Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Malhotra, S. L. , Leonard, J. and Thomas, M.(1977) 'Polymerization of α-Methylstyrene in Cyclohexane with Potassium as Initiator. IV. Thermodynamic Study and Gel-Permeation Chromatographic Analyses of the Polymers', Journal of Macromolecular Science, Part A, 11: 12, 2213 — 2232

To link to this Article: DOI: 10.1080/00222337708061360

URL: http://dx.doi.org/10.1080/00222337708061360

J. MACROMOL. SCI.–CHEM., A11(12), 2213-2232 (1977)

Polymerization of α-Methylstyrene in Cyclohexane with Potassium as Initiator. IV. Thermodynamic Study and Gel-Permeation Chromatographic Analyses of the Polymers

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ABSTRACT

Polymerization of α-methylstyrene in cyclohexane containing traces of tetrahydrofuran (THF) has been carried out at 40°C with potassium as initiator. The conversion of monomer to polymer was very slow, and a solution with $[M]_0$ of 5.15 mole/liter, carrying 0.110 mole/liter of the living ends [LE], required two months to reach a stationary state. The gel-permeation chromatographic (GPC) analyses of these polymers showed them to have multimodal distributions which could be split into components D+A, B, and C similar to those found for poly-α-methylstyrene prepared in THF and p-dioxane as solvents. Furthermore, under identical conditions of $[M]_0$ and [LE], the GPC distributions of poly-α-methylstyrene prepared in cyclohexane, p-dioxane, and THF were the same, in spite of their different dielectric constants. Under identical conditions

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of $[M]_0$ but with different [LE], the effect of excessive [LE] on the GPC distributions of the polymers prepared in cyclohexane was not limited to the component D+A as was the case when THF or p-dioxane were the solvents, but also on the component C which increased its contribution $[P]_e$ to the polymer.

INTRODUCTION

Gel-permeation chromatographic (GPC) molecular weight distribution studies on poly-α-methylstyrene prepared in tetrahydrofuran (THF) [1, 2] and in p-dioxane [3] have been reported earlier from this laboratory. It was found that in THF, as well as in p-dioxane, the GPC distributions of polymer initiated with potassium metal alone were multimodal in character which could be split into three distinct components. These were termed D+A, B, and C, where D represents dead polymer; A is dormant polymer; B is polymer due to a solvent-separated ion-pair mechanism, and C is that due to a contact pair. This parallel was drawn on the basis of the reported mechanisms [4] in the anionic polymerizations at different temperatures.

Species responsible for component B were found to yield reversible propagation, whereas those for component C gave irreversible propagation. In polymerizations where potassium-naphthalene was used as initiator, the extent of reversibility was found to increase and was attributed to the presence of a coordinate complex of potassium-naphthalene as suggested by Podolsky and Korotkov [5], which yields a different type of propagation. Polymers prepared under identical conditions at 40°C in THF [2] and in p-dioxane [3] gave GPC curves which were very similar in shape in spite of the different dielectric constants of the two solvents used. Thus it was thought of interest to study the GPC distributions of poly-α-methylstyrene prepared in a solvent with a lower dielectric constant, e. g., cyclohexane than that of THF or p-dioxane. Since potassium metal alone does not initiate the polymerization of α-methylstyrene in cyclohexane, traces of THF were incorporated with cyclohexane to facilitate initiation. Because of a higher (37°C) theta temperature for the system poly-α-methylstyrene-cyclohexane, all reactions had to be carried out at 40°C. Thus the comparison of the GPC results for the polymers prepared in the three solvents, viz., cyclohexane, p-dioxane, and THF, can be made only in those cases where polymerization was carried out at 40°C or higher. The principal results of this study are presented in this communication.

EXPERIMENTAL

Cyclohexane (Fisher Certified) was kept over calcium hydride and degassed on the vacuum line for nearly two weeks. It was distilled under vacuum on a mirror of potassium and preserved over it. After every fortnight the solvent was transferred to a fresh mirror of the metal.

Purification of the monomer, experimental procedure, monomer analysis, and characterization of the polymer formed has been described in previous publications [1, 6] and need not be repeated here. The only change in the experimental procedure from that reported earlier was in the distillation of a trace of THF on the potassium mirror prior to the addition of the solvent cyclohexane. As mentioned earlier, this was necessitated because it was not possible to initiate the reaction with potassium in a solution of α-methylstyrene and cyclohexane alone.

RESULTS AND DISCUSSION

In Fig. 1 is presented a kinetic curve, prepared at 40°C for 5.17 $\underline{M}$ solution of α-methylstyrene in cyclohexane, polymerization having been initiated with potassium mirror. The progress of the reaction was followed periodically in a dilatometric ampoule. It may be noted that with a concentration of living ends [LE] of 0.021 mole/liter as calculated from the viscosity-average molecular weight $\overline{M}_v$, the reaction needed 61 days to reach a stationary state and yielded a total of 2.15 base-mole/liter of the polymer, which corresponds to 36% conversion. It may be remarked here that under identical conditions the times taken to reach a stationary state in p-dioxane and in THF were of the order of 5 days and 2 days, respectively. Because of the length of time (2 months) required to reach equilibrium even with [LE] values of the order of 0.021 mole/liter, it was not encouraging to study the reaction with lower [LE] or at higher temperatures, both of which, in all probability, would prolong the time of polymerization.

However, six other ampoules were also kept in the bath at 40°C along with the dilatometric run, and all of these were analyzed for $[P]_e$ and $[M]_e$. These values are presented in Table 1. Based on these values, a plot of $[M]_e$ versus $[P]_e$ was made (but not shown here), and it yielded a straight line. The extrapolated value of the monomer concentration at zero polymer was found to be 5.1 mole/liter. Under similar conditions this value in p-dioxane [6] was 3.6 mole/liter, and in THF [1] it was 3.8 mole/liter. Leonard [7], on the basis of his theoretical calculations, had predicted this value to be much less than that in THF. From the slope of $[M]_e$ versus $[P]_e$ curve and

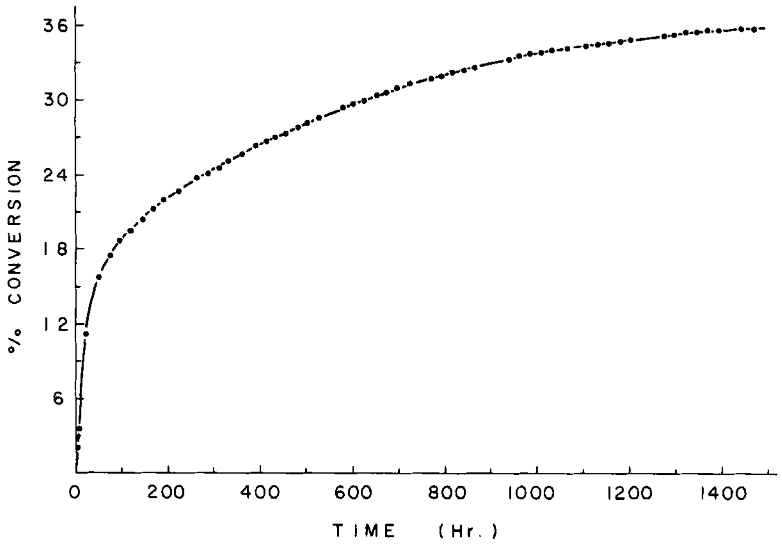

FIG. 1. Kinetic curve presenting the conversion vs. time for the polymerization of a 5.17 M solution (polymer 44) of α-methylstyrene in cyclohexane containing traces of THF, with initiation by a potassium mirror.

with the value of 5.1 mole/liter for the monomer concentration at zero polymer, the value of the free energy of polymerization $\Delta G_{\ell c}$, was computed by making use of the equation suggested by Ivin and Leonard [8]. A comparison of the $\Delta G_{\ell c}/RT$ values for poly-α-methylstyrene in cyclohexane, in p-dioxane, and in THF showed them to have values of -0.426, +0.100, and +0.150, respectively.

Although the extrapolated $[M]_e$ values for zero $[P]_e$ in three solvents (but the same monomer) may be different, by the definition of the free energy of polymerization, the $\Delta G_{\ell c}$ values in the three cases should be the same. The values of 0.1 and 0.15 for poly-α-methylstyrene in p-dioxane and in THF are of the same magnitude. However, this value in the case of cyclohexane is totally different. This clearly suggests that there are certain abnormalities in the polymerization of α-methylstyrene initiated by potassium metal in cyclohexane. In the earlier studies [1-3] it was noted that the [LE] concentration computed from the number-average molecular weight $\overline{M}_n$ and those from $\overline{M}_v$ were quite far apart. It could be possible that

TABLE 1. GPC Analysis Showing $[P]_e$ and [LE] Associated with Different Components in Poly-α-methylstyrene Prepared at 40°C with Potassium as Initiator

			$[P]_e$ (base-mole/liter)								[LE] (mole/liter) (GPC)							
No.	Solvent[a]	$[M]_0$ (mole/ liter)	Dead tetramer	D+A	D+A+B	B	B+C	C	Total $[P]_e$	$[M]_e$ (mole/ liter)	Dead tetramer	D+A	D+A+B	B	B+C	C	Effective [LE][b]	$\frac{[LE]}{\overline{M}_v}$ (mole/ liter)
40	THF	4.95	0.08	1.23	-	-	0.60	-	1.83	3.45	0.041	0.104	-	-	0.003	-	0.107	0.014
47	CHEX	5.17	0.05	1.10	-	-	0.73	-	1.92	3.60	0.026	0.089	-	-	0.007	-	0.096	0.022
44	CHEX	5.17	-	1.29	-	-	0.86	-	2.15	3.40	-	0.103	-	-	0.007	-	0.110	0.021
46	CHEX	5.60	0.11	-	0.97	-	1.82	-	2.90	3.15	0.055	-	0.055	-	0.007	-	0.062	0.012
26	DIOX	5.55	0.04	-	0.99	-	1.77	-	2.80	3.25	0.021	-	0.047	-	0.008	-	0.055	0.013
43	CHEX	5.80	0.05	1.94	-	-	1.21	-	3.20	3.10	0.025	0.183	-	-	0.007	-	0.190	0.027
42	CHEX	5.85	-	2.31	-	0.99	-	1.90	5.20	1.50	-	0.279	-	0.004	-	0.002	0.285	0.016
48	CHEX	6.35	0.05	-	0.89	-	1.76	-	2.70	4.20	0.027	-	0.041	-	0.008	-	0.049	0.011
45	CHEX	6.35	-	1.63	-	1.32	-	2.47	5.42	1.85	-	0.155	-	0.011	-	0.003	0.169	0.016

[a] Solvents: THF = tetrahydrofuran; DIOX = p-dioxane; CHEX = cyclohexane.
[b] Effective [L E] does not include the contribution of dead tetramers formed early in the reaction.

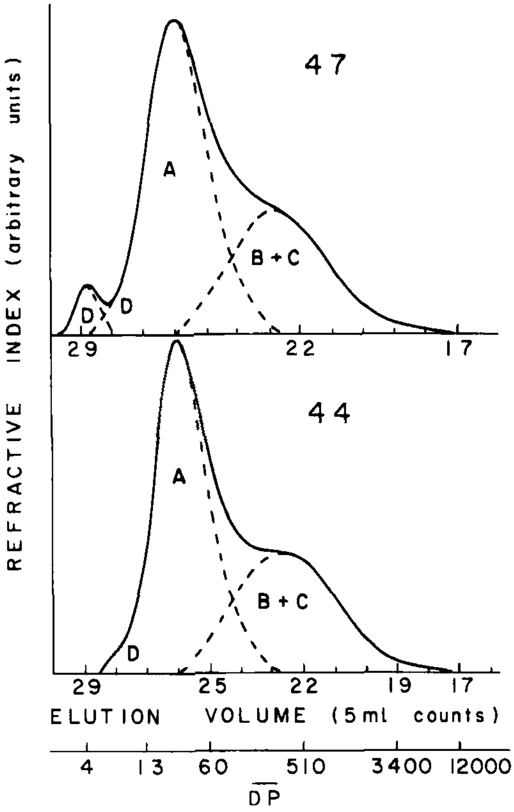

FIG. 2. GPC molecular weight distributions of poly-α-methylstyrene samples 47 and 44 prepared from 5.17 $\underline{M}$ solutions of α-methylstyrene in cyclohexane with identical concentrations of living ends [LE]. See Table 1 for other data.

same is true in the present study and in reality the [LE] concentrations may be higher than those found by $\overline{M}_v$. With a view to clarify this point a GPC study on the polymers was carried out.

In Fig. 2 are shown the GPC chromatograms of two poly-α-methylstyrenes, samples 47 and 44, both prepared from 5.17 $\underline{M}$ solutions of α-methylstyrene in cyclohexane and initiated with potassium. The total [LE] as calculated from $\overline{M}_n$ (GPC) in the case of polymer 47 was 0.122 mole/liter. However, it appears that out of that, 0.026 mole/liter [LE] was killed in the beginning of the reaction yielding tetramers, leaving only 0.096 mole/liter as $[\mathrm{LE}]_{\mathrm{effective}}$. In polymer 44, which was prepared in the dilatometer, there was no apparent killing in the beginning, and the total [LE] is 0.110 mole/liter. [LE] values in these two experiments as calculated from $\overline{M}_v$ were of the order of 0.02 mole/liter. This once again suggests that viscosity data should not be used to compute [LE]. Due to an excess [LE] of 0.014 mole/liter in polymer 44, the yield was higher (2.15 base-mole/liter) than that of polymer 47 (1.92 base-mole/liter). In spite of this little difference in [LE] and $[P]_e$, their GPC molecular weight distributions (Fig. 2) are identical in shape. These are bimodal in character, having one maximum at an elution count of 26 ($\overline{DP}$ = 25) and the other at about 23 ($\overline{DP}$ = 250). If there were no killing or there were only one type of reactive species propagating the reaction, the expected $\overline{DP}$ of the polymer would be about 40.

The presence of a bimodal distribution with components having two maxima instead of one may be attributed either to the process of killing or to the presence of different reactive species. In order to affirm one of these two possibilities, these GPC chromatograms were split into different components as was done in the case of THF [1, 2] and p-dioxane [3]. The analyses of polymers 47 and 44 in terms of components has been presented in Table 1. Component D+A in polymer 44 has 60% of $[P]_e$ associated with it and 73% of [LE] attached to it and has a narrow distribution. In order to explain the narrow polydispersity of the polymer in the low molecular weight region one has to assume that this was produced in the early stages of the reaction and then was killed in some way. However, the visual analysis of the conversion versus time curve gives no impression of the formation of this low molecular weight product, as there are no abrupt beginnings or endings in the kinetic curve.

It may also be argued that the reaction is comparatively faster in the first 48 hr as compared to the rest of the time; however this produces a maximum of only 0.90 base-mole/liter, which corresponds to 40% of the total polymer and not 60% as found out by component tracing. Furthermore, it is not logical to assume that 93% of [LE] was killed in the first one week and the remainder 7% survived a period of seven weeks. If there was to be such a remote possibility, there ought to be a drastic change in the intensity of the red color because of the killing of 93% [LE]. However no such change was noticed. This explanation is not intended to rule out the possibility of some killing taking place in the reaction because it would be unimaginable to assume that a solution of α-methylstyrene in cyclohexane when kept at 40°C for two months did not decompose at all. The motive is to justify that $[P]_e$ of 1.29 base-mole/liter and [LE] of 0.103 mole/liter associated with component D+A is not solely as a result of killing. The possibility of killing may further be ruled out on the basis of the GPC chromatogram of the polymer 47. Under more or less identical conditions, the distribution of molecular weights is also identical. Here as well, the component D+A has 60% of the total $[P]_e$ and 93% of the total [LE].

After having established that the phenomenon of killing is not solely responsible for the formation of the low molecular weight polymer, the question now arises as to what is the origin of this polymer. On the basis of the GPC studies alone it is very difficult to make any prediction. However if one draws a parallel from the earlier studies, D and A in this study may also denote a dead and a dormant polymer. The high molecular weight component having a maximum at an elution count of 23 may be attributed to component C, as the presence of contact ion-pair mechanism is the most likely explanation especially in a solvent with a very low dielectric constant. This polymer though has been attributed to component B+C simply on the basis that the presence of component B cannot be ruled out. Component B in the earlier studies [1-3] has been related to the solvent-separated ion-pair mechanism and has the same meaning in the present text as well. Although the presence of a solvent-separated ion-pair mechanism in a solvent like cyclohexane with a bulk dielectric constant of 2.02 is not likely yet, there is a remote possibility that the presence of trace of THF might solvate the ion-pair by increasing the conductance of the solution as reported in the literature [9, 10].

On the basis of the above experiments it may safely be said that the GPC bimodal distributions of poly-α-methylstyrene are indeed the results of different reactive species. If such were the case, then the effect of [LE] on the distribution of molecular weights should be very prominent, as was the case when p-dioxane as well as THF were the solvents used. In Fig. 3 are shown GPC chromatograms of two polymer samples 43 and 42 prepared from 5.80 and 5.85 M solutions of α-methylstyrene in cyclohexane. In polymer 43, the $[\overline{LE}]_{\text{effective}}$ was 0.190 mole/liter and 3.20 base-mole/liter of polymer was recovered, whereas in polymer 42 the $[LE]_{\text{effective}}$ was 0.285 mole/liter and a $[P]_e$ of 5.20 base-mole/liter was obtained. It is quite normal that from two solutions of same molarity but having different [LE], the solution with higher [LE] should yield more polymer. This was the case when THF [1, 2] and p-dioxane [3] were the solvents used. However, there is one peculiarity in the distribution of polymer 42 which has higher [LE]: the excess polymer seems to be on the higher molecular weight side. This is contrary to what was recorded when the effect of [LE] was studied in THF [1] and p-dioxane [3], where higher [LE] yielded more polymer but all of it was associated with the low molecular weight polymer.

The GPC chromatograms in Fig. 3 were split into different components, and the values of $[P]_e$ and [LE] associated with these are

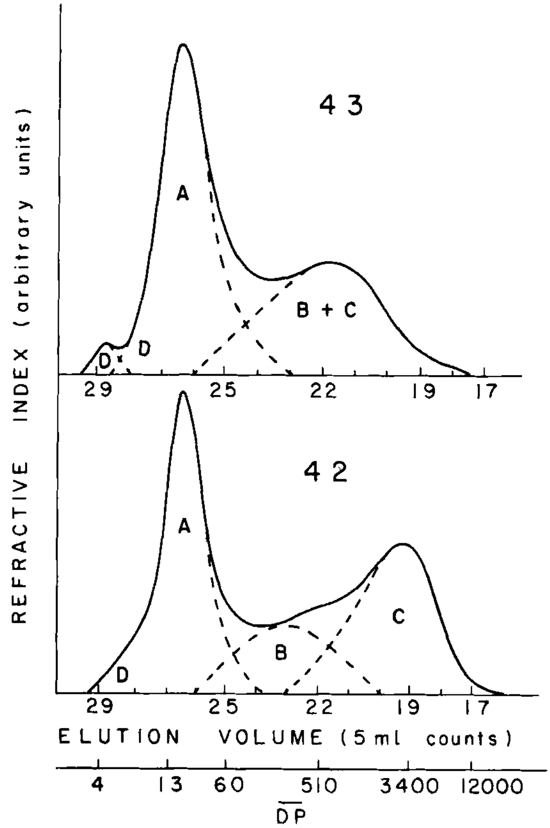

FIG. 3. GPC molecular weight distributions of poly-α-methylstyrene samples 43 and 42 prepared from 5.80 and 5.85 M solutions of α-methylstyrene in cyclohexane with different [LE] concentrations. See Table 1 for other data.

presented in Table 1. It may be noted that the GPC distribution of polymer 43 can at best be split into component D+A and B+C, whereas in polymer 42, because of higher [LE], the GPC distribution may be split into three components, viz., D+A, B, and C. Based on these values of $[P]_e$ and [LE] (Table 1) one notes that the effect of higher [LE] is associated with component D+A as well as with component C. Out of an $[LE]_{effective}$ of 0.285 mole/liter, 0.279 mole/liter is associated with component D+A, 0.004 mole/liter with component B, and 0.002 mole/liter with component C. On the other hand, out of an

$[LE]_{effective}$ of 0.190 mole/liter, component D+A carries 0.183 mole/liter, and the remaining 0.007 mole/liter may be attributed to component B+C. As far as the values of $[P]_e$ are concerned, component D+A in polymer 42 has 0.37 base-mole/liter in excess to that in polymer 43, whereas component B+C in the former has about 1.59 base-mole/liter in excess to that of component B+C in the latter. This analysis yields the overall differences in the values of $[P]_e$ and [LE] associated with different components. However, in order to ascertain the precise distribution of the excess [LE] of 0.095 mole/liter (0.285-0.190 mole/liter) in polymer 42, an alternate approach is necessary.

The GPC chromatograms of polymers 43 and 42 may be weight-normalized, and the base-mole/liter at various elution counts be calculated. On the basis of these data curves be traced for the two polymers and superimposed as shown in Fig. 4a. It may be noted that the shaded area is in excess of that in polymer 43. These areas may be converted in terms of distribution [11, 12] as shown in Fig. 4b. It is clear that the excess [LE] of 0.095 mole/liter in polymer 42 has resulted in additional polymer having two distinct distributions, one $(+)_1$, situated between the elution counts of 25 and 28, having a $[P]_e$ of 0.60 base-mole/liter and carrying 0.093 mole/liter of [LE] with it. The other, $(+)_2$, is situated between the elution counts of 16.5 and 22.5, has a $[P]_e$ of 1.49 base-mole/liter, and carries 0.002 mole/liter of [LE]. Thus the excess [LE] of 0.095 mole/liter is distributed in the low and high molecular weight region as 0.093 for the former and 0.002 mole/liter for the latter.

One might wonder whether or not this effect of [LE] on GPC distributions of polymers prepared in cyclohexane is reproducible. In a polymerization system which takes two months to reach a stationary state, testing of reproducibility is not feasible. However similar results are obtained on analysis of two other polymers where the starting monomer concentration was the same but the [LE] in the two were different. In Fig. 5 are shown the GPC chromatograms of two polymer samples, 48 and 45, prepared from two solutions of molarity 6.35 and $[LE]_{effective}$ of 0.049 mole/liter for the former and 0.169 mole/liter for the latter. Polymer 48 yielded a $[P]_e$ of 2.70 base-mole/liter; on the other hand polymer 45 yielded a $[P]_e$ of 5.42 base-mole/liter. The GPC chromatograms of the two polymers were split into different components and analyzed in terms of $[P]_e$ and [LE] associated with these. The GPC distribution of polymer 48 can at best be split into two components, viz., A+B and

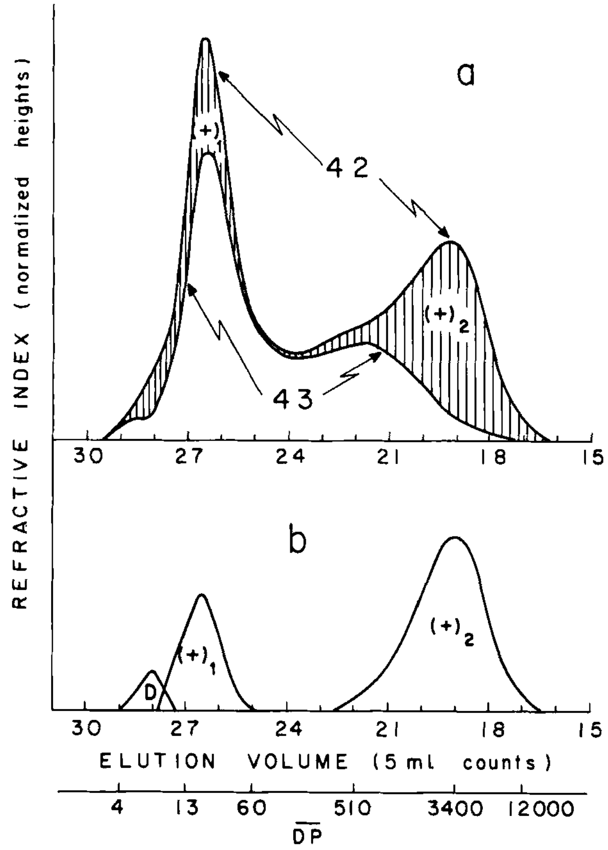

FIG. 4. Graphical method of analysis by which the GPC chromatograms are broken down into different components: case of poly-α-methylstyrene samples 43 ([LE] = 0.190 mole/liter) and 42 ([LE]) = 0.285 mole/liter).

B+C, whereas that of polymer 45 has the usual D+A, B, and C components. The lowest molecular weight component in polymer 48 has been attributed to A+B because it does not elute at the count of 26.5, where normally D+A should elute. Thus it might carry the contribution to component B whose contribution extends further in component C as well. The comparison of the GPC analysis of these two experiments shows that the effect of excess [LE] is felt in the lower as well as the higher molecular weight zone. Out of 0.169 mole/liter of [LE] in polymer 45, 0.155 mole/liter is associated with component D+A,

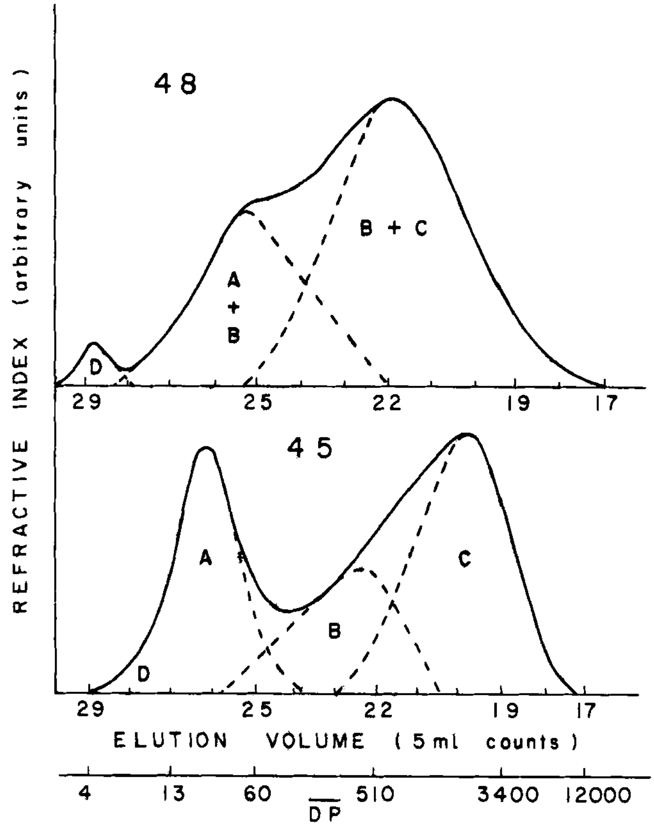

FIG. 5. GPC molecular weight distributions of poly-α-methylstyrene samples 48 and 45 prepared from 6.35 M solutions of α-methylstyrene in cyclohexane with different [LE] concentrations. See Table 1 for other data.

0.011 mole/liter with component B, and 0.003 mole/liter with component C. In polymer 48, out of the effective [LE] of 0.057 mole/liter, component A+B has 0.045 mole/liter and component B+C has 0.012 mole/liter. As far as the values of $[P]_e$ are concerned, component B+C has 1.8 base-mole/liter in excess of B+C in polymer 48. The other 1.0 base-mole/liter of excess polymer in polymer 45 is associated with the low molecular weight component.

In order to get a better picture of the situation, the traced weight normalized curves were superimposed (Fig. 6a). It may be remarked

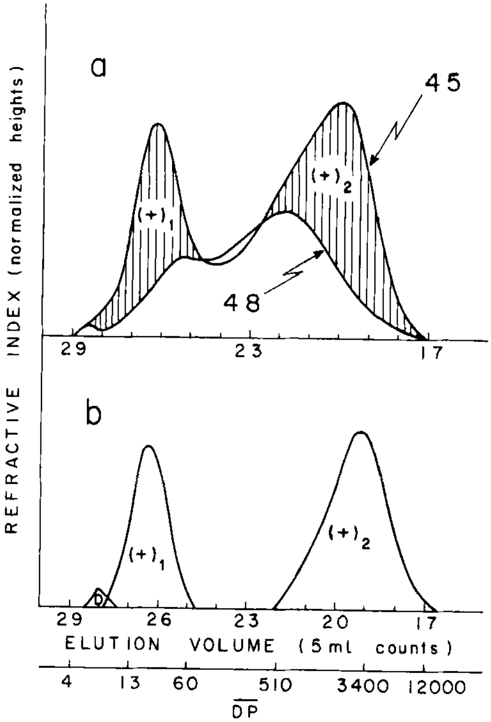

FIG. 6. Graphical method of analysis by which the GPC chromatograms are broken down into different components: case of poly-α-methylstyrene samples 48 ([LE] = 0.049 mole/liter) and 45 ([LE] = 0.190 mole/liter).

that the shaded area is in excess because of the higher [LE] in polymer 45. This area, when transformed into molecular weight distributions, yielded two distinctly separate distributions, one $(+)_1$ situated between the elution counts of 25 and 28, having a $[P]_e$ of 1.04 base-mole/liter and carrying 0.110 mole/liter of [LE]; the other $(+)_2$, situated between the elution counts of 17 and 22, having a $[P]_e$ of 1.72 base-mole/liter and carrying 0.002 mole/liter of [LE]. Thus, once again, the excess [LE] of 0.112 mole/liter is distributed in the low and high molecular weight region as 0.110 mole/liter for the former and 0.002 mole/liter for the latter. However, it is difficult to ascribe any reasonable explanation for the different effects of [LE] concentration on polymers prepared in cyclohexane as compared to those in p-dioxane or in THF.

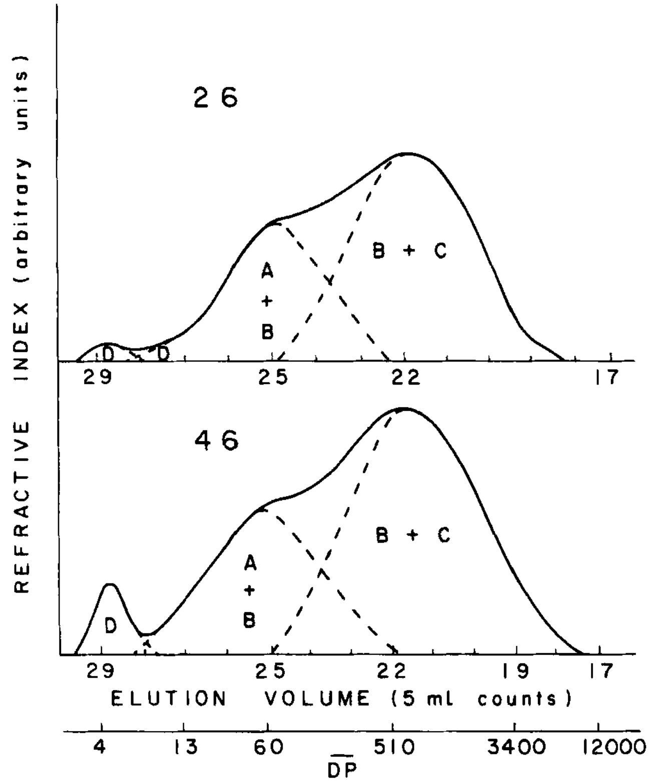

FIG. 7. GPC molecular weight distributions of poly-α-methylstyrene samples 26 and 46, the former prepared from a 5.55 M solution of α-methylstyrene in p-dioxane and the latter from 5.6 M solution of α-methylstyrene in cyclohexane. See Table 1 for other data.

With a view to obtaining additional information about the distribution of [LE] or $[P]_e$ in polymerizations carried out under similar conditions of $[M]_0$ and [LE] but in different solvents, the GPC chromatograms of the polymer samples 46 and 26, the former having been prepared from a 5.6 M solution of α-methylstyrene in cyclohexane and the latter from a 5.55 M solution of α-methylstyrene in p-dioxane are compared in Fig. 7. Polymer 46 required two months to reach a stationary state, and with an $[LE]_{effective}$ of 0.62 mole/liter it yielded 2.90 base-mole/liter polymer. Polymer 26, on the other hand, required about 5 days to reach a stationary state, and with an $[LE]_{effective}$ of 0.055 mole/liter it yielded 2.80 base-mole/

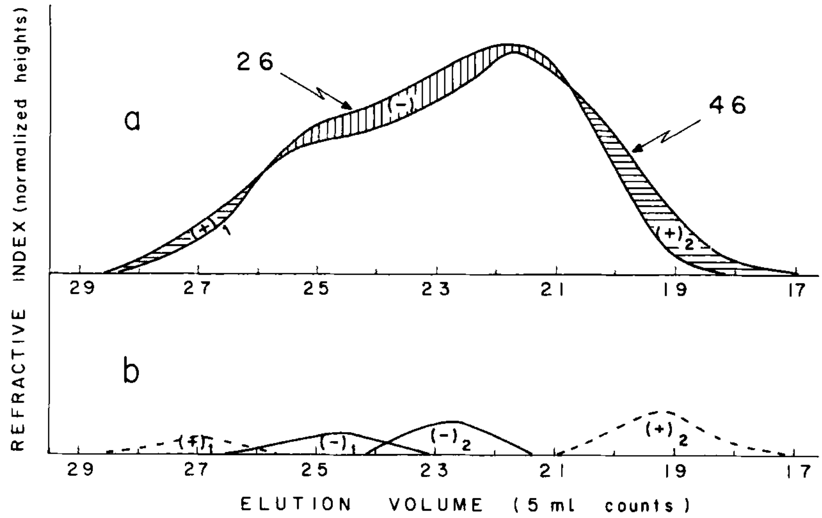

FIG. 8. Graphical method of analysis for comparing the weight-normalized GPC distributions of polymers: case of poly-α-methylstyrene samples 26 (in 5.55 M solution in p-dioxane) and 46 (in 5.6 M solution in cyclohexane) prepared with 0.055 and 0.062 mole/liter of [LE], respectively.

liter of polymer. The analyses of the GPC chromatograms in terms of different components and the values of $[P]_e$ and [LE] associated with these are presented in Table 1. The GPC chromatograms of two polymers (26, 46) can be split into components A+B and B+C only; however the values of $[P]_e$ and [LE] with these in the two experiments are remarkably identical in spite of the considerable difference in the time taken by the two to reach a stationary state.

A more rigorous analysis of these two experiments is shown in Fig. 8a, where weight-normalized curves of 26 and 46 are traced and superimposed. It may be remarked that in polymer 46 the area $(+)_2$ with horizontal shading appearing between the elution counts of 17 and 21 as well as between the elution counts of 26 and 28, $(+)_1$, is in excess to that in polymer 26. Correspondingly in polymer 26 the area (-) with vertical shading appearing between the elution counts of 21 and 26 is in excess to that in polymer 46. These areas may be transformed in terms of molecular weight distributions (Fig. 8b). The area (-) between the elution counts of 21 and 26 was found to be built up of two distinctly separate distributions $(-)_1$ and $(-)_2$. The $[P]_e$ of polymer associated with $(-)_1$ is 0.09 base-mole/liter with an [LE] of 0.002 mole/liter, whereas in $(-)_2$ the $[P]_e$ value is 0.13 base-mole/liter with an associated [LE] of 0.001 mole/liter. On the other hand, the $[P]_e$ value for $(+)_2$ in cyclohexane is 0.18 base-mole/liter but has [LE] of only 0.001 mole/liter. The excess [LE] of 0.007 mole/liter in polymer 46 is associated with component $(+)_1$ which has a $[P]_e$ value of 0.06 base-mole/liter. Thus, on the basis of these results, one could say that in cyclohexane containing traces of THF the splitting of the species is very much marked, whereas in p-dioxane the species do not separate far from one another. However, on keeping in mind the limitations in the reproducibility of the experimental data and the GPC chromatograms coupled with the method of analyses of $[P]_e$ and [LE], it would be more reasonable to say that the two systems are identical as far as the distribution of the reactive species is concerned. This is what one would expect as well on the basis of their similar bulk dielectric constants.

In order to study the effect of dielectric constant of the medium on the separation of the reactive species GPC chromatograms of two polymer samples 40 and 47 the former having been prepared from a 4.95 $\underline{M}$ solution of α-methylstyrene in THF and the latter from a 5.17 $\underline{M}$ solution in cyclohexane are shown in Fig. 9. In polymer 40 the $[LE]_{effective}$ was 0.107 mole/liter and it yielded 1.83 base-mole/liter, whereas in polymer 47 the $[LE]_{effective}$ was 0.096 mole/liter and it yielded 1.92 base-mole/liter of the polymer. The analyses of these chromatograms in terms of $[P]_e$ and [LE] are shown in Table 1. The $[P]_e$ associated with component D+A in both experiments is more or less the same, and so is the average degree of polymerization $\overline{DP}$ in the two cases. Similarly, the value of $[P]_e$ associated with the component B+C in the case of solvent THF is 0.60 base-mole/liter and that in the case of p-dioxane is 0.73 base-mole/liter. However the distribution of molecular weight of component B+C in THF is narrow ($\overline{P_d}$ = 1.5) whereas that in cyclohexane it is broad ($\overline{P_d}$ = 2.8) in nature, in spite of the fact that there is more polymer associated with component B+C in cyclohexane and carries more of the high molecular weight polymer. The [LE] analyses of this component B+C in the two solvents shows that out of an $[LE]_{effective}$ of 0.107 in mole/liter in THF only 0.003 mole/liter is attached to it, whereas out of an $[LE]_{effective}$ of 0.096 mole/liter in cyclohexane, 0.007 mole/liter is attached to it. This would indicate that separation

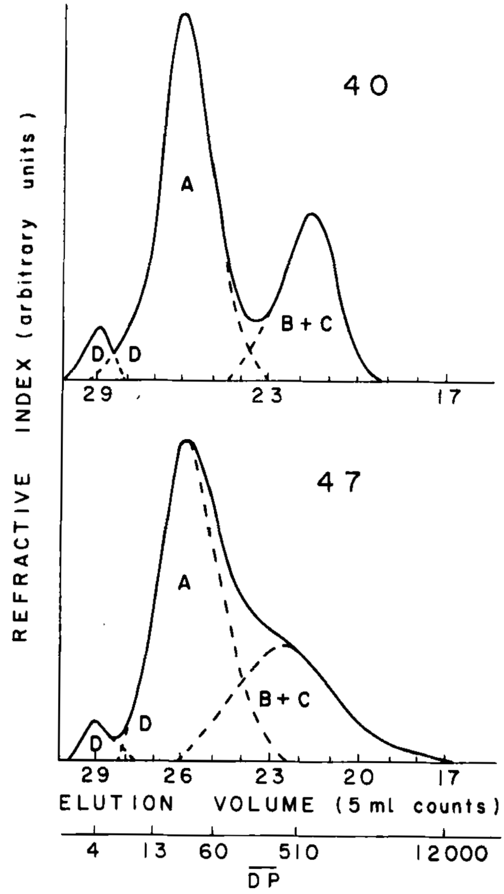

FIG. 9. GPC molecular weight distribution of poly-α-methylstyrene samples 40 and 47, the former prepared from a 4.95 $\underline{M}$ solution of α-methylstyrene in THF and the latter from a 5.17 $\underline{M}$ solution in cyclohexane. See Table 1 for other data.

of the reactive species in THF is superior to that in cyclohexane because of the higher dielectric constant of the former solvent.

In order to have a better picture of the situation, the base-mole/liter of polymer at various elution counts was calculated, and on the basis of these data the traced weight-normalized curves were superimposed as shown in Fig. 10a. The area (+) with horizontal shading

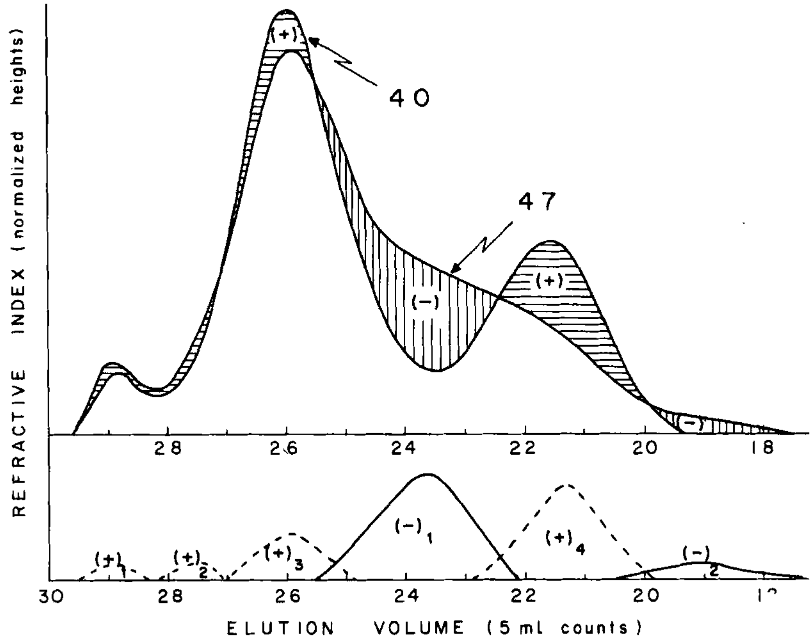

FIG. 10. Graphical method of analysis for comparing the weight-normalized GPC distributions of polymers: case of poly-α-methylstyrene samples 40 (4.95 M solution in THF) and 47 (in 5.17 M solution in cyclohexane) prepared from 0.107 and 0.096 mole/liter of [LE], respectively.

in the distribution of polymer 40 is in excess to that in polymer 47 and that $(-)_1$ with vertical shading in the distribution of the latter is in excess to that in the former. These areas may be converted in terms of their respective distributions as shown in Fig. 10b. The distributions marked $(+)_1$ and $(+)_2$ in THF may be discarded because these represent the dead polymer formed in the beginning of the reaction. Similarly, the distribution marked $(-)_2$ in cyclohexane may be discarded because the $[P]_e$ associated with it is very low (0.03 base-mole/liter), although it has an [LE] of 2.2×10^{-5} mole/liter attached to it. The remainder of the three distributions $(+)_3$, $(-)_1$, and $(+)_4$ in Fig. 10b may now be analyzed more closely.

The first observation one makes is that the separation of distributions $(+)_3$ and $(+)_4$ in THF is quite pronounced, compared to that of $(-)_1$ in cyclohexane. The distribution $(+)_3$ lying between the elution counts of 25 and 27 has a $[P]_e$ of 0.07 base-mole/liter and and [LE] of 0.005 mole/liter, whereas $(+)_4$ situated between the elution counts of 20 and 23 has a $[P]_e$ value of 0.17 base-mole/liter and an [LE] of 5×10^{-4} mole/liter. The distribution $(-)_1$ in cyclohexane has a $[P]_e$ value of 0.24 base-mole/liter and an [LE] of 0.004 mole/liter. From that analysis it may be said that in a medium of high dielectric constant (THF) the effect of higher [LE] is such that more than 98% of [LE] is associated with a component of $\overline{DP} = 25$ whereas the rest of the 2% [LE] splits far away from these and produces a narrowly distributed polymer. Similarly in a solvent of low dielectric constant (cyclohexane) the effect of higher [LE] is such that 93% of [LE] is associated with a component of $\overline{DP} = 25$, whereas the remaining 7% of [LE] is not split apart and yields a polymer with broad molecular weight distribution.

If for a moment it is considered that component $(-)_2$ of cyclohexane may not be rejected, it could also be concluded that the difference in the separation of reactive species in the two solvents in such that a major portion of the polymer is formed in THF due to species with low [LE] of 5×10^{-4} and a minor portion that due to high [LE] 6×10^{-3} mole/liter, whereas in cyclohexane the reverse is the case, a major portion being formed due to high [LE] of 3.6×10^{-3} and a minor portion due to low [LE] of 2.2×10^{-5} mole/liter.

In concluding it may be said that the polymerization of α-methylstyrene at 40°C in cyclohexane, although very slow, yields polymers with bimodal distribution where the high molecular weight part of the polymer has a broad distribution. Under identical conditions of $[M]_0$ and [LE], but on replacing cyclohexane by p-dioxane, these distributions do not show much improvement. However if the solvent used is THF, the high molecular weight component appears to have polymer with low polydispersity. In the polymerization of α-methylstyrene in cyclohexane but with very high [LE], the GPC distribution of polymer produced resembles that of poly-α-methylstyrene prepared in THF but with relatively low [LE]. It would appear that on replacing cyclohexane by THF or using high [LE] but keeping cyclohexane as solvent, the equilibrium between the reactive species which yield components D+A, B, and C shifts in a fashion that there is high [LE] associated with component D+A but more monomer is left for the species B or C carrying relatively low [LE].

NMR studies on the characterization of polymers prepared in THF, p-dioxane, cyclohexane and yielding multimodal distributions are under way, and the results will be published in due course.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support received from the National Research Council of Canada and the Department of Education of the Province of Quebec.

This work has been carried out as part of the general research program of the Groupe de Recherche en Science Macromoléculaire at this University.

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Accepted by editor September 2, 1977
Received for publication September 12, 1977