03	0.04	+0.01	-	0.03	-	-	0.04	-	-	-	-
34	0.03	0.04	+0.01	-	0.03	-	-	0.04	-	-	-	-

34.5	0.02	0.03	+0.01	0.02	-	-	-	0.03	-
35	0.02	0.02	-	0.02	-	-	-	0.02	-
35.5	0.01	0.01	-	0.01	-	-	-	0.01	-
Σ [P] e	2.84	2.07	0.77	0.26	1.26	0.67	0.65	0.26	0.42
									1.39

^aL-109: initiated at 25°C with potassium-naphthalene and polymerized at 25°C.

^bL-107: polymerized at 5°C and depolymerized at 25°C.

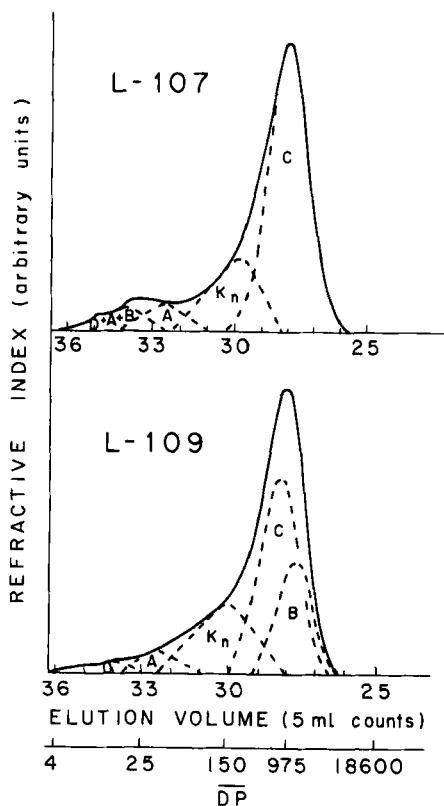


FIG. 16. GPC molecular weight distribution of polymers L-109 and L-107 in terms of various component traced on the basis of Fig. 15. See Tables 1, 3 and 7 for other data.

all distributions can not exceed that of the parent distribution, the rest of the distributions in L-107 can easily be traced. The distribution marked K_n in L-107 may be another part of the distribution $(-)_2$ which depropagated from the same elution counts in L-109 and thus can be added to it in order to make its distribution complete as it was present in the parent distribution L-109 before depropagation. The total of these two distributions as well as the distribution $(-)_1$ depropagating from L-109 between the elution counts of 26 and 29 may be fitted in L-109 thereby tracing the distribution of its component C. The other distributions can now be easily drawn.

The $[P]_e$ values associated with different components in the

polymerized (L-109) and the depolymerized (L-107) polymers are given in Table 7. Out of 2.84 base-mole/liter of polymer in L-109, 0.26 is attached to component (D + A), 1.26 to B, 0.67 to Kn, and 0.65 base-mole/liter to component C. On depolymerization at 25°C (L-107) the 1.26 base-mole/liter of B depropagates completely, 0.67 base-mole/liter of Kn depropagates to yield 0.42 of Kn, whereas the component C in L-109 which has only 0.65 base-mole/liter associated with it now has 1.38 base-mole/liter after depropagation. This observation is very similar to the one observed in an earlier work [7], where the depropagating species overshoot the limits of depropagation but after that postpolymerize. The active species C at 25°C consume all the depropagated monomer and grow. The proof that the two C components, in L-109 as well as in L-107, are due to the same species may be found in the fact that although the values of base-mole/liter of $[P]_e$ associated with them are different, both have 0.004 mole/liter of $[LE]$ attached with them (cf. Tables 1, 3).

Effect of Abrupt Killing

Throughout this communication it has been repeatedly stated that the multimodal distributions in p-dioxane are due to the presence of different reactive species and not due to killing of the bifunctional initiators as suggested in the literature [3, 5]. Brower and McCormick [5] had 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 distribution: (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 this hypothesis, a 2.60 M/solution of α -methylstyrene (polymer 16) was initiated and polymerized at 25°C with potassium as the initiator. It was observed that in the first 15 min the intensity of the red color in solution diminished throughout the solution, indicating that there were some impurities present either in the monomer or in the solvent. The polymerization in this reaction, however, continued, and once the reaction attained a steady state, it was opened to air and killed. This polymer 16 yielded 0.90 base-mole/liter of polymer and thus satisfied the thermodynamic requirements. The GPC chromatogram of polymer 16 is shown in Fig. 17, and compared with another polymer L-3 prepared from a 2.75 molar solution and in the same solvent. It may be remarked here that there was no drastic killing of the living ends in L-3 as was observed in polymer 16. In the latter polymer, where there was killing in the early stages of the reaction, 0.08 mole/liter of tetramer with an $[LE]$ of 0.026 mole/liter were formed, whereas in L-3 there is no such indication although there must be some dead tetramers in it. The component (A + B)

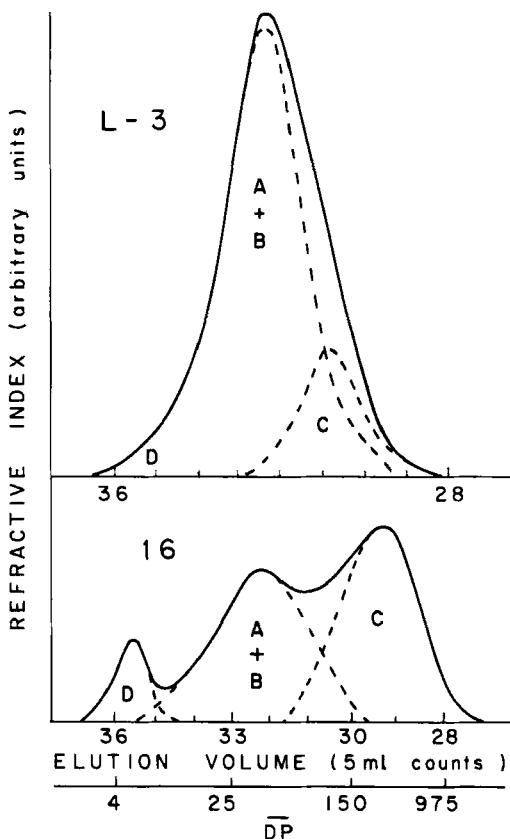


FIG. 17. A comparison of the GPC molecular weight distribution of poly- α -methylstyrene L-3 and 16, prepared at 25°C with potassium as initiator. L-3 shows no visible killing during polymerization; Polymer 16 shows killing in the very beginning of polymerization. See Table 3 for other data.

in the two samples appears at the same elution count and has an \overline{M}_w of about 5.0×10^3 in both cases. The component C however has an \overline{M}_w value of 3.8×10^4 in polymer 16 whereas in L-3 its value is only 1.3×10^4 . It would appear that the part of the monomer which was supposed to be utilized by the component (A + B) is now consumed by component C. The values of $[P]_e$ associated with components

(A + B) and C in the two polymers support this cause. In polymer L-3, $[P]_e$ associated with (A + B) is 0.66 base-mole/liter, whereas in polymer 16 it is only 0.35 base-mole/liter. Component C, on the other hand, has 0.15 base-mole/liter of polymer associated with it in L-3, whereas in polymer 16 it is 0.47 base-mole/liter (cf. Table 3).

If one has to base one's judgment solely on the results of these two experiments, the obvious conclusion would be that killing of the bifunctional initiators is responsible for it. The GPC chromatogram of polymer 16 fits, though partly, the description provided by Figini [3], Wenger [4], and McCormick [5] of a polymer produced in a medium where the solvent reacts with the growing polymer. However the other results of this study paint a different picture of the apparent situation. In the opinion of the authors, killing of polymers in p-dioxane does exist, but not in the shape of bimodal distributions. The long tails in the lower molecular weight region of the polymers are the effects of killing.

In conclusion, it may be said that in the polymerization of α -methylstyrene at low temperature in p-dioxane as solvent and with potassium as initiator there is a possibility of the presence of a solvent-separated ion-pair mechanism along with that due to a contact ion-pair. The presence of naphthalene yields an additional reactive species, and it may be a coordinate complex mechanism as suggested by Korotkov and co-workers [12], giving reversible propagation.

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