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Polymerization of α-Methylstyrene in Tetrahydrofuran with Potassium as Initiator. II. Gel-Permeation Chromatographic Analyses of Polymers

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ABSTRACT

Polymerization of α-methylstyrene initiated with potassium and potassium naphthalene in tetrahydrofuran as solvent has been carried out in the temperature range of -78 to 55°C. The type of propagation—whether reversible or irreversible—has been verified in these polymerizations at -78, -25, -5, and 25°C by comparing the gel-permeation chromatographic molecular weight distributions of polymers before and after depropagation. It has been postulated that in the polymerization of α-methylstyrene at 25°C with potassium alone as initiator, the propagation attributed to contact ion-pair mechanism is irreversible in nature. Contribution towards propagation at -25°C where solvent-separated ion-pairs are known to be active has been shown to be completely reversible. It has also been shown that at -78°C, where free ions are most reactive, the propagation may also be irreversible. In the presence of naphthalene in reactions at 25°C, the extent of reversibility has been shown to increase. This has been attributed to the tendency of naphthalene to form coordinate complexes with

potassium, which are quite capable of propagating the polymerization reaction thus leaving lesser monomer for the contact ion-pair propagation which is irreversible.

INTRODUCTION

In an earlier study [1] on the polymerization of α-methylstyrene at high temperatures with potassium as initiator and tetrahydrofuran (THF) as solvent, it was observed that the values of the polymer concentration at equilibrium $[P]_e$ were unusually high. The viscosity-average molecular weights $\overline{M}_v$, of these polymers were also quite high, considering that near the ceiling temperature only low molecular weight products should be obtained. The gel-permeation chromatographic (GPC) analyses of these products had shown them to possess multimodal distributions made up of polymers with average degree of polymerization $\overline{DP}$ ranging from 4 to 1000 and sometimes even greater than that.

Theoretical studies on the formation of multimodal distributions in living polymerizations initiated with bifunctional initiators are reported in the literature [2, 3]. The prime reason for such distributions is said to be the terminating agents which attack the growing ends indiscriminately and thus yield three types of polymers: dead polymers, polymers having only one growing end, and polymers possessing two growing ends. Bimodal distributions [4] in the anionic polymerization of methyl methacrylate have been attributed to the formation of helical structure with $\overline{M}_w$ of about 2000 along with a normal polymer of molecular weight 27,000. Sigwalt and coworkers [5], in their study on the anionic polymerization of propylene sulfide at -30° C in tetrahydrofuran as solvent, have shown that once the "living ends" [LE] exceed 10^{-3} mole/liter, their association or aggregation takes place. This, in our opinion, could also lead to bimodal distributions. Recently Schmitt and Schulz [6], in their studies on the polymerization of styrene in 3-methyltetrahydrofuran initiated with α-methylstyrene oligomers, have observed bimodal molecular weight distributions for their reaction products. According to these authors [6], different ion-pairs may have been responsible for these bimodal distributions.

In the previous study [1], the multimodal distributions were found to consist of four components D, A, B, and C. The low molecular weight components, D and A, were tentatively attributed to dead and dormant polymers, respectively. Components B and C were suspected to be correlated with the presence of various types of ion-pairs. It was also speculated that one of these species responsible for the formation of high molecular weight polymer at 25° C, yielded irreversible propagation.

In the present study an approach is developed to test the concept of reversibility in the anionic polymerization of α-methylstyrene in THF as solvent with potassium and potassium-naphthalene as initiators. Based on the knowledge of the active species said to be responsible for carrying out the propagation at different temperatures and based on the reversibility test, species yielding irreversible propagation have been singled out. The principal results of this study are presented in this communication.

EXPERIMENTAL

Materials and Procedure

The purification of materials and the experimental procedure employed in the present study have been discussed in detail elsewhere [1, 7]. In the present case, when potassium-naphthalene (Kn) was used as the initiator, the apparatus was, however, slightly different from that used in the earlier study [7], where in each experiment there was a provision for the formation of fresh potassium mirror for the purpose of initiation.

The potassium-naphthalene initiator used in the present work was prepared separately by distilling under vacuum a stoichiometric quantity of naphthalene on a mirror of potassium already formed along the walls of a glass tube attached to one wing of a Pyrex vessel whose other wing carried twelve calibrated side tubes each equipped with a break-seal and an iron bar encased in a Pyrex ampoule as the seal breaker [8]. A desired amount of THF was then distilled to dissolve the potassium-naphthalene complex. After distributing equal amounts of the potassium-naphthalene complex solution in the ampoules, these were removed one by one from the parent apparatus. These were generally used within a week of their preparation and were refrigerated at all times to avoid any decompositions.

Depending upon [LE] required for a given experiment, the corresponding number of initiator ampoules were attached to the apparatus. After having distilled the monomer and the solvent in the apparatus it was sealed off the vacuum line, allowed to attain the room temperature of 25° C, the contents mixed thoroughly, and then with the help of a bar magnet the potassium-naphthalene solution was mixed with that of the monomer, yielding instant initiation.

Gel-Permeation Chromatographic Analysis (GPC)

The procedure concerning the analysis of GPC has been discussed in an earlier paper [1] in detail and thus has not been repeated. However, some points pertinent to this study have been retained. In the present case, as in the earlier study [1], two sets of columns were used to find out the GPC molecular weight distributions. In set (a), four columns with maximum rated porosity of 1×10^6, 1.5×10^5, 3×10^3, and 250 Å were used in series. The length of the first two columns was 3 ft each, whereas the other two were each 4 ft long. In set (b), three 4-ft columns with maximum rated porosity of 1×10^6, 1.5×10^5 and 3×10^3 Å were used.

In order to demonstrate that the analyses of $[P]_e$ and [LE] associated with different components, for a sample of poly-α-methylstyrene passed through these two sets of columns, does not vary by much, in Fig. 1 are shown the GPC chromatograms of polymer 68. The separation in the high molecular weight region with set (b) is better than that with set (a) due to the extra length of the former set of columns. In the lower molecular weight region, in set (a) the component D elutes as a long tail but with set (b) the resolution is improved by a great deal. The values of $[P]_e$ associated with components (D + A), B and C in 68a were 0.69, 0.50 and 0.77 base-mole/liter respectively whereas with 68b, for the same components, these values read as 0.65, 0.53 and 0.78 base-mole/liter respectively. The values of [LE], on the other hand, for components (D + A), B, and C in 68a were 0.097, 0.005, and 0.001 mole/liter, respectively whereas in 68b for the same components these were 0.130, 0.004, and 0.01 mole/liter. One notes that the error lies only in the [LE] values for very low molecular weight component, (D + A). This error arises out of the fact that it is very difficult to obtain low molecular weight pure oligomers for the purpose of instrument calibration.

RESULTS AND DISCUSSION

Polymerization at 25°C

It has been reported [9] that the bulk polymerization of α-methylstyrene initiated with BuLi is irreversible. A similar experiment was attempted in this laboratory to verify the reversibility of poly-α-methylstyrene prepared with potassium as initiator. Polymerization was carried out in a dilatometer and its progress followed by noting the changes in the miniscus height. After about 24 hr the miniscus appeared to have reached a stationary state. At this stage the

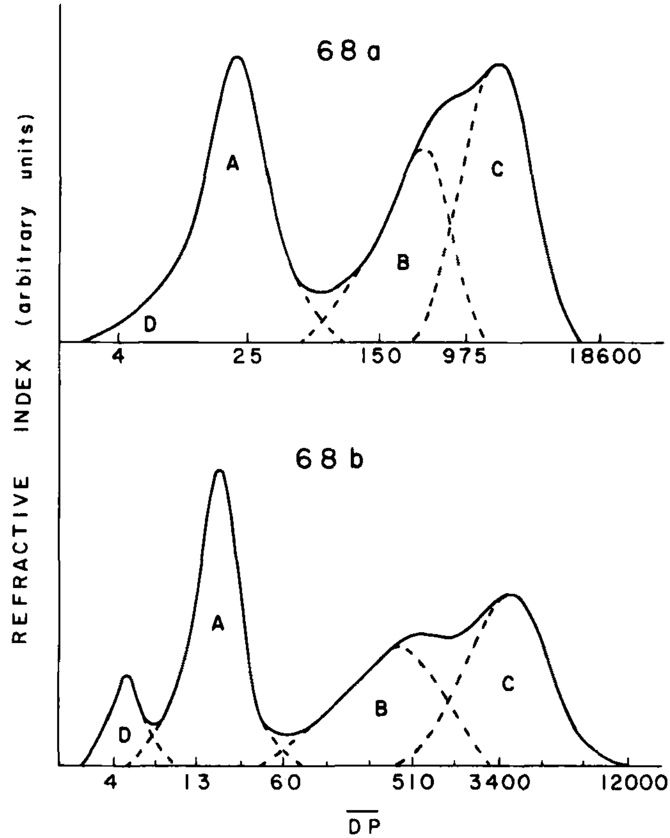

FIG. 1. GPC chromatograms of poly-α-methylstyrene sample 68 resulting from two different sets of column arrangement. (a) four columns; two 3-ft long columns having porosity of 1.0×10^6 and 1.5×10^5 A, respectively, and two others, each 4 ft long with porosity of 3×10^3 and 250 Å, respectively; (b) three 4-ft columns with porosity of 1.0×10^6, 1.5×10^5, and 3.0×10^3 Å, respectively.

dilatometer was immersed in an oil bath set at 60°C. It was observed that, besides the volume change due to the thermal expansion due to the increase in temperature from 25 to 60°C, there were no other volume changes because of depropagation. The solid polymer was recovered by breaking the dilatometer and the red color in the polymer persisted for about 16 hr before it disappeared completely. This may be attributed to the inability of air to diffuse through the solid polymer. It is apparent that if the disappearance of the red color is related with the killing of living ends by oxygen, the propagation of the active species formed under these conditions is irreversible because the reversible species would have depropagated before they were destroyed by oxygen.

In order to stay away from such unfavorable conditions, solutions having slightly lower initial monomer concentration ($[M]_0$ between 4.0 to 6.0 mole/liter), than those used in the bulk conditions (7.2 mole/liter) were prepared. In Fig. 2 are shown GPC distributions of polymers L-96 and L-97 which were initiated with potassium at 25°C, polymerized at 25°C, and depolymerized at 40°C for 3 days. It was noted that these do not depropagate to yield $[P]_e$ values expected at 40°C [1], as presented in Table 1. The initial monomer concentrations in L-96 and L-97 were 4.0 mole/liter and the expected theoretical values for $[P]_e$ at 25 and 40°C are about 2.5 and 0.65 mole/liter, respectively [1]. The experimental $[P]_e$ values of 3.08 for L-96 and 2.35 for L-97 at 40°C are closer to those expected theoretically at 25°C. The reason for the different $[P]_e$ values in the case of L-96 and L-97 arises out of the different initial [LE] used in these two polymers (cf. Table 1). Because of the higher [LE] in L-96, the low molecular weight component (D + A) is more important than that in L-97. Components B and C in the two polymers have more or less the same $[P]_e$ associated with them. However, the [LE] associated with component C is different in L-96 and L-97, although component B has the same [LE] in the two cases.

In Fig. 3 are shown the GPC distributions of poly α-methylstyrene samples L-90 and L-91, prepared from solutions of $[M]_0 = 4.50$ mole/liter at 25°C and depolymerized at 40°C. The $[P]_e$ values after depolymerization do not correspond to those expected at 40°C (Table 1). The GPC molecular weight distributions of the two polymers appears similar, the higher proportion of (D + A) in L-90 resulting because of the higher [LE] used. The $[P]_e$ and [LE] values associated with components B and C in the two polymers are also identical.

In Fig. 4 are shown the GPC chromatograms of poly-α-methylstyrene samples L-93 and L-94 prepared under exactly identical conditions from a 5.0 $\underline{M}$ solution with potassium as initiator. These were once again polymerized at 25°C and depolymerized at 40°C. The $[P]_e$ and [LE] values associated with different components in the two experiments (Table 1) are very close reflecting on the reliability of the data.

The high values of $[P]_e$ which are observed here show that depropagation in the system under study is not prominent. However,

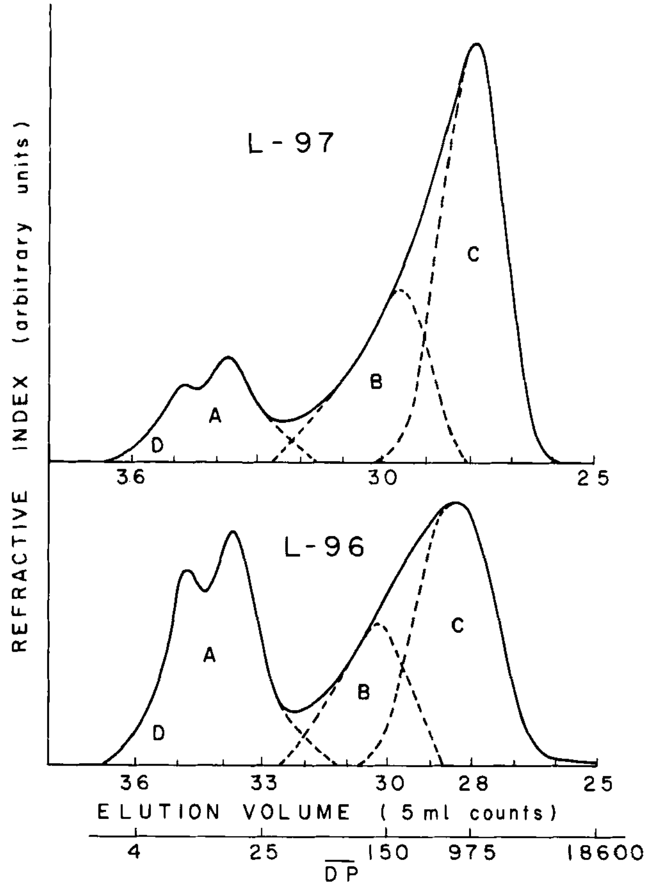

FIG. 2. GPC molecular weight distributions of poly-α-methylstyrenes (L-96, L-97) initiated and polymerized with potassium at 25°C from a 4.0 M solution of α-methylstyrene in THF and depolymerized at 40°C. (See Table 1 for other data).

it is possible that these reactions are reversible to a certain extent which can be checked through dilatometry as was done in the case of bulk polymerization. In an experiment, two 5.5 M solutions of monomer were initiated at 25°C with potassium and polymerized at this temperature till an equilibrium had been reached. One of these (L-81) was terminated at 25°C and yielded 5.55 base-mole/liter of polymer which represents 82% conversion. The other

TABLE 1. GPC Analysis of $[P]_e$ and [LE] Associated with Different Components in Depolymerized Samples of Poly-α-methylstyrene Prepared at 25°C[a]

		$[P]_e$ at depolymerization temperature (base-mole/liter)						[LE] (mole/liter)			
No.	$[M]_0$ (mole/liter)	(D + A)	B	C	Total $[P]_e$	Expected $[P]_e$ at 25°C (base-mole/liter)[b]	Expected $[P]_e$ at depolymerization temperature (base-mole/liter)[b]	(D + A)	B	C	Total [LE]
L-97	4.0	0.43	0.65	1.27	2.35	2.50	0.65	0.074	0.010	0.003	0.087
L-96	4.0	1.20	0.62	1.26	3.08			0.216	0.012	0.006	0.234
L-91	4.5	0.52	0.92	2.32	3.76	3.50	1.30	0.097	0.015	0.005	0.117
L-90	4.5	1.23	1.12	2.07	4.42			0.224	0.020	0.007	0.251
L-94	5.0	0.49	0.81	2.63	3.94	4.00	1.60	0.082	0.016	0.005	0.103
L-93	5.0	0.50	1.02	2.56	4.08			0.096	0.016	0.005	0.117
L-80	5.5	0.54	1.38	4.33	6.25	5.55	1.31	0.065	0.015	0.006	0.086
L-81	5.5	0.58	2.03	2.94	5.55			0.060	0.018	0.006	0.084

[a] Conditions: Polymers L-90 to L-97 were initiated and polymerized at 25°C and depolymerized at 40°C. L-80 and L-81 were initiated and polymerized at 25°C, however L-80 was depolymerized at 50°C. Potassium mirror was used for initiation purposes.

[b] Prediction based on Léonard and Malhotra [1].

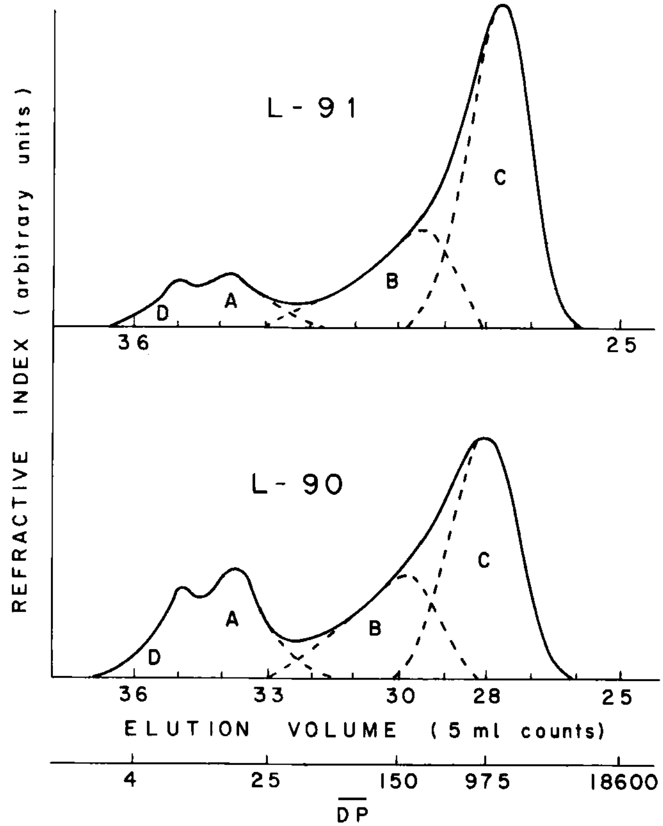

FIG. 3. GPC molecular weight distributions of poly-α-methylstyrenes (L-90, L-91) initiated and polymerized with potassium at 25°C from a 4.5 M solution of α-methylstyrene in THF and depolymerized at 40°C. See Table 1 for other data.

solution (L-80) was depolymerized in a dilatometer at 50°C. Upon raising the temperature it was observed that the volume of the solution increased beyond the volume expected due to thermal expansion. After about 1 hr, the volume reached a stationary state and then started decreasing indicating that after depolymerization, polymerization had restarted. Once the reaction was over the $[P]_e$ of the polymer produced was found to be 6.25 base-mole/liter (93% conversion). The expected value of $[P]_e$ at 50°C for this experiment is 1.31 base-mole/liter (Table 1).

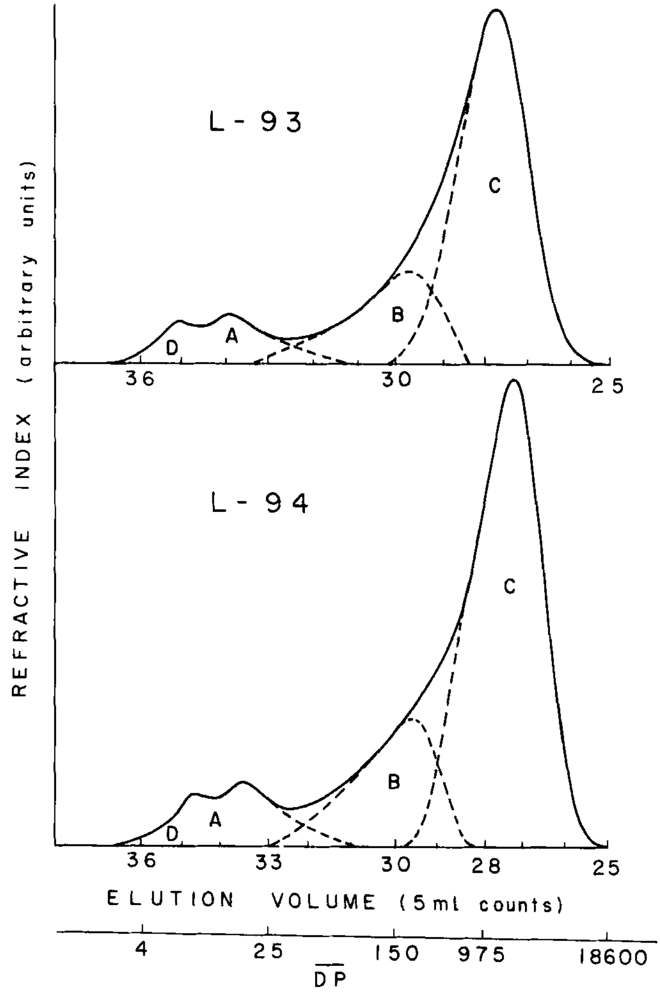

FIG. 4. GPC molecular weight distributions of poly-α-methylstyrenes (L-93, L-94) initiated and polymerized with potassium at 25°C from a 5.0 M solution of α-methylstyrene in THF and depolymerized at 40°C. See Table 1 for other data.

In view of this unusual behavior, the chromatograms of polymers L-80 and L-81 were analyzed more extensively. This has been achieved by a graphical superimposition [10] of the normalized molecular weight distribution of L-80 and L-81 (see Fig. 5) traced on the basis of GPC analyzed weights of these two polymers at various elution counts as presented in Table 2. It may be noted that polymer b, between the elution counts of 28 and 33 (lower molecular weights) and marked with vertical hash lines, disappears, whereas another c between the elution counts of 25 and 28 (higher molecular weights) and marked here with horizontal hash lines, appears on depropagation of L-81 at 50°C. The first conclusion one is liable to make from these observations is that polymer b picks up some of the depropagated monomer and yields component c. This, however, is not necessarily true, as can be shown in the following way. The areas under the hash lines may be transformed in terms of molecular weight distributions b and c meeting at an elution count of 27.7. In reality, there may be some overlapping of the two distributions in such a way that the tail of distribution c and the head of distribution b are placed at the same elution count as shown in Fig. 5, by the broken lines. The tracing of these broken lines is based essentially on the overall shape of the curves, be they broad, gaussian, or other in distribution but these are at best only a first approximation. The calculated $[P]_e$ of the polymer attributed to component b, on the basis of its surface area under the broken line, is 0.90 base-mole/liter with a GPC calculated [LE] of 3.3×10^{-3} mole/liter. The $[P]_e$ of component c, on the other hand, is 1.62 base-mole/liter. If component c were to have its origin from component b, then the maximum $\overline{M}_n$ of c could not have exceeded 1.0×10^5. However, a $\overline{M}_n$ value of 2.95×10^5 for component c with a GPC-calculated [LE] of 1.3×10^{-3} mole/liter rules out its origin solely from component b. The $\overline{M}_w$ values for components b and c are 1.08×10^5 and 4.13×10^5, respectively.

In order to find out the origin of component c in L-80, the GPC chromatograms of L-80 and L-81 (Fig. 6) were analyzed for $[P]_e$ and [LE] associated with each component (see Table 1). The tracing of these components was carried out as discussed in the following text. From Fig. 6 one notes that in the GPC chromatogram L-80, one can easily draw the left-hand distribution of the high molecular weight component appearing between the elution counts of 25 and 30 by simply tracing the mirror image of its right-hand side distribution. The distributions of the remainder components B and (D + A) pose no problem if one keeps in mind that the sum area of all the components should not exceed the total area under the GPC envelope. The distributions of components b (from Fig. 5) and B (from L-80 in Fig. 6) may now be added together and inserted in the distribution of L-81 (Fig. 6) to derive component C. A comparison of the $[P]_e$ and the molecular weight values of components B + b with B and C + c with C is presented in Table 2. It may be noted that the $[P]_e$ (2.93 base-mole/liter) and $\overline{M}_w$ (2.03×10^5) of component C in L-81 after depropagation

TABLE 2. GPC Analyzed Weights of Poly-α-methylstyrene at Various Elution Counts and Concentration of Polymer Associated with Each Component

No. of 5 ml counts	L-80 (base-mole/liter)[a]	L-81 (base-mole/liter)[b]	(L-81) - (L-80) (base-mole/liter)	From L-81 (base-mole/liter)			From L-80 (base-mole/liter)		
				(D + A)	(B + b)	C	(D + A)	B	(C + c)
25.5	0.05	0.01	0.04	-	-	0.01	-	-	0.05
26.0	0.33	0.07	0.26	-	-	0.07	-	-	0.33
26.5	0.79	0.31	0.48	-	-	0.31	-	-	0.79
27.0	1.19	0.72	0.47	-	0.08	0.64	-	-	1.19
27.5	0.99	0.91	0.08	-	0.17	0.74	-	-	0.99
28.0	0.70	0.86	-0.16	-	0.25	0.61	-	0.11	0.59
28.5	0.50	0.69	-0.19	-	0.29	0.40	-	0.20	0.30
29.0	0.36	0.49	-0.13	-	0.36	0.13	-	0.27	0.09
29.5	0.28	0.34	-0.06	-	0.31	0.03	-	0.28	-
30.0	0.22	0.23	-0.01	-	0.23	-	-	0.22	-
30.5	0.15	0.17	-0.02	-	0.17	-	-	0.15	-
31.0	0.12	0.14	-0.02	0.04	0.10	-	0.02	0.10	-
31.5	0.09	0.12	-0.03	0.06	0.06	-	0.04	0.05	-
32.0	0.08	0.10	-0.02	0.09	0.01	-	0.08	-	-
32.5	0.05	0.09	-0.04	0.09	-	-	0.05	-	-
33.0	0.05	0.08	-0.03	0.08	-	-	0.05	-	-

33.5	0.07	0.06	+0.01	0.06	-	-	0.07	-	-
34.0	0.08	0.05	+0.03	0.05	-	-	0.08	-	-
34.5	0.07	0.03	+0.03	0.03	-	-	0.07	-	-
35.0	0.08	0.05	+0.03	0.05	-	-	0.08	-	-
35.5	0.00	0.03	-0.03	0.03	-	-	0.00	-	-
$\Sigma[P]_e$	6.25	5.55	0.69	0.58	2.03	2.94	0.54	1.38	4.33
Molecular weight $\overline{M_w}$ (GPC) × 10^{-4}				-	6.04	20.3	-	3.84	30.60

[a] L-81: initiated with potassium and polymerized at 25° C.

[b] L-80: initiated with potassium, polymerized at 25° C and depolymerized at 50° C.

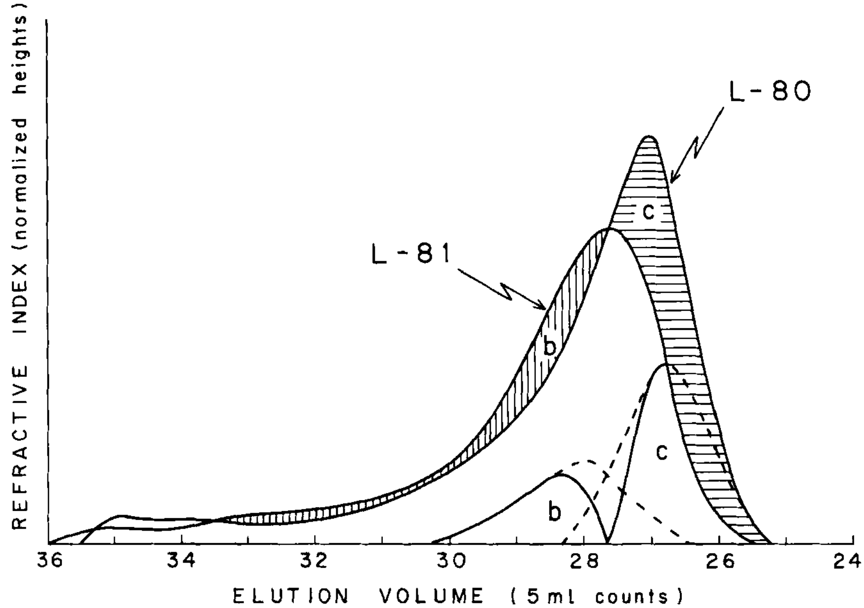

FIG. 5. Graphical method of analysis by which GPC distribution curves are broken down into their components: the case of poly-α-methylstyrenes initiated and polymerized with potassium at 25°C (L-81) and depolymerized at 50°C (L-80). See Tables 1 and 2 for other data.

at 50°C (L-80) had increased to a $[P]_e$ of 4.35 base-mole/liter and an $\overline{M_w}$ of 3.06×10^5. The new component is represented in L-80 as (C + c). Furthermore the $[P]_e$ [2.03 base-mole/liter and $\overline{M_w}$ (6.04×10^4)] of component (B + b) in L-81 on depropagation at 50°C decreased to a $[P]_e$ of 1.38 base-mole/liter and an $\overline{M_w}$ of 3.84×10^4. An analysis of the [LE] values associated with (B + b) (0.018 mole/liter) and B (0.015 mole/liter) as well as components (C + c) (0.006 mole/liter) and C (0.006 mole/liter) shows that component b with [LE] of 0.003 mole/liter has depropagated to yield very low molecular weight products (oligomers) and component C has picked up the liberated monomer to form a new component (C + c) with higher $[P]_e$ and $\overline{M_w}$ values.

Based on the analyses of Figs. 2 to 6 and the data of Tables 1 and 2,

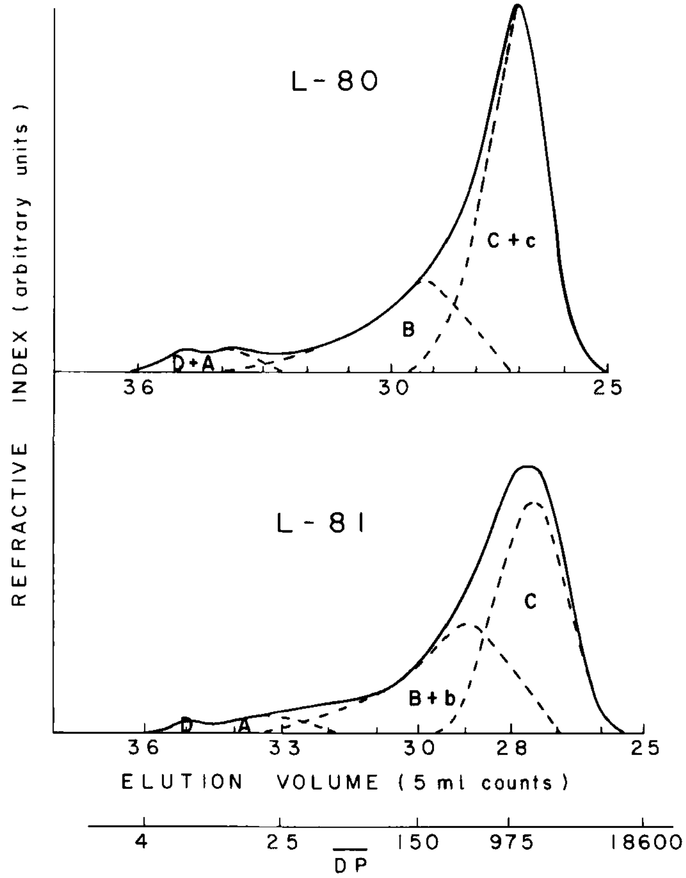

FIG. 6. GPC molecular weight distributions of poly-α-methylstyrenes showing the distribution changes in the components on depolymerization at 50° C (L-80) on a polymer prepared at 25° C (L-81). See Table 1 for other data.

one ought to conclude that upon raising the temperature, a major part of the propagation gets an irreversible characteristic. If one correlates this observation with the mechanism of propagation thought [11] to be responsible for polymerization at 25° C, one would have to say that the contact ion-pairs yield irreversible propagation. There are, however other postulations which can be made to explain these irreversible reactions. For example it may be that besides the contact ion-pairs there is yet another active species present (under the reaction conditions used in the present experiments, cf. Tables 1 and 2, Figs. 2 to 6) which would have more covalent character as compared to that of the contact ion-pair and yield irreversible propagation. It is also possible that, on raising the temperature, a part of the conventional contact ion-pairs are transformed into the alleged irreversible species.

Polymerization at -5° C

All of the studies reported earlier in the text were carried out with $[M]_0$ values ranging from 4.0 to 7.2 mole/liter. It has been mentioned in these experiments that the initiation at 25° C was slow, and some polymer was formed during the period of initiation, the quantity of polymer being formed depended on the value of $[M]_0$. Since in most of the experiments the process of initiation was performed at 25° C it is difficult to evaluate as to what amount of polymer was formed during initiation. This does not pose any problem when the propagation is carried out at 25° C; however, in propagations performed at lower temperatures, the absolute contribution towards propagation at these temperatures is difficult to estimate, if one uses initial concentrations $[M]_0$ higher than 2.0 mole/liter. The reason for this lies in the fact that the monomer concentration at equilibrium $[M]_e$ at 25° C for the present system is 2.5 mole/liter, and thus any solution having $[M]_0$ of about 2.0 and higher will have polymer formation during the process of initiation. The quantity of polymer formed though is significant only in cases where $[M]_0$ higher than 2.5 mole/liter is employed. In order to overcome this problem in polymerizations at -5° C, these were first polymerized completely at 25° C in duplicate before the reaction vessel was brought to -5° C for further polymerization. The difference between the two polymer concentrations at -5 and 25° C yielded contributions towards propagation exclusively at -5° C.

In Fig. 7 are shown the GPC chromatograms of polymers L-104, L-105, and L-106, prepared from a 2.0 <u>M</u> solution of α-methylstyrene in THF as solvent and potassium as initiator. The three experiments were carried out at 25° C, and once these had attained stationary states, L-106 was opened at 25° C whereas the other two (L-105 and L-104) were further-polymerized at -5° C. Polymer L-105 was opened at -5° C but L-104 was brought back to 25° C. Polymer L-106 had a $[P]_e$ value of 0.38 base-mole/liter and showed multimodal distributions when passed through GPC. These multimodal distributions were split into components (D + A), B, and C. The $[P]_e$ and $[LE]$ values associated with these components is presented in Table 3. Polymer L-105 had a $[P]_e$ of 2.0 base-mole/liter thus indicating that

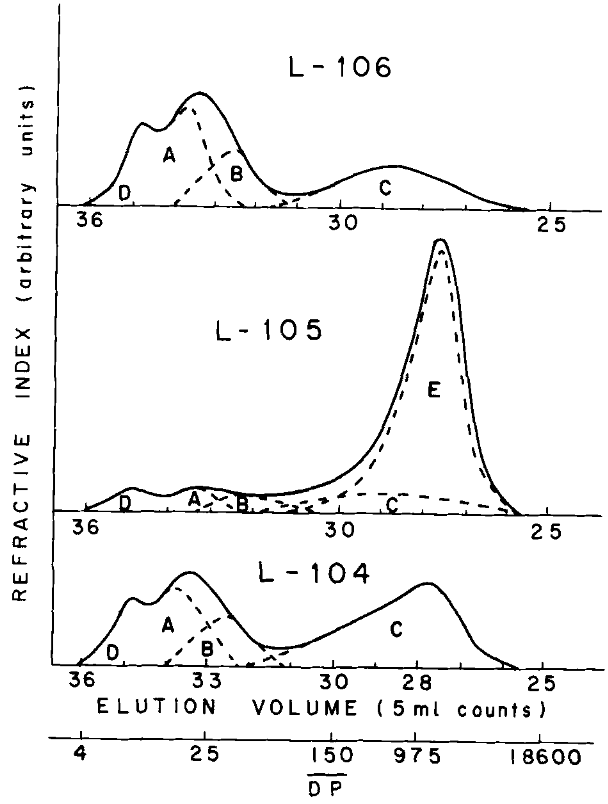

FIG. 7. GPC molecular weight distributions of poly-α-methylstyrenes initiated and polymerized at 25°C with potassium from a 2.0 M solution of α-methylstyrene in THF (L-106), further polymerized at -5°C (L-105) and depolymerized at 25°C (L-104). See Table 3 for other data.

1.62 base-mole/liter of this was formed at -5°C whereas 0.38 base-mole/liter came out of propagation reaction at 25°C. Polymer L-104 which was polymerized at 25°C, further-polymerized at -5°C and depolymerized at 25°C yielded 0.41 base-mole/liter of polymer indicating that the polymer formed at -5°C is completely reversible.

The GPC analyses of L-104, L-105 and L-106 show (Fig. 7, Table 3) that component (D + A) which was present in the parent distribution (L-106) is still present in L-105 after polymerization at -5°C. Some parts of component B in L-106 seem to have further-polymerized and

TABLE 3. GPC Analysis of $[P]_e$ and [LE] Associated with Different Components in Polymerized and Depolymerized Samples of Poly-α-methylstyrene Prepared at Different Temperatures

No.	Temperature of polymerization (°C)	Temperature of depolymerization (°C)	$[M]_0$ (mole/liter)	$[P]_e$ (base-mole/liter)				$[M]_e$ (mole/liter)	[LE] (mole/liter)			
				(D + A)	B	C	Total $[P]_e$		(D + A)	B	C	Total [LE]
L-106	25	-	2.0	0.18	0.08	0.12	0.38	1.69	0.031	0.005	0.001	0.037
L-105	25, -5	-	2.0	0.16	0.06	0.12	2.00	0.25	0.030	0.005	0.001	0.041
				E = 1.66					E = 0.005			
L-104	25, -5	25	2.0	0.14	0.07	0.20	0.41	1.68	0.026	0.004	0.001	0.031
L-101	25	-	3.0	0.16	0.46	0.30	0.92	2.24	0.031	0.022	0.004	0.057
L-103	25, -5	-	3.0	0.29	0.75	0.39	3.00	0.25	0.061	0.036	0.005	0.106
				E = 1.57					E = 0.004			
L-102	25, -5	25	3.0	0.23	0.49	0.43	1.15	2.05	0.045	0.029	0.007	0.081
L-116	25, -78	-	4.0	0.12	2.98	0.60	5.00	0.10	0.018	0.004	0.007	0.032
				F = 1.29					F = 0.003			
L-118	25, -78	25	4.0	0.12	0.26	0.58	2.25	2.13	0.021	0.004	0.007	0.035
				F = 1.29					F = 0.003			

reappeared between the elution counts of 25 to 31 and thus while analyzing this zone in L-105 one may erroneously conclude that it is the component C in L-106 which picks up the monomer and yields 1.62 base-mole/liter of additional polymer at -5° C. In order to clarify this point, one may refer to Table 3, where the values of [LE] for all the components of L-106 and L-105 are presented. It may be noted that the [LE] associated with component C in L-106 is 0.001 mole/liter whereas in L-105 component E, which is located at the same elution counts of 25 to 31 as for C in L-106, has a [LE] value of 0.005 mole/liter indicating that E in L-105 does not have its origin from component C in L-106. A comparison of the GPC distributions of L-105 with that of L-104 reveals that, on depolymerization, component E disappears from L-105 and the GPC distribution of the depolymerized polymer L-104 resembles that of L-106, confirming the earlier conclusion that polymer formed at -5° C is completely reversible.

In Fig. 8 are shown the GPC distributions of three polymers, L-101, L-103, and L-102, prepared from a 3.0 <u>M</u> solution of α-methylstyrene in THF. The procedure adopted for these three was the same as that for L-106, L-105 and L-104 described earlier. L-101 represents a polymer prepared at 25° C, L-103 polymerized at 25° C and further polymerized at -5° C, whereas L-102 was polymerized at 25° C, further polymerized at -5° C, and depolymerized at 25° C. The analyses of their chromatograms are also presented in Table 3. It may be noted from Table 3 and Fig. 8 that component E in L-103 is completely reversible when depolymerized at 25° C. The GPC distributions of the depolymerized polymer L-102 resembles that of L-101. From these results one may safely conclude that the predominant propagating species at -5° C, which are the solvent-separated ion-pairs [11], are reversible in nature.

Polymerization at -78° C

The species thought to be most effective [11] in the polymerization of α-methylstyrene at -78° C with THF as solvent are the free ions and also to some extent the solvent-separated ion-pairs. After having established that the solvent-separated ion-pairs yield reversible propagation, it was thought of interest to know the type of propagation rendered by the free-ions. In an experiment, two 4.0 M solutions of α-methylstyrene in THF as solvent were initiated at 25° C with potassium as initiator and polymerized at -78° C. One of these (L-116) was opened at -78° C, and it yielded 5.0 base-mole/liter of polymer. The other (L-118), polymerized at -78° C and depolymerized at 25° C, yielded 2.25 base-mole/liter of polymer. These values of $[P]_e$ at -78° C (5.0 base-mole/liter) and at 25° C (2.25 base-mole/liter) agree well with the expected $[P]_e$ values

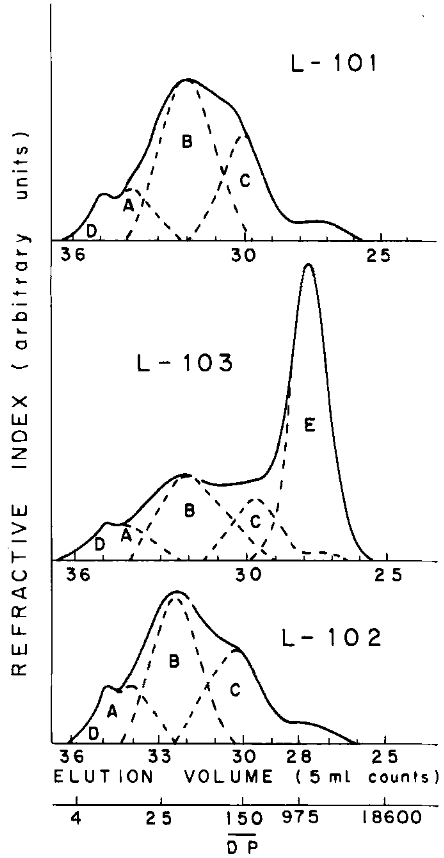

FIG. 8. GPC molecular weight distributions of poly-α-methylstyrenes initiated and polymerized at 25°C with potassium from a 3.0 M solution of α-methylstyrene in THF (L-101), further polymerized at -5°C (L-103) and depolymerized at 25°C (L-102). See Table 3 for other data.

for a 4.0 M solution at these temperatures. Based on these results one would be tempted to conclude that the propagation rendered by the free ions as well as the solvent-separated ion-pairs is completely reversible. However a GPC analyses of these polymers shows that the above statement is partly true, and only the latter of the two propagations is reversible in nature. The approach used in this analysis was similar to the one mentioned earlier in the text for the cases L-80 and L-81.

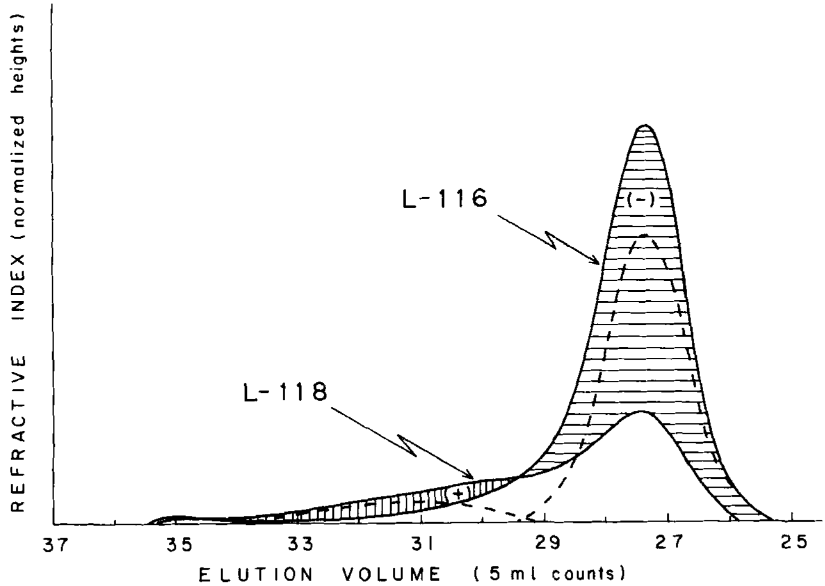

FIG. 9. Graphical method of analysis by which GPC distribution curves are broken down into their components: the case of poly-α-methylstyrenes initiated at 25° C and polymerized with potassium from a 4.0 M solution of α-methylstyrene in THF at -78° C (L-116), and depolymerized at 25° C (L-118). See Tables 3, 4 for other data.

In Fig. 9 are superimposed the normalized molecular weight distributions of L-116 (-78° C) and L-118 (-78 and 25° C) traced on the basis of the GPC-analyzed weights of the two polymers at various elution counts as presented in Table 4. The polymer between the elution counts of 25 to 29.5, under the area marked with horizontal hash lines has disappeared on depropagating the reaction at 25° C, and part of it has reappeared between the elution counts of 30 to 34. The disappeared polymer surface has been transformed into its molecular weight distribution and is shown in Fig. 9.with the dotted lines. It may be remarked that the maximum peak elution count for the depolymerized (L-118) and the one which is not depolymerized (L-116); is the same at about 27.7. This would mean that a part of the polymer, prepared at -78° C and having its maxima at an elution count of 27.7, on depolymerization yields lower molecular weight component with its maxima at an elution count of 31.5, whereas the other part does not depolymerize. The depolymerization reaction in a polymer with a $[P]_e$ of 5.0 base-mole/liter and an $\overline{M_w}$ of

TABLE 4. GPC Analyzed Weights of Poly-α-methylstyrenes at Various Elution Counts, Polymer Concentrations, and [LE] Associated with Each Component

No. of 5 ml counts	L-116 (base-mole/liter)	L-118 (base-mole/liter)	(L-116) - (L-118) (base-mole/liter)	From L-116 (base-mole/liter)				From L-118 (base-mole/liter)			
				(D + A)	B	C	F	(D + A)	B	C	F
25.5	0.03	0.00	-0.03	-	0.03	-	0.00	-	-	-	0.00
26.0	0.14	0.02	-0.12	-	0.12	-	0.02	-	-	-	0.02
26.5	0.53	0.13	-0.40	-	0.40	-	0.13	-	-	-	0.13
27.0	1.11	0.29	-0.82	-	0.82	-	0.29	-	-	-	0.29
27.5	1.27	0.35	-0.92	-	0.92	-	0.35	-	-	-	0.35
28.0	0.83	0.28	-0.55	-	0.52	0.05	0.26	-	-	0.02	0.26
28.5	0.41	0.21	-0.20	-	0.17	0.08	0.15	-	-	0.06	0.15
29.0	0.21	0.16	-0.05	-	-	0.14	0.07	-	-	0.09	0.07
29.5	0.13	0.14	+0.01	-	-	0.11	0.02	-	-	0.12	0.02
30.0	0.09	0.13	+0.04	-	-	0.09	-	-	-	0.13	-
30.5	0.06	0.12	+0.06	-	-	0.06	-	-	0.03	0.09	-
31.0	0.04	0.10	+0.06	-	-	0.04	-	-	0.05	0.05	-
31.5	0.03	0.09	+0.06	-	-	0.03	-	-	0.07	0.02	-
32.0	0.03	0.07	+0.04	0.03	-	-	-	-	0.07	-	-
32.5	0.02	0.05	+0.03	0.02	-	-	-	0.02	0.03	-	-
33.0	0.01	0.04	+0.03	0.01	-	-	-	0.03	0.01	-	-

33.5	0.01	0.03	+0.02	0.01	-	-	-	0.03	-	-	-
34.0	0.01	0.02	+0.01	0.01	-	-	-	0.02	-	-	-
34.5	0.01	0.01	+0.00	0.01	-	-	-	0.01	-	-	-
35.0	0.03	0.01	-0.02	0.03	-	-	-	0.01	-	-	-
$\Sigma[P]_e$	5.00	2.25	-2.75	0.12	2.98	0.60	1.29	0.12	0.26	0.58	1.29
		$\overline{M_w}$ (GPC) × 10^{-4}		-	26.00	3.45	19.80	-	0.80	2.75	19.80

2.95×10^5 (as is the case for L-116) to a polymer with $[P]_e$ of 2.25 base-mole/liter (L-118) should yield a polymer having $\overline{M_w}$ of about 1.25×10^5. When the $\overline{M_w}$ value of the depolymerized polymer does not change, it could mean three things: (a) that the polymer which is irreversible is a dead polymer; (b) that the polymer is made up from two types of species and by a sheer coincidence these yield polymers having the same maxima; or (c) that the phenomenon resembles that of thermal degradation of polystyrene ($\overline{M_w} = 1.03 \times 10^4$) [10], which has also been explained in terms of complete depolymerization of the radical bearing chains, where a random proportion of polymer leaves the reaction medium and this is independent of molecular weights. However, keeping in mind, the process of depolymerization in the present studies (Figs. 7 and 8), it would appear that explanations (a) and (b) have more weight to them as compared to (c), where very high temperatures (300-400°C) were used for depolymerization. If one retains explanation (a), for the present study it would mean that the free-ion mechanism yields reversible propagation. However if the explanation (b) is considered to be true, it could also mean that the part of the polymer which is reversible may be attributed to solvent-separated ion-pairs, whereas the other which does not depolymerize and is formed exclusively at -78°C may be due to a free-ion mechanism.

In order to trace different components in the GPC chromatograms of L-116 and L-118 for the purpose of computing $[P]_e$ and [LE] associated with various species, one may proceed as follows. The distribution of the depolymerized portion of the polymer L-116 (shown with dotted lines in Fig. 9) may be subtracted from the total envelope of L-116, thus yielding components B, F, C, and (D + A) (Fig. 10, L-116). In the GPC chromatogram of L-118, the distribution of the highest molecular weight polymer (elution counts 25-30) may be traced on the basis of its right hand side distribution. Once again the distributions of D + A, B and C are easy to trace. The calculated values of $[P]_e$ and [LE] associated with different components, viz., (D + A), B, C, and F in L-118 and L-116 are presented in Table 3. Based on these results it would appear that L-116 (-78°C) is built up of 0.12 base-mole/liter of (D + A), 0.60 base-mole/liter of C, 1.29 base-mole/liter of F, and 2.98 base-mole/liter of component B. On depolymerization, the component B (2.98 base-mole/liter) depropagates and yields a lower molecular weight polymer with a $[P]_e$ value of 0.26 base-mole/liter. This component B has been attributed to be originating from a solvent-separated ion-pair, F has been designated to a free-ion and C that due to a contact ion-pair mechanism. The assignment of polymer C to a contact ion-pair mechanism has been

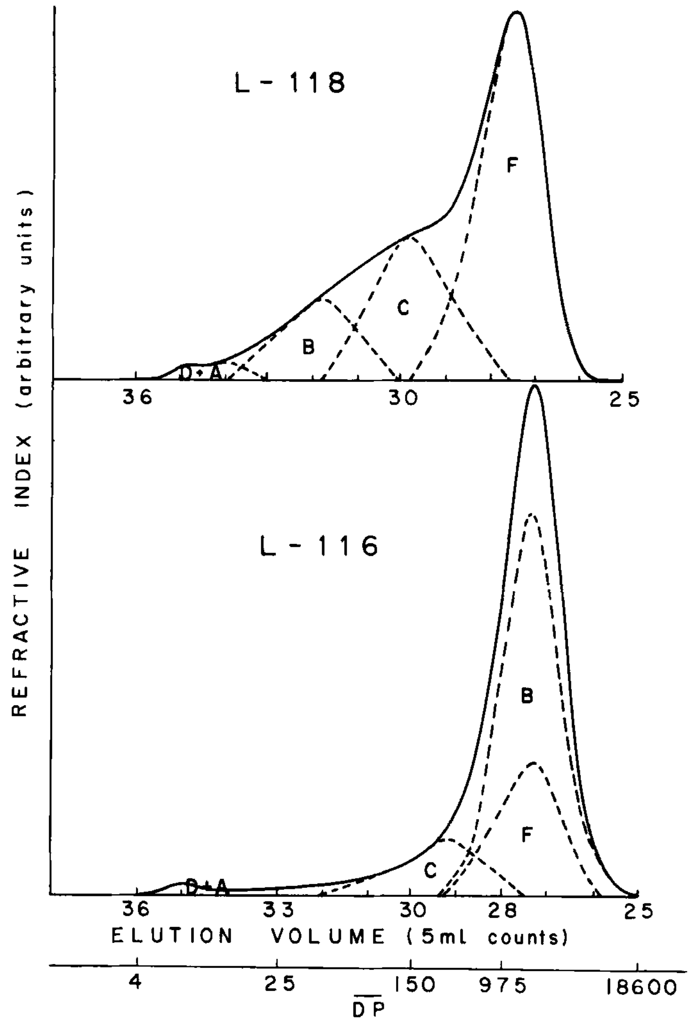

FIG. 10. GPC molecular weight distributions of poly-α-methylstyrenes showing the distribution changes in the components on depolymerization at 25°C (L-118) on a polymer prepared at -78°C (L-116). See Table 3 for other data.

done exclusively on the supposition that contact ion-pairs do not take part in the growth of the polymer at -78° C. This part C of the polymer has, in all probability, its origin from the period of initiation at 25°C. The values of [LE] associated with different components in L-118 and L-116, as listed in Table 3, show a complete agreement.

Polymerizations with Potassium-Naphthalene as Initiator

The role of naphthalene in anionic polymerizations is generally confined to the initiation process without any reference to the propagation. This is indeed the most likely conclusion to be drawn from the existing data at low temperatures and in solutions with high solvent content, where the initiation process with or without naphthalene is quite rapid. A group of research workers [12], however, believes that with the sodium-naphthalene-initiated polymerizations the propagation step is carried out by a "coordinate catalytic" mechanism [13-15] along with the stepwise mechanism. These workers have shown that, for the polymerization of α-methylstyrene ($[M]_0 = 2.0$ mole/liter) at -78°C initiated with naphthylsodium ($[LE] = 0.017$ mole/liter), the distribution of molecular weights should be broad for a stepwise mechanism and bimodal for a coordinate mechanism. From their experimental curves, the distribution of molecular weights was found to be built of a mixture of polymers due to stepwise and coordination mechanism. With this in mind, the polymerization experiments at high temperatures in α-methylstyrene-potassium-tetrahydrofuran system [1] were also performed by replacing the initiator with potassium-naphthalene.

In Fig. 11 are shown GPC distributions of two polymers M-29 and 54, prepared from 6.4 M solutions of α-methylstyrene in THF at 50°C, the initiation having been carried out at 25°C with potassium-naphthalene for M-29 and potassium alone in polymer 54. The bimodal distribution of the polymer formed with potassium alone are rendered to a near unimodal distribution due to the presence of naphthalene. It may be mentioned here that, even for a $[M]_0 = 6.4$ mole/liter, the process of initiation is instantaneous with naphthalene in solution, whereas in its absence polymer 54 needed 15 min for introducing a comparable [LE].

The analyses of these GPC distributions in terms of $[P]_e$ and [LE] associated with different components are presented in Table 5. For a total [LE] of 0.065 mole/liter in polymer 54, 0.059 mole/liter is attributed to the low molecular weight component (D + A) whereas in the presence of naphthalene (M-29) for a total [LE] of 0.058 mole/liter, only 0.024 mole/liter is assigned to the component (D + A), indicating the changes in the reactivity of species in the absence and

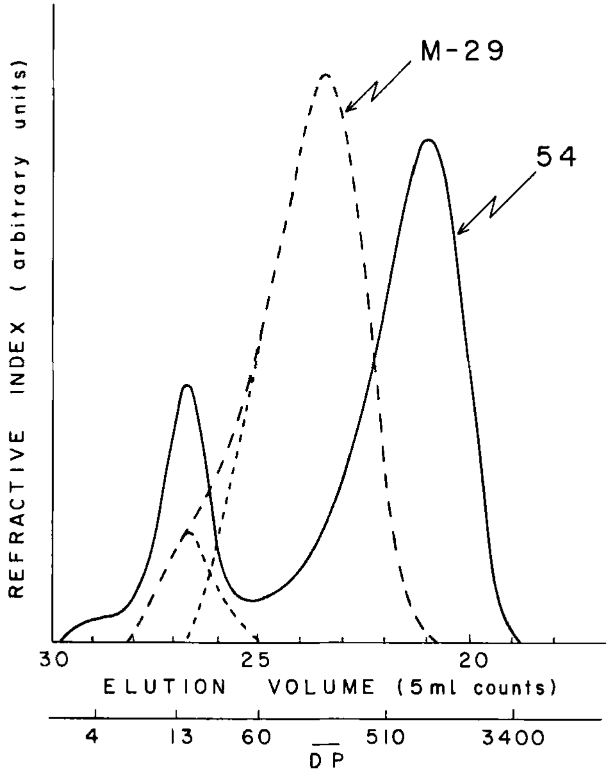

FIG. 11. GPC molecular weight distributions of two poly α-methylstyrene samples: in one case the polymer was initiated with potassium (54) and in the other with potassium-naphthalene (M-29). Both were polymerized from 6.4 M solutions of α-methylstyrene in THF at 50°C. See Table 5 for other data.

presence of naphthalene. Out of a total $[P]_e$ of 1.72 base-mole/liter in polymer 54, 0.38 base-mole/liter is associated with component (D + A), 0.24 base-mole/liter with component B, and 1.10 base-mole/liter with component C. In M-29, out of a total $[P]_e$ of 2.0 base-mole/liter only 0.18 base-mole/liter is attributed to (D + A), none to component B or C, and 1.82 base-mole/liter to potassium-naphthalene (Kn).

In another experiment, two 6.7 M solutions of α-methylstyrene in THF were polymerized at 55°C, the initiation having been carried

TABLE 5. GPC Analysis of $[P]_e$ and [LE] Associated with Different Components in Samples of Poly-α-methylstyrene Prepared with Potassium and Potassium-Naphthalene as Initiator[a]

			$[P]_e$ (base-mole/liter)					[LE] (mole/liter)				
No.	$[M]_0$ (mole/liter)	Initiator	(D + A)	B	Kn	C	Total $[P]_e$	(D + A)	B	Kn	C	Total [LE]
54	6.4	K	0.38	0.24	-	1.10	1.72	0.059	0.003	-	0.003	0.065
M-29	6.4	Kn	0.18	-	1.82	-	2.00	0.024	-	0.034	-	0.058
68	6.7	K	0.77	0.50	-	0.69	1.96	0.097	0.005	-	0.001	0.103
M-4	6.7	Kn	0.55	-	1.45	-	2.00	0.077	-	0.026	-	0.103
M-7	6.4	Kn	0.29	-	1.01	-	1.30	0.050	-	0.022	-	0.072

[a] Polymers 54 and M-29 were prepared at 50° C, whereas the rest of the data were collected at 55° C.

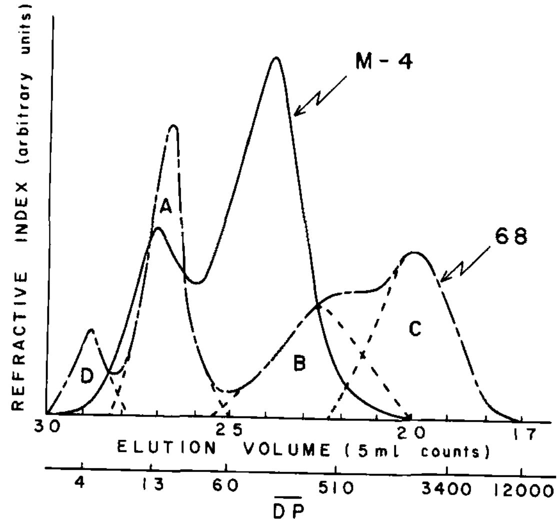

FIG. 12. Comparison of GPC molecular weight distributions of two poly-α-methylstyrene samples: in one case the polymer was initiated at 25°C with potassium (68) and in the other with potassium-naphthalene (M-4). Both were polymerized at 55°C from 6.7 M solutions of α-methylstyrene in THF. See Table 5 for other data.

out at 25°C with potassium alone (polymer 68) as well as with potassium-naphthalene (M-4). The GPC distributions of these polymers is shown in Fig. 12. There is a remarkable difference in the distributions of polymers M-4 and 68, indicating that the presence of naphthalene does improve the distribution of molecular weights but does not eliminate the phenomenon of multimodal distributions. The highest molecular weight component in polymer 68 between the elution counts 17 and 22 is completely missing in M-4. However component (D + A) in the two polymers elutes at the same count of 27. The analyses of these two chromatograms in terms of $[P]_e$ and [LE] are also presented in Table 5. It may be noted that in polymer 68, out of total [LE] of 0.103 mole/liter, 0.097 mole/liter is attributed to (D + A), whereas for the same concentration of [LE] only 0.077 mole/liter is assigned to (D + A) in the case of polymer M-4, where naphthalene is present.

Based on the results of these experiments it may be said that the presence of naphthalene eliminates the formation of high molecular weight polymers present in the potassium-initiated polymerizations. Furthermore it reduces the [LE] associated with the component

D + A and thus reduces the contribution due to these low molecular weight oligomers.

Reversibility in Potassium-Naphthalene-Initiated Polymerizations at 25 °C

Earlier in this report it was shown that potassium-initiated polymerizations at 25°C involved irreversible propagation. After having seen the effect of the presence of naphthalene on the GPC distributions (Figs. 11 and 12), it was thought of interest to study the concept of irreversible propagations in the potassium-naphthalene-initiated polymerizations at 25°C. These studies were carried out in a dilatometer which was precisely calibrated, and thus the changes in volume due to depropagation could be accurately determined. In a dilatometric experiment a 6.5 M solution of α-methylstyrene in THF, initiated at 25°C with potassium-naphthalene (LE = 0.035 mole/liter) was polymerized at 25°C. The changes in volume due to polymerization with time were duly recorded till the reaction attained a stationary state. Now the dilatometer was brought to 40°C and once again the volume changes due to depropagation between 25 and 40°C were noted. As soon as the depropagation at 40°C was complete, the temperature of the bath was increased to 50°C, and the volume changes due to depropagation between 40 and 50°C were noted down. After making the necessary corrections for volume changes due to the thermal expansion, the overall volume changes during polymerization at 25°C and during depropagation at 40 and 50°C were transformed into $[P]_e$ values making use of the molar volumes of α-methylstyrene at different temperatues [16]. The values of $[P]_e$ at 25, 40 and 50°C calculated from the recorded volume changes were 9.0. 5.2 and 3.0 base-mole/liter respectively. If one polymerizes three different solutions of α-methylstyrene with $[M]_0$ of 6.5 mole/liter and [LE] 0.01 mole/liter directly at 25, 40, and 50°C, one should get $[P]_e$ values of 8.5, 4.5, and 2.0 base-mole/liter respectively [1]. It may be noted that the two sets of values are not that far apart. The difference in these values may arise out of the different [LE] used in the two sets of experiments, or the fact that the depropagation is not complete.

In another experiment a 7.0 M solution of α-methylstyrene in THF initiated with potassium-naphthalene complex (LE = 0.400 mole/liter) was divided into two parts. One of these was polymerized at 55°C (L-98), and it yielded 4.4 base-mole/liter of polymer. The other was polymerized at 25°C ($[P]_e$ = 9.0 base-mole/liter) and depolymerized at 55°C. This polymerization also yielded 4.4 base-mole/liter of polymer. There was, however, a curious observation made in this depropagation study. When the polymer solution at

25°C was depolymerized at 55°C, the volume of the solution increased beyond the volume expected due to thermal expansion. After about 1 hr the volume reached a stationary state and then started decreasing. It gave the impression that on depropagation, the reaction yields back more monomer than necessary to meet the thermodynamic requirement; however, it readjusts itself and some additional monomer polymerizes (post-polymerization) to yield the required $[P]_e$ at 55°C. In such reactions the values of $[P]_e$ and $[M]_e$ do correspond to those desired by the thermodynamics of the solution, but the molecular weight distribution of these polymers obtained after depropagation at a certain temperature are quite different from those prepared directly at that temperature.

This is confirmed by the GPC molecular weight distributions of L-98 and L-69 as shown in Fig. 13. Polymer L-98 (55°C) has a bimodal distribution, where the lower molecular weight component has a $\overline{DP} = 19$ with $[P]_e = 3.96$ base-mole/liter and the higher molecular weight component has a $\overline{DP} = 200$ with $[P]_e = 0.44$ base-mole/liter. The other polymer L-69 (25°C, depropagated at 55°C),also has a bimodal distribution; however, in this case the lower molecular weight component has a $\overline{DP} = 14$ with $[P]_e = 2.96$ base-mole/liter. It would appear that the difference in the GPC distributions of L-69 and L-98 originates for one or both of the following reasons.

(a) The conversion of contact ion-pairs into potassium-naphthalene complex pairs [Eq. (1)] is never complete and there are always some species [M_x K in Eq. (6)] which do not yield reversible propagation. This would mean that the higher molecular weight component in L-69 is built, in part, of irreversible propagation, and the one with lower molecular weight has contribution from the potassium-naphthalene complex polymer (which is reversible) along with the contributions due to the usual (D + A) component. Because of the high $[P]_e$ (1.44 base-mole/liter) associated with the high molecular weight component in L-69. On depropagation at 55°C, more monomer has to be released by the reversible part of this polymer in order to meet the thermodynamic requirements of $[M]_e$ in the system. This reduces the $\overline{DP}$ of the lower molecular weight component to 14 instead of 19 as was the case with L-98. The other part of the high molecular weight component in L-69 may be attributed to the post-polymerization phenomenon discussed earlier.

(b) The conversion of contact ion-pairs into potassium-naphthalene complex pairs is complete, but the complex dissociates during the reaction, thereby yielding some species which also yield irreversible propagation. Such a reaction may be written as follows:

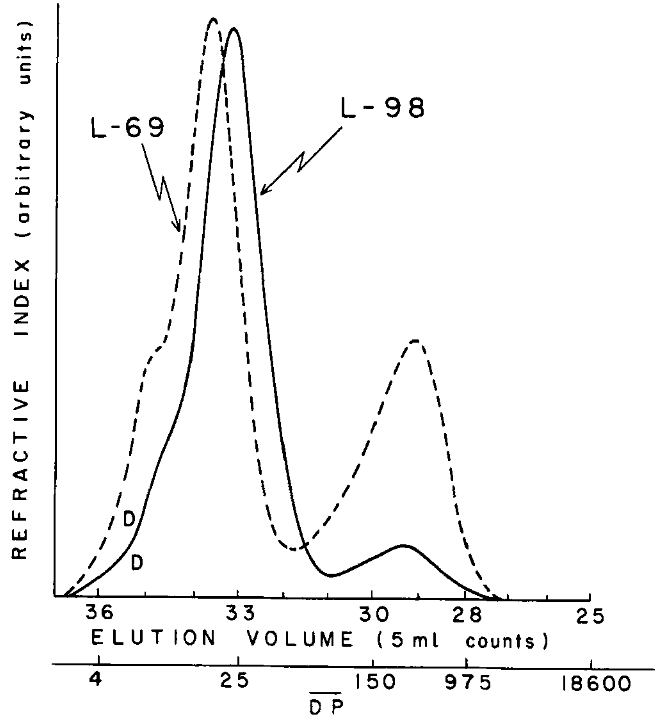

FIG. 13. Comparison of GPC molecular weight distributions of two poly-α-methylstyrene samples: in one case the polymer was initiated at 25°C with potassium-naphthalene and polymerized from 7.0 M solution of α-methylstyrene in THF at 55°C (L-98) the other was polymerized at 25°C and depolymerized at 55°C (L-69).

$$\mathrm{Kn} + \mathrm{M} \xrightarrow[\text{fast}]{k_i} [\mathrm{M}^-\,\overset{+}{\mathrm{Kn}}] \tag{1}$$

$$[\mathrm{M}^-\,\overset{+}{\mathrm{Kn}}] + \mathrm{M} \overset{k_{p_1}}{\rightleftharpoons} [\mathrm{M}_2^-\overset{+}{\mathrm{Kn}}] \text{ ---- } [\mathrm{M}_{x-1}^-\overset{+}{\mathrm{Kn}}] + \mathrm{M} \overset{k_{p_{x-1}}}{\rightleftharpoons} [\mathrm{M}_x^-\overset{+}{\mathrm{Kn}}] \tag{2}$$

$$[\mathrm{M}_x^-\overset{+}{\mathrm{Kn}}] + \mathrm{M} \overset{k_{p_x}}{\rightleftharpoons} [\mathrm{M}_{x+1}^-\ \mathrm{Kn}] \text{ ---- } [\mathrm{M}_{n-1}^-\overset{+}{\mathrm{Kn}}] + \mathrm{M} \overset{k_{p_{n-1}}}{\rightleftharpoons} [\mathrm{M}_n^-\overset{+}{\mathrm{Kn}}] \tag{3}$$

$$[M_x^- \overset{+}{Kn}] \underset{}{\overset{\text{dissociation}}{\overset{k_d}{\rightleftharpoons}}} \text{naphthalene} + M_x^- K^+ \qquad (4)$$

$$M_x^- K^+ + M \overset{k_{p_x}'}{\rightleftharpoons} M_{x+1}^- \; K^+ \qquad (5)$$

$$M_x^- K^+ \xrightarrow[\text{transformation}]{k_t} M_x \; K + M \xrightarrow{k_{p_x}''} M_{x+1} \; K \qquad (6)$$

When this scheme is applied to the present studies, it means that the reversible part B or Kn of the polymer initiated with $[M^- \overset{+}{Kn}]$ [Eq. (1)] takes its origin from reaction (2) to (5), whereas the irreversible part has contributions of reaction (6). Thus, in a solution of poly α-methylstyrene in THF at 25°C, with potassium-naphthalene as the initiator, there are four possible types of polymer present: dead polymer, dormant polymer, polymer due to potassium-naphthalene complex, and polymer due to a contact ion-pair. In a polymer solution at -25°C, however, the situation could be still more complicated as shown in the following sections.

Depropagation from a Polymer Prepared at -25°C with Potassium-Naphthalene as Initiator

Besides the four types of polymers produced at 25°C, at -25°C there is the additional possibility of polymers due to the solvent-separated ion-pairs and the coordinate catalytic mechanism of Korotkov and co-workers [12-15]. In the GPC distribution of the polymer prepared at -25°C it is difficult to find the contributions due to each of the reactive species. However, if one depolymerizes the polymer prepared at -25°C, at higher temperature one can have a better view of the situation.

With this in mind, a 6.5 M solution of α-methylstyrene in THF was initiated with potassium-naphthalene at 25°C and divided into two parts. Both of these were polymerized at -25°C and allowed to reach a stationary state. One of these (L-119) was opened at -25°C, and it yielded 8.0 base-mole/liter of polymer. The other (L-99) was depolymerized at 55°C, and 4.31 base-mole/liter polymer was recovered. From the GPC distributions of these polymers, base-mole/liter polymer associated with different elution counts was calculated and this is presented in Table 6. On the basis of these data, normalized molecular weight distributions of L-99 and L-119 were traced and superimposed as shown in Fig. 14a.

TABLE 6. GPC Analyzed Weights of Poly-α-methylstyrene at Various Elution Counts, Polymer Concentrations, and [LE] Associated with Each Component

No. of 5 ml counts	L-119 (mole/liter)[a]	L-99 (mole/liter)[b]	(L-119) - (L-99) (mole/liter)	L-119 (mole/liter)						L-99 (mole/liter)				
				1 (D + A)	2	3 (Kn)	4	5 (E)	6 (C)	1 (D + A)	2	3 + 5 (Kn + E)	4	6 (C)
26.5	0.00	0.06	+0.06	-	-	-	-	-	-	-	-	-	-	0.06
27.0	0.02	0.21	+0.19	-	-	-	-	-	0.02	-	-	-	-	0.21
27.5	0.16	0.41	+0.25	-	-	-	-	0.05	0.11	-	-	-	-	0.41
28.0	0.46	0.48	+0.02	-	-	-	-	0.23	0.24	-	-	-	-	0.48
28.5	0.97	0.40	-0.57	-	-	-	0.06	0.64	0.26	-	-	-	0.06	0.34
29.0	1.29	0.31	-0.98	-	-	-	0.14	0.97	0.18	-	-	-	0.14	0.17
29.5	1.26	0.21	-1.05	-	-	-	0.17	0.99	0.11	-	-	-	0.16	0.04
30.0	0.99	0.15	-0.84	-	-	0.14	0.13	0.71	-	-	-	-	0.13	0.01
30.5	0.70	0.10	-0.60	-	-	0.26	0.10	0.35	-	-	-	-	0.10	-
31.0	0.48	0.07	-0.41	-	-	0.39	0.06	0.04	-	-	0.02	-	0.06	-
31.5	0.35	0.07	-0.28	-	0.05	0.27	0.02	-	-	-	0.04	-	0.03	-
32.0	0.25	0.11	-0.14	-	0.13	0.12	-	-	-	-	0.11	-	-	-
32.5	0.20	0.27	+0.07	0.02	0.18	-	-	-	-	0.02	0.17	0.08	-	-
33.0	0.18	0.45	+0.27	0.07	0.11	-	-	-	-	0.08	0.09	0.28	-	-
33.5	0.16	0.40	+0.24	0.13	0.02	-	-	-	-	0.16	-	0.24	-	-
34.0	0.15	0.24	+0.09	0.16	-	-	-	-	-	0.16	-	0.08	-	-

34.5	0.12	0.17	+0.05	0.12	-	-	-	-	-	0.16	-	0.01	-	-
35.0	0.12	0.11	-0.01	0.12	-	-	-	-	-	0.11	-	-	-	-
35.5	0.08	0.06	-0.02	0.08	-	-	-	-	-	0.06	-	-	-	-
36.0	0.06	0.03	-0.03	0.06	-	-	-	-	-	0.03	-	-	-	-
$\Sigma [P]_e$	8.00	4.31	-3.69	0.76	0.49	1.18	0.68	3.98	0.92	0.78	0.43	0.69	0.68	1.72
[LE] (mole/liter)	0.257	0.260	-	0.153	0.029	0.030	0.009	0.036	0.004	0.145	0.024	0.066	0.009	0.004

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[a] L-119: initiated with potassium-naphthalene and polymerized at -25° C.

[b] L-99: initiated with potassium-naphthalene, polymerized at -25° C and depolymerized at 55° C.

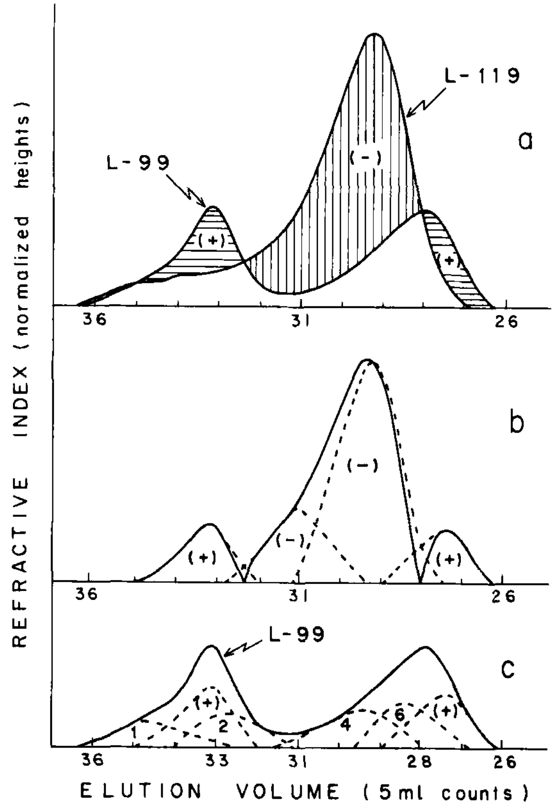

FIG. 14. Graphical method of analysis by which the GPC curves are broken down into components: the case of poly-α-methylstyrene initiated with potassium-naphthalene at 25° C and polymerized from a 7.0 M solution of α-methylstyrene in THF at -25° C (L-119) and the other polymerized at -25° C but depolymerized at 55° C (L-99). See Table 6 for other data.

The polymer between the elution counts of 28 to 32.5 and marked with vertical hash lines has disappeared (-) from the polymer prepared at -25° C (L-119) and reappeared (+) at the elution counts 26 to 28 and 32.5 to 35 as marked with the horizontal hash lines. The area under the hash lines may be transformed into their respective molecular weight distributions as shown in Fig. 14b. In tracing the distributions, it has been once again assumed that the distributions having abrupt ending just like the one denoted by (+) and lying in the elution count range 26 to 28, may in reality have their tail merged in the head distribution of another such as (-) between the elution counts of 28 to 32.5. This correction has been shown by the dotted lines which also intersect at the elution count of 28. Similar corrections have also been applied to the curves (-) between the elution counts of 28 to 32.5 and (+) between the elution counts of 32.5 to 35, which meet at the count of 32.5. It may further be noted that the distribution (-) which has disappeared on depolymerization is made up of two distinct distributions, and these are also shown in Fig. 14b. The excessive distributions (+), which were not originally present in L-99 but are the result of depolymerization, may be subtracted from the normalized distribution of L-99 and the remainder area be transformed into distributions as shown in Fig. 14c. This yields distributions 1, 2, 4, and 6.

After having calculated the base-mole/liter of all these distributions (see Table 6), these may be placed in the original GPC molecular weight distribution curves as shown in Fig. 15, and more precise components 1 to 6 be traced. It is noteworthy that components 5 and 3, which had 3.97 base-mole/liter and 1.19 base-mole/liter polymer associated with them, respectively, at -25°C, have depolymerized on heating at 55°C, yielding 0.69 base-mole/liter polymer. The sum [LE] of components 5 and 3 in the polymerized and depolymerized state is 0.066 mole/liter. Furthermore it may also be noted that component 6, which had only 0.92 base-mole/liter of polymer with a [LE] value of 0.004 mole/liter, now has after depolymerization 1.72 base-mole/liter polymer and the same 0.004 mole/liter of [LE]. The other components, viz., 1, 2, and 4, remain unchanged on depolymerization.

If one tries to correlate these different components with the type of polymer these belong to, one may say that component 1 is (D + A) (combination of dead and dormant polymer), component 6 is that due to a contact pair, the reversible components 5 and 3 may be representing solvent-separated ion-pairs or naphthalene-complex ion-pairs, and the other two components (2 and 4) may have been produced during the initiation period. The latter two could also be attributed to the coordinate catalytic mechanism proposed by Korotkov and co-workers [12-15]. Indeed, these workers had found bimodal distributions in their study on the polymerization of α-methylstyrene at -78°C with potassium-naphthalene as initiator and had suggested the presence of a coordinate catalytic mechanism even at -78°C. The present studies, however, show that only two mechanisms as suggested by Korotkov and co-workers [12-15], cannot explain the results obtained. These in combination with ion-pair and free ion mechanisms [11], would help in explaining some of the unusual GPC molecular weight distributions obtained for the polymers prepared in this study.

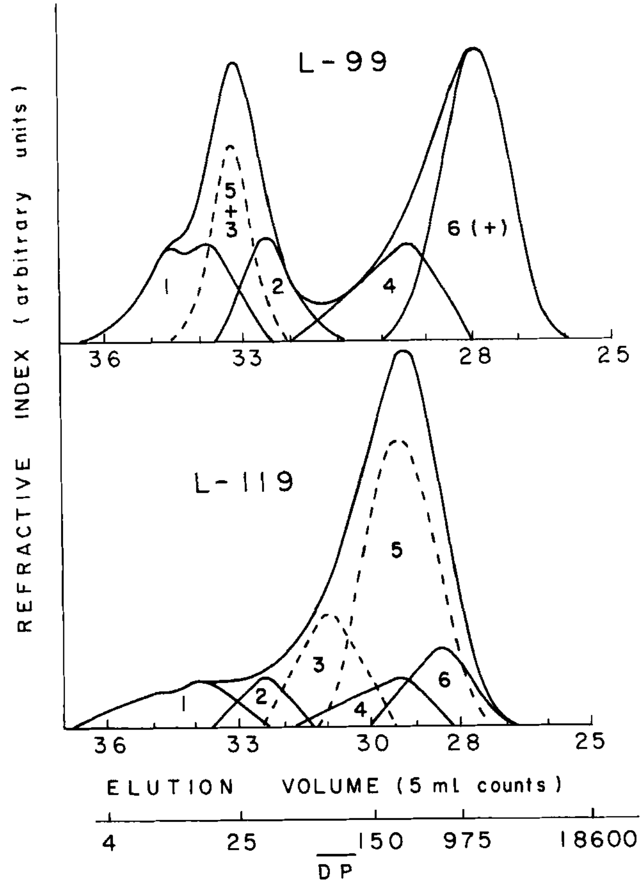

FIG. 15. GPC molecular weight distributions of poly-α-methylstyrenes (L-99, L-119) showing the distribution changes in the components of depolymerization at 55°C (L-99) in a sample prepared at -25°C (L-119).

CONCLUSION

The principal conclusions to be drawn from this work can be outlined briefly as follows.

In the polymerization of α-methylstyrene in THF with potassium as initiator, the propagation at 25°C is irreversible. Correlating these observations with the mechanistic hypothesis [11] it may be said: (a) that the contact ion-pairs yield irreversible propagation; (b) that the contact ion-pairs yield reversible propagation but in the present case these get transformed into irreversible species on raising the temperature, and (c) that besides the contact ion-pairs there are other ion-pairs present, which could have more covalent character as compared to that of the conventional contact ion-pairs and yield irreversible propagation. Of these three, explanation (a) has been retained for the present because it is generally accepted that at 25°C contact ion-pairs are very active in the polymerizations of α-methylstyrene.

The propagation at -25°C attributed [11] to the solvent-separated ion-pairs is completely reversible.

The propagation at -78°C which is not completely reversible may be attributed to the presence of dead polymer or to the free-ion mechanism which is very active at such low temperatures. The latter explanation has been retained on the grounds that even at elevated temperatures the living ends were found quite stable.

On the addition of naphthalene, the propagation at 25°C becomes reversible and may be attributed to the formation of naphthalene complex pairs which yield reversible propagation. The presence of naphthalene reduces the formation of (D + A) type of polymer.

The concept of reversibility is being tested on other systems where p-dioxane and cyclohexane were used in place of THF. The results of these studies shall be published later on.

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REFERENCES

[1] J. Léonard and S. L. Malhotra, J. Macromol. Sci.–Chem., A10, 1273 (1976).
[2] R. V. Figini, Makromol. Chem., 44-46, 497 (1961).
[3] T. A. Orofino and F. Wenger, J. Chem. Phys., 35, 532 (1961).
[4] D. L. Glusker, I. Lysloff, and E. Stiles, J. Polym. Sci., 49, 315 (1961).

[5] P. Guérin, S. Boileau, and P. Sigwalt, Eur. Polym. J., 7, 1119 (1971).

[6] B. J. Schmitt and G. V. Schulz, Makromol. Chem., 175, 3261 (1974).

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

[8] F. S. Dainton, K. J. Ivin, and R. T. Laflair, Eur. Polym. J., 5, 379 (1969).

[9] I. Mita and H. Okuyama, J. Polym. Sci. A-1, 9, 3137 (1971).

[10] S. L. Malhotra, J. Hesse, and L. P. Blanchard, Polymer, 16, 81, 269 (1975).

[11] M. Szwarc, Carbanions: Living Polymers and Electron Transfer Process, Interscience-Wiley, New York, 1968, pp. 23, 212.

[12] A. E. Podolsky and A. A. Korotkov, J. Polym. Sci. C, 16, 3667 (1968).

[13] A. A. Korotkov, paper presented at IUPAC International Symposium on Macromolecular Chemistry, Prague, 1957, paper 66.

[14] A. A. Korotkov and G. Rakova, Vysokomol. Soedin, 10, 1462 (1961).

[15] A. A. Korotkov, S. P. Mitsengendler, and V. N. Krasulina, J. Polym. Sci., 53, 217 (1961).

[16] K. Ivin and J. Léonard, Eur. Polym. J., 6, 331 (1970).

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