Polymerization of α-Methylstyrene at High Temperatures in Tetrahydrof uran with Potassium as Initiator. I. Thermodynamic Study and Gel-Permeation Chromatographic Analyses of the Polymers

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ABSTRACT

Polymerization of α-methylstyrene in tetrahydrofuran with potassium as initiator has been studied in the -25 to 60°C temperature range. Variation of the monomer concentration at equilibrium $[M]_e$, with its own polymer $[P]_e$, was found to be linear at 25 and 40°C. The experiments carried out at 50, 55, and 60°C yielded high values of $[P]_e$ and polymers with high viscosity. The GPC distributions of these polymers were found to be multimodal in character, yielding four components D, A, B, and C with an average degree of polymerization, $\overline{DP}$, of about 4, 16, 250, and 1000, respectively. It was found that the living end concentration, $[LE]$ calculated from the viscosity-average molecular weight $\overline{M}_v$ differs to a

considerable extent from those calculated on the basis of number-average molecular weight, $\overline{M}_n$(GPC). In spite of these initial high [LE] values (10^{-1} and 10^{-2}), component C had [LE] of the order of 10^{-3} mole/liter associated with it. The formation of high molecular weight-polymer at high temperatures in solution with high [M]$_0$ was found to be the products of slow initiation and rapid propagation at 25°C which did not depropagate when kept at 50 or 60°C although active ends were still present. In solutions with low [M]$_0$ and high [LE], where initiation was instantaneous, the GPC distributions were also multimodal. It has been speculated that these multimodal distributions are a result of dead and dormant polymers in combination with polymers due to different ion pairs.

INTRODUCTION

Thermodynamic studies on the anionic equilibrium polymerization have been extensively dealt with in the literature [1-6]. It has been reported that the equilibrium monomer concentration [M]$_e$ at a given temperature is not unique but varies linearly with the concentration of the polymer [P]$_e$. Making use of the extrapolated [M]$_e$ at zero polymer concentration as well as the slope of the [M]$_e$ versus [P]$_e$ curve, the values of $\Delta G_{\ell c}$, the free energy change for the conversion of 1 mole of pure liquid monomer to 1 base-mole of amorphous polymer, can be calculated. In the temperature range reported (-20 to +20°C), the variation of $\Delta G_{\ell c}/RT$ with $1/T$ was shown to be linear.

In an attempt to extend these studies to higher temperatures, polymerization of α-methylstyrene in tetrahydrofuran was carried out at 25, 40, 50, 55, and 60°C, potassium mirror being the initiator used. The polymer samples thus obtained were characterized by viscometry and gel-permeation chromatography. The principal results of this study form the subject of this communication.

EXPERIMENTAL

Materials

α-Methylstyrene (Baker analyzed reagent) was kept over calcium hydride and degassed over a period of two weeks. It was distilled

under vacuum, the head and tail fractions being discarded. Vapor-phase chromatography of the middle fraction showed it to contain small amounts of cumene, but the presence of no other materials could be detected. Prior to its use, the monomer was further puri-fied by distilling it on a mirror of sodium or potassium metal. Tetra-hydrofuran (Fisher Scientific ACS) was purified in the same manner as described above for α-methylstyrene.

Procedure

Polymerizations were carried out in precision calibrated ampoules by use of high vacuum-techniques. Calibration of the ampoules, initia-tion over a potassium mirror, polymerization, and determination of polymer and unreacted monomer have been described elsewhere [7]. Initiation was performed at 25°C in most cases. In the case of mix-tures with initial monomer concentration higher than 5 mole/liter, the formation of the red color was not instantaneous. The initiation period ranged from 2 to 5 min; this includes the time required for the transfer of the mixture from the potassium mirror to the cali-brated ampoule and the sealing of the ampoule. The ampoule contain-ing the solution was immersed in a bath set at a desired temperature and the decrease in volume due to polymerization was followed till the reaction reached a stationary state. The polymerization was then terminated according to the procedure previously described [7].

Monomer Analysis

Determination of unreacted monomer was carried out through gas chromatography with cumene as an internal standard. Analyses were performed with a Perkin-Elmer chromatograph at 170°C on a UCON oil column LB-550-X with the use of a thermal conductivity detector, helium being the carrier gas.

Molecular Weights

Viscometry

An Ubbelohde viscometer was used to measure the flow time of the solvent toluene and the polymer solution at 25°C. From these data the intrinsic viscosity [η] of the polymer was calculated using the one-point method [8]. Molecular weights were computed from the relation [9]:

$$[\eta] = 7.81 \times 10^{-5} \overline{M}_V^{0.73} \tag{1}$$

where $\overline{M}_V$ is the viscosity-average molecular weight.

Gel-Permeation Chromatography (GPC)

The GPC molecular weight distributions of poly-α-methylstyrene were obtained with a Waters Associates (model 200) gel-permeation chromatograph equipped with three columns connected in series, each one being packed with crosslinked polystyrene gel having, according to the Waters method a maximum rated porosity of 1×10^6, 1.5×10^5, and 3×10^3 Å, respectively. A few samples were also run with four columns, this additional column having a maximum-rated porosity of 250 Å. In order to avoid "concentration effects" on the peak positions, the concentration was limited to 0.125%, and tetrahydrofuran purged with nitrogen at a flow rate of 1 ml/min was the solvent used. The calibration of the instrument was performed with narrowly distributed polystyrenes and poly-α-methylstyrenes. Molecular weights were computed as suggested in Waters' manual [10]. The GPC curves analyzed in this text are the raw curves, and no "resolution correction" has been applied to them.

RESULTS AND DISCUSSION

Thermodynamics

Equilibrium monomer concentrations $[M]_e$ and equilibrium polymer concentrations $[P]_e$ for the anionic polymerization of α-methylstyrene in tetrahydrofuran at 25, 40, 50, 55, and 60°C are shown in Table 1 together with $[LE]$, the living end concentration as computed from Eq. (2), assuming two "living ends" per chain

$$[LE] = 2w/\overline{M}_V V_e$$

$$= 2 \times 118.2 [P]_e / \overline{M}_V \text{ mole/liter} \tag{2}$$

where w is the weight of polymer (in grams) present at equilibrium in the volume V_e (in liters). Figure 1 shows the plot of $[M]_e$ versus

TABLE 1. Equilibrium Values of Monomer and Polymer Concentrations and Living End Concentrations at Various Temperatures

Sample no.	Temperature ($^\circ$C)	$[M]_0$ (mole/liter)	$[M]_e$ (mole/liter)	$[P]_e$ (base-mole/liter)	$[\eta]$	$[LE] \times 10^3$ (mole/liter)
L-106	25	2.00	1.69	0.38	0.13	4.
J-1	25	2.81	2.55	0.32	—	9.
L-5	25	3.00	2.25	0.90	0.05	22.
L-101	25	3.00	2.24	0.92	0.13	10.
J-2	25	3.23	2.20	1.25	—	9.
J-3	25	3.36	2.25	1.35	—	9.
J-4	25	3.60	2.00	1.95	—	9.
J-5	25	3.83	2.10	2.10	—	9.
L-97	25	4.00	1.90	2.55	0.30	8.
L-91	25	4.48	1.60	3.50	0.40	7.
L-94	25	5.00	1.10	4.75	0.55	6.
L-81	25	5.55	1.00	5.55	0.42	9.
L-83	25	6.00	0.90	6.25	0.64	5.
L-86	25	6.00	0.55	6.65	0.45	10.
L-78	25	6.50	0.75	7.00	—	—

(continued)

TABLE 1. (Continued)

Sample no.	Temperature (°C)	$[M]_0$ (mole/liter)	$[M]_e$ (mole/liter)	$[P]_e$ (base-mole/liter)	$[\eta]$	$[LE] \times 10^3$ (mole/liter)
L–52	25	7.00	0.45	8.00	0.30	24.
L–49	25	7.50	0.30	9.00	0.64	10.
36	40	4.20	3.42	0.95	0.23	4.
38	40	4.35	3.73	0.76	0.27	2.
41	40	4.54	3.64	1.10	0.37	2.
40	40	4.95	3.45	1.83	0.15	14.
L–92	40	5.00	3.67	1.62	–	–
39	40	5.35	3.45	2.32	0.42	4.
37	40	6.50	3.15	4.13	0.55	5.
56	50	5.82	5.30	0.63	0.23	3.
58	50	5.85	5.20	0.78	0.12	9.
59	50	5.80	4.73	1.31	0.09	24.
54	50	6.40	5.00	1.72	0.28	65.
57	50	6.44	4.92	1.88	0.23	76.
69	50	6.45	4.80	2.00	0.20	107.

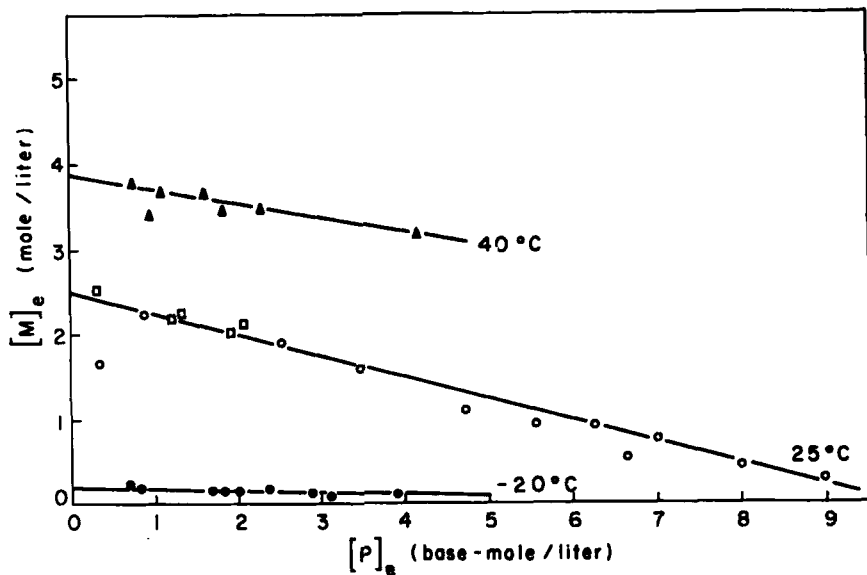| 53	55	6.25	3.65	3.16	0.28	12.
60	55	6.25	3.17	3.75	0.13	30.
65	55	6.25	3.09	3.85	0.12	45.
67	55	6.70	5.83	1.06	0.10	17.
68	55	6.70	5.10	1.96	0.25	9.
66	55	6.70	4.20	3.05	0.40	7.
64	60	6.70	5.50	1.47	0.11	114.
63	60	6.70	5.00	2.10	0.25	73.
62	60	7.20	5.90	1.58	0.57	12.
61	60	7.20	5.40	2.10	0.55	23.

FIG. 1. Variation of $[M]_e$ with $[P]_e$ for the equilibrium polymerization of α-methylstyrene in tetrahydrofuran at -20, 25, and 40°C. Squares and full circles are from ref. [5].

$[P]_e$ obtained at -20, 25, and 40°C. It is apparent that the variation of $[M]_e$ with $[P]_e$ is linear in nature, especially at 25°C where the relationship can be extended to include the near bulk conditions. $\Delta G_{\ell c}$, the free energy change for the conversion of 1 mole of pure liquid monomer to 1 base-mole of amorphous polymer, may be computed [5, 6] from the variation of $[M]_e$ with $[P]_e$ which can be expressed by

$$[M]_e = a + b [P]_e \tag{3}$$

with

$$A = aV_m \tag{4}$$

$$B = b(V_m/V_p) \qquad\qquad\qquad (5)$$

$$B = (\chi_{mp} - \beta)/(\beta + \chi_{mp} - 1/A) \qquad\qquad (6)$$

where V_m and V_p are the volume of 1 mole of monomer and 1 base-mole of polymer, respectively; χ_{mp} is the free energy interaction parameter between monomer and polymer; β is an interaction parameter for the solvent. Then it follows that

$$\Delta G_{\ell c}/RT = 1 + \ln A + \beta(1 - A) - \chi_{mp}A \qquad\qquad (7)$$

From the experimental values of a, b, V_m, and V_p given in Table 2, values of A, B, β, and $\Delta G_{\ell c}/RT$ are readily obtained by using Eqs. (4) to (7) assuming χ_{mp} = 0.4. The values of $\Delta G_{\ell c}/RT$ shown in Table 2 are in good agreement with those previously obtained from the equilibrium polymerization in dioxane [7].

Because at high temperature the range of allowed initial monomer concentrations for a given temperature is small and because, as it will be seen later, the concentration of short chains formed under these conditions is quite high, it was not possible to use our data as such for the computation of thermodynamic parameters at 50, 55, and 60°C for the sake of comparison with the results obtained at 25 and 40°C.

At 50°C the variation of $[M]_e$ with $[P]_e$ is also linear (not shown in Fig. 1). However, from the data presented in Table 1, the initial monomer concentration $[M]_0$ being identical in the case of experiments 56, 58, and 59, it is found that, contrary to expectation, the values of $[M]_e$ and $[P]_e$ are not identical. The same observation can be made for experiments carried out at 50, 55, and 60°C, where it seems that in solutions with identical $[M]_0$, $[M]_e$ varies with $[LE]$.

The present equilibrium monomer concentrations are much lower than the ones reported by McCormick for shorter times of polymerization [1]. From Table 1 and from the GPC curve analysis shown in Tables 3-5, it is observed that the variation of $[M]_e$ goes along with the variation of $[LE]$ and this can be associated with the presence of low molecular weight polymer.

TABLE 2. Parameters of the Equilibrium Polymerization at 25 and 40°C

T (°C)	a (mole/liter)	b	V_m (liter/mole)[a]	V_p (liter/base-mole)[a]	$\Delta G_{\ell c}/RT$	
					This work	Ref. [7]
25	2.53 ± 0.04	-0.27 ± 0.01	0.1305	0.1071	-0.71	-0.63
40	3.85 ± 0.06	-0.17 ± 0.02	0.1325	0.1077	+0.17	+0.15

[a]Extrapolated from data of Ivin and Leonard [5].

TABLE 3. GPC Analysis of Poly-α-methylstyrene Prepared at 60° C^a

No.	[M]$_o$ (mole/liter)	[P]$_e$ (base-mole/liter)				[LE] (GPC) (mole/liter)				[LE] from Eq. (2) (mole/liter)
		A + D	B	C	Total [P]$_e$	A + D	B	C	Total [LE]	
62	7.2	0.10	0.33	1.15	1.58	0.009	0.002	0.001	0.01	0.002
61	7.2	0.10	0.52	1.48	2.10	0.01	0.006	0.003	0.02	0.003
63	6.70	0.39	0.76	0.94	2.10	0.06	0.007	0.002	0.07	0.008
64	6.70	0.66	0.29	0.52	1.47	0.11	0.004	0.002	0.12	0.019

[a] Initiation time at room temperature: samples 62 and 61, about 30 min; samples 63 and 64, about 20 min.

TABLE 4. GPC Analysis of Poly-α-methylstyrene Prepared at 55° C[a]

No.	[M]$_0$ (mole/liter)	[P]$_e$ (base-mole/liter)				[LE] (GPC) (mole/liter)				[LE] from Eq. (2) (mole/liter)
		A + D	B	C	Total [P]$_e$	A + D	B	C	Total [LE]	
53	6.25	1.18	0.59	1.39	3.16	0.12	0.005	0.002	0.13	0.012
60	6.25	2.02	0.77	0.96	3.75	0.25	0.006	0.002	0.26	0.030
65	6.25	2.38	0.99	0.48	3.85	0.61	0.018	0.002	0.63	0.045
67	6.70	0.63	0.16	0.27	1.06	0.10	0.003	0.001	0.10	0.017
68	6.70	0.77	0.50	0.69	1.96	0.10	0.005	0.001	0.10	0.009
66	6.70	0.55	0.90	1.60	3.05	0.09	0.005	0.001	0.10	0.007

[a]Initiation time at room temperature: sample 53, 10 min; sample 60, 20 min; sample 65, 30 min; sample 67, 25 min; sample 68, 35 min; sample 66, 50 min.

TABLE 5. GPC Analysis of Poly-α-methylstyrene Prepared at 50°C[a]

No.	$[M]_o$ (mole/liter)	$[P]_e$ (base-mole/liter)				$[LE]$ (GPC) (mole/liter)				$[LE]$ from Eq. (2) (mole/liter)
		A + D	B	C	Total $[P]_e$	A + D	B	C	Total $[LE]$	
56	5.82	0.14	0.06	0.43	0.63	0.02	0.001	0.002	0.02	0.003
58	5.85	0.31	0.16	0.31	0.78	0.04	0.003	0.002	0.04	0.009
59	5.80	0.65	0.20	0.46	1.31	0.09	0.002	0.002	0.09	0.024
54	6.40	0.38	0.24	1.10	1.72	0.06	0.003	0.003	0.07	0.006
57	6.44	0.51	0.29	1.08	1.88	0.07	0.003	0.003	0.08	0.009
69	6.45	0.75	0.39	0.86	2.00	0.10	0.003	0.002	0.11	0.012

[a]Initiation time at room temperature: samples 56, 58, and 59, 10 min; samples 54, 57 and 69, 15 min.

It has been shown that equilibrium between active short-chain polymer and monomer differs to a considerable extent from equilibrium involving long-chain polymer [6]. However, in the present case the situation is more complex, since it involves an equilibrium between monomer and both short- and long-chain polymers. In order to see the effect of short-chain polymer on the equilibrium, one can make use of an approach which combines the fundamental equations for homo and copolymerizations. The free energy of polymerization can be written as the sum of four terms which is equal to zero under equilibrium conditions:

$$-\Delta \overline{G}_m + \Delta G_{\ell c} + x(\Delta \overline{G}_p/n) + x^*(\Delta \overline{G}_p^*/n^*) = 0 \qquad (8)$$

The first term represents the change in free energy associated with the removal of 1 mole of monomer from the equilibrium mixture without changing its concentration. $\Delta G_{\ell c}$ is the change in free energy for the conversion of 1 mole of pure liquid monomer into x base-mole of amorphous high molecular weight polymer with a degree of polymerization of n and $x^*(x + x^* = 1)$ base-mole of amorphous low molecular weight polymer with a degree of polymerization of n^*. $\Delta \overline{G}_p$ and $\Delta \overline{G}_p^*$ are the partial molar free-energy change for the addition of 1 mole of high and low molecular weight polymer, respectively. Using the Flory-Huggins expression for the free energy of mixing, differentiating in order to get expressions for $\Delta \overline{G}_m$, $\Delta \overline{G}_p$, and $\Delta \overline{G}_p^*$ and neglecting the terms divided by n, one finally obtains:

$$\Delta G_{\ell c}/RT = \ln \phi_m + 1 + (V_m/V_s)(\chi_{sm} - \chi_{sp})\phi_s$$

$$+ \chi_{mp}(\phi_p - \phi_m) - (1 - x)[(\ln \phi_p^* + 1)/n^*] \qquad (9)$$

where ϕ is the volume fraction of any species under equilibrium conditions and χ is the interaction parameter between any two components of the system, the polymer-polymer interaction parameter being zero. Subscripts m, s, p* refer to monomer, solvent, and low molecular weight polymer, respectively. The subscript p denotes the whole polymer, so that ϕ_p is the volume fraction of the total polymer. V_m and V_s are the molar volumes of the monomer and the solvent, respectively.

The last term of Eq. (9) can be related to the concentration of living ends [LE] * and the degree of polymerization n* of the low molecular weight polymer through the equality

$$\phi_p^* = V_p [LE]^* n^*/2 \tag{10}$$

where V_p is the volume of one base-mole of polymer, assuming two living ends per chain. Equation (9), together with Eq. (10), clearly shows the effect of the active low molecular weight polymer on the equilibrium. This is in accordance with the results shown in Table 1 as has been already mentioned. Unfortunately the present results do not allow a quantitative comparison and extensive studies on this aspect alone would be required in order to draw any firm conclusion. It is worth noting that if the low molecular weight polymer is inactive ("dead"), the last term of Eq. (9) disappears, whereas ϕ_p still refers to the total polymer volume fraction.

Gel-Permeation Chromatography

The presence of low molecular weight polymer is easily detectable through gel-permeation-chromatographic analysis. Component tracing of the multinodal distributions was carried out according to the procedure suggested by Robb et al. [11], who extended the approach of Bartlet and Smith [12] applicable to gas chromatographic traces. Computations have been based on the assumption that the recorded signal height is directly proportional to the polymer concentration irrespective of the molecular weight [13]. This is not strictly true but, since the discussion is based on a qualitative analysis of the GPC chromatograms, this approximation is considered satisfactory.

Figures 2 to 14 show GPC chromatograms of polymers prepared under various experimental conditions, all polymerizations being carried out with high initial monomer concentrations and high living end concentrations. In Fig. 2 are shown the chromatograms of two samples prepared by polymerizing pure monomer with traces of solvent at 60° C (near bulk polymerization), initiation being carried out at 25° C. These experiments represent typical cases of slow initiation, and these distributions could be considered as unimodal with a long tail in the low molecular weight region resulting from the deactivation of chains alongside with their propagation. However, if the peaks are assumed to be symmetrical, these distributions might be associated with the presence of four components D, A, B, and C.
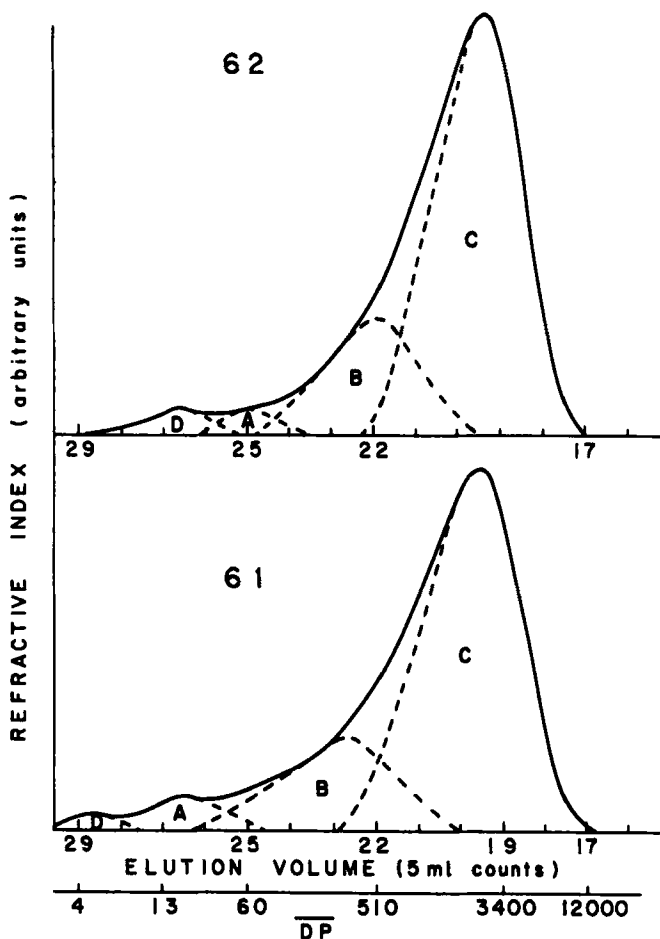
FIG. 2. GPC chromatograms of poly-α-methylstyrene (samples
62, 61) initiated at 25° C and polymerized at 60° C under near bulk
conditions. (See Table 3 for other data.)

The multimodal character of the distributions is enhanced by further
addition of tetrahydrofuran as can be seen from Fig. 3 and Table 3.
In Table 3 $[M]_0$ is the initial monomer concentration and $[LE]$ is
computed both from Eq. (2) and from GPC results. $[LE]$ associated
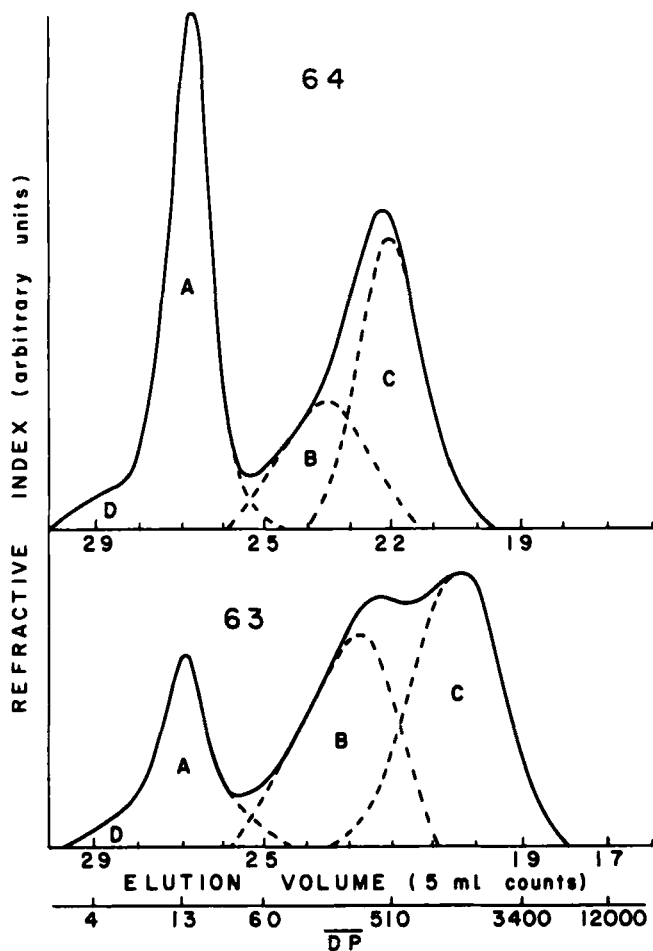with the various components of the chromatograms are computed by

FIG. 3. GPC chromatograms of poly-α-methylstyrene (samples 64, 63) initiated at 25° C and polymerized at 60° C from 6.7 mole/liter solutions of α-methylstyrene. (See Table 3 for other data.)

using $\overline{M}_n$ as determined by GPC and the concentration of polymer (in base-mole/liter) obtained from the total $[P]_e$ and the relative area of the various peaks. In cases 63 and 64, the initiation is relatively more rapid and the total living end concentration is much higher than

it is in the previous case. Components D and A appear everywhere at the same elution volumes, the average degree of polymerization $\overline{DP}$ being of the order of 4 for D, whereas A has a $\overline{DP}$ ranging between 15 and 20. From Table 3 it is observed that the concentration of chains associated with peak C remains approximately constant and does not seem to vary much in the case of peak B. It seems that additional formation of chains contributes to the increase of species A, as can be seen from Table 3. From Table 3 one also notes that the total [LE] computed from viscosity and that computed from $\overline{M}_n$ (GPC)

differ to a considerable extent. The values of [LE] computed these ways represent the total concentration of polymer chain ends rather than the real living ends concentration, since part of the active centers could have been already deactivated when the reaction is terminated by the addition of methanol.

Polymers obtained at 40, 50, and 55° C present a similar pattern of distribution. Figure 4 shows the chromatograms of polymers prepared at 55° C (initiated at 25° C). In this case [LE] is very high and differs considerably for the three experiments presented in Table 4, [LE] ranging from 0.13 to 0.63 mole/liter. However [LE] associated with component C remains at 0.002 mole/liter, whereas the relative amount of components B and (A + D) increases with increasing [LE]. Figure 5 shows anomalous chromatograms, since, as $[M]_0$ and total [LE] are identical, all chromatograms of samples 66 and 68 should be identical. The difference between these distributions seems to arise from the fact that the three samples were left at 25° C for various periods of time prior to their being brought to 55° C as is mentioned in Table 4. The proportion of components B and C increases with the time during which the reaction solution was left at 25° C.

Polymers prepared at 50° C, for which results are presented in Table 5 and Figs. 6 and 7, show similar trends. For two different initial monomer concentrations, the concentration of low molecular weight polymer chains (A + D) increases with increasing total [LE]. The same type of observation applies to polymerizations carried out at 40° C and the results are shown in Table 6 and Fig. 8.

The presence of low molecular weight polymer in this set of experiments is in accordance with the thermodynamic treatment. Because of the high molecular weight component in the multimodal distributions, the high proportion of polymer molecules having a low $\overline{DP}$ was not detectable through simple viscosity measurements as can be seen from Tables 3-6. In the same way, the very high concentraion of living ends did not allow for measurements of [LE] through UV spectroscopy. If the distributions were unimodal, with such high [LE] the formation of relatively low molecular weight
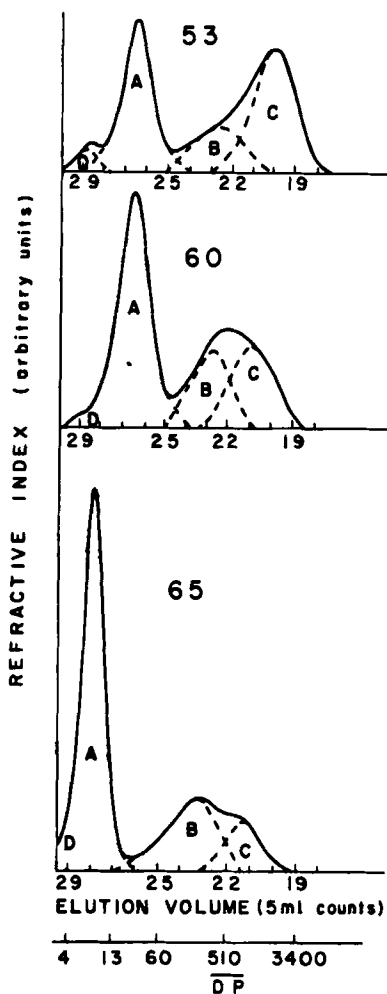
FIG. 4. GPC chromatograms of poly-α-methylstyrene (samples 53, 60, 65) initiated at 25°C and polymerized at 55°C from 6.25 mole/liter solutions of α-methylstyrene. (See Table 4 for other data.)
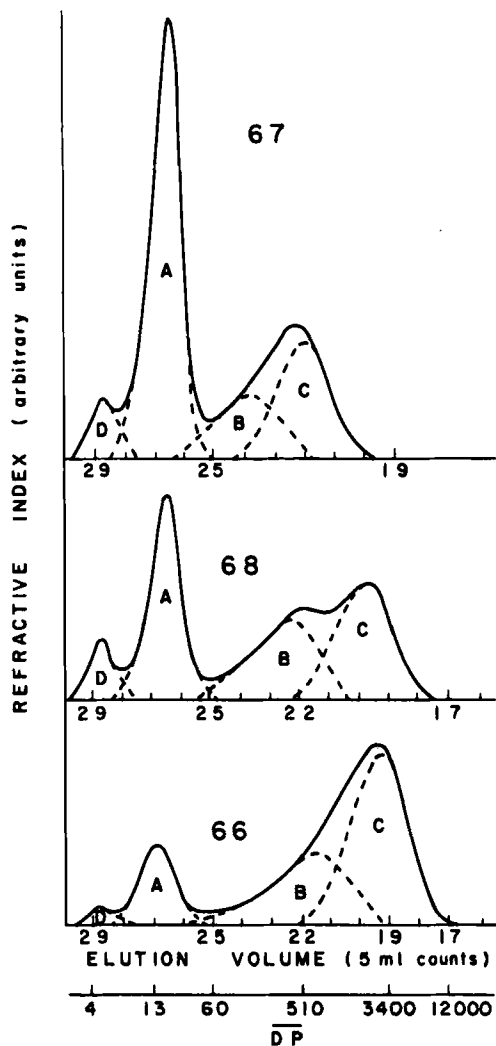
FIG. 5. GPC chromatograms of poly-α-methylstyrene (samples 67, 68, 66) initiated at 25° C and polymerized at 55° C from 6.7 mole/liter solutions of α-methylstyrene. (See Table 4 for other data.)
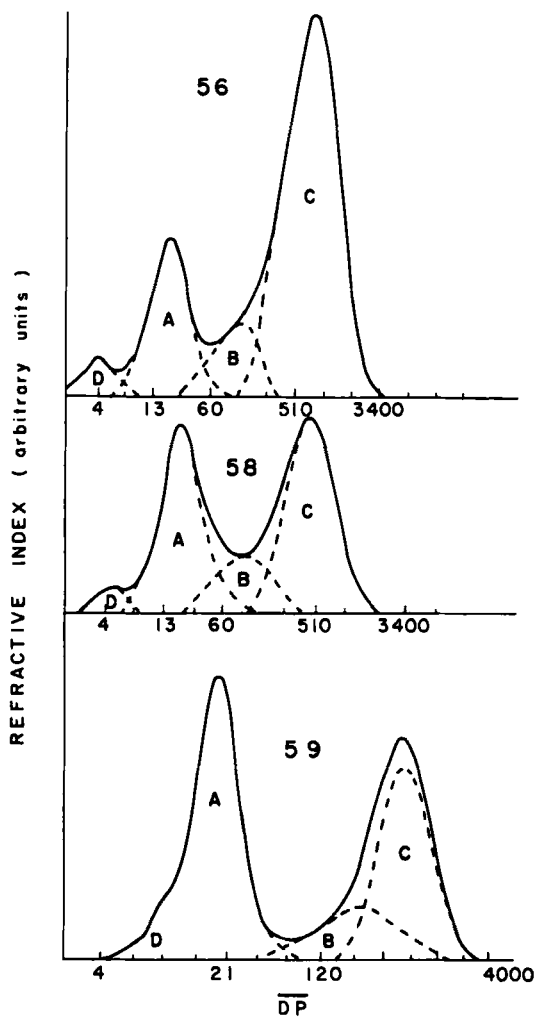
FIG. 6. GPC chromatograms of poly-α-methylstyrene (samples 56, 58, 59) initiated at 25° C and polymerized at 50° C from 5.8 mole/liter solutions of α-methylstyrene. (See Table 5 for other data.)
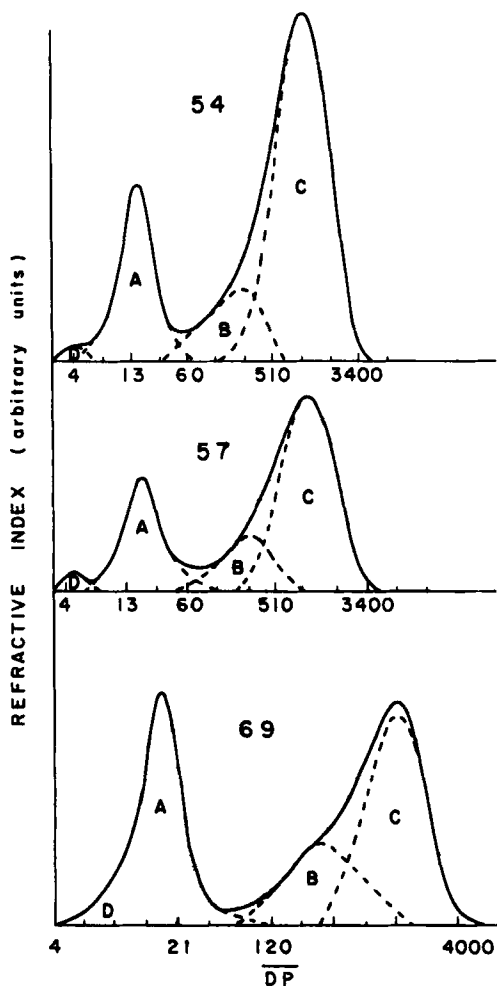
FIG. 7. GPC chromatograms of poly-α-methylstyrene (samples 54, 57, 69) initiated at 25° C and polymerized at 50° C from 6.4 mole/liter solutions of α-methylstyrene. (See Table 5 for other data.)
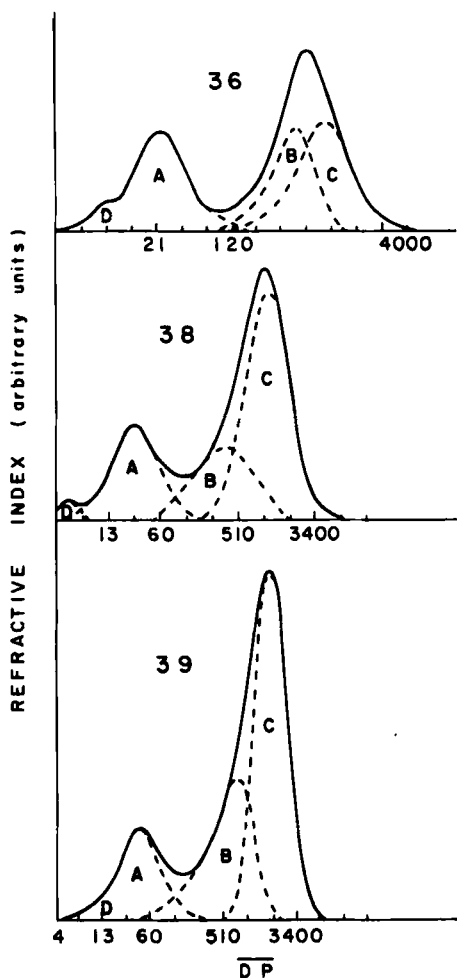
FIG. 8. GPC chromatograms of poly-α-methylstyrene initiated and polymerized at 25°C from solutions of α-methylstyrene with $[M]_0$ values of 4.20 (sample 36), 4.35 (sample 38) and 5.35 (sample 39) mole/liter. (See Table 6 for other data.)

TABLE 6. GPC Analysis of Poly-α-methylstyrene Prepared at 40° C[a]

No.	[M]$_0$ (mole/liter)	[P]$_e$ (base-mole/liter)				[LE] (GPC) (mole/liter)				[LE] from Eq. (2) (mole/liter)
		A + D	B	C	Total [P]$_e$	A + D	B	C	Total [LE]	
36	4.20	0.34	0.26	0.35	0.95	0.04	0.001	0.001	0.04	0.004
38	4.35	0.19	0.17	0.40	0.76	0.02	0.001	0.001	0.02	0.003
40	4.95	1.23	(0.60)		1.83	0.15	(0.003)		0.15	0.014
39	5.35	0.43	0.67	1.22	2.32	0.03	0.003	0.001	0.03	0.004
37	6.50	0.54	1.21	2.37	4.12	0.02	0.009	0.002	0.03	0.005

[a]Initiation time at room temperature: 10 min for sample 37; 5 min for all other ones.

polymer would be expected. However multimodal distributions with a low molecular weight species having a given $\overline{DP}$ and a high molecular weight component remain to be explained.

The multimodal distributions may arise from the fact that the first part of the polymerization takes place at 25°C. It may be thought that at 25°C the distribution is unimodal and consists of high molecular weight species. Upon raising the temperature, most of the active species would depropagate (low molecular weight peak) while part of them would not (high molecular weight peak). The latter peak may consist of deactivated species or nonreversible species formed at 25°C which do not depropagate at higher temperature. This speculation takes its origin from the work of Wenger [14], who suggested that depropagation has a high activation energy and thus, in order to avoid the formation of nonreversible species, initiation should be carried out at high temperature. If deactivation occurs at high temperature, this can be found with the help of UV spectrophotometry. However, for practical reasons this could not be done in the present work, and it remains to be done.

In order to check the effect of the initiation temperature on the distribution, two solutions with the same initial monomer and living end concentrations were initiated at 25° (L-83) and 50°C (L-86) and polymerized at 25°C. Figure 9 and Table 7 show similar distributions in both cases. In Fig. 10 are shown the GPC chromatograms of polymers L-52, L-53, and L-78 (see Table 7) prepared from a 7.0 M solution with very high [LE], initiation being carried out at 50°C and polymerization at 25°C. One observes that the low molecular weight component (D + A) increases with increasing concentration of living ends, yet one finds high molecular weight components B and C. It may be argued that near bulk conditions one is likely to get anomalous results due to numerous factors.

Slow initiation and inefficient mixing may lead to anomalous distributions. It is known [15] that in order to obtain unimodal Poisson-type molecular weight distribution initiation ought to be instantaneous and the spatial distribution of all reagents uniform throughout the polymerization system. It has been reported that inefficient mixing [16-19] and slow initiation [20, 21] both lead to a broadening of distribution rather than multimodal distributions. Figure 11 shows the chromatograms of the polymer obtained using systems with initial monomer concentrations of 2.0 (L-106), 3.0 (L-101), and 5.5 (L-81) mole/liter. The initiation in the cases of L-106 and L-101 is instantaneous, and there is no possibility of any large amount of polymer being formed during initiation. One notes that these two polymers as well have the same four components (D, A, B, and C) with a similar criterion as that of L-81 where one can imagine some polymerization
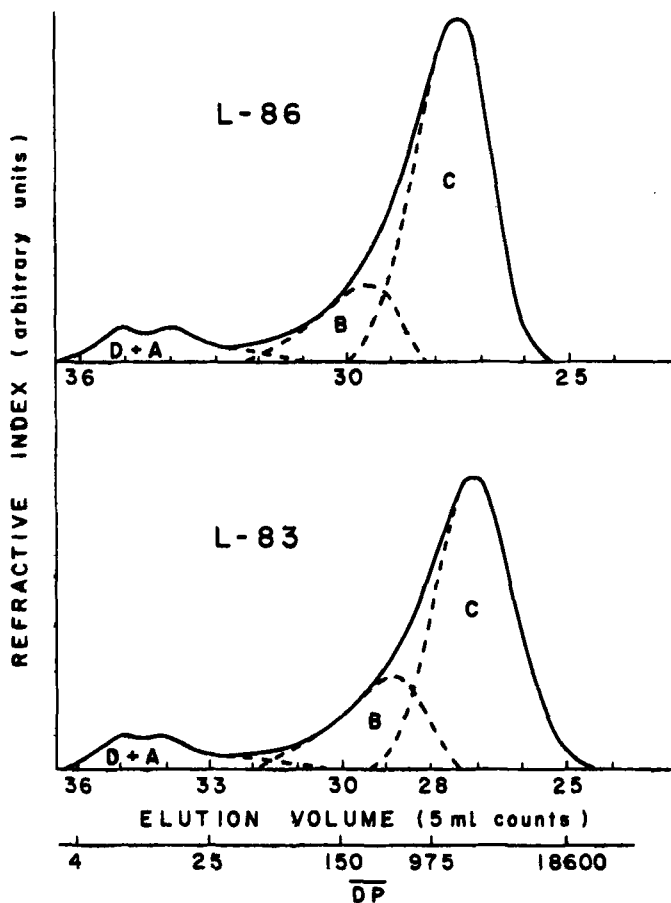
FIG. 9. Comparison of GPC chromatograms of poly-α-methylstyrene initiated at 25°C (sample L-83) and 50°C (sample L-86) from 6.0 mole/liter solutions of α-methylstyrene. (See Table 7 for other data.)

during initiation at 25°C. In all the three chromatograms the components B and C contribute towards the growth of the polymer, where as A and D elute at the same place. The analyses of these chromatograms is shown in Table 7. Based on all these experiments one can safely say that in the polymerization of α-methylstyrene with potassium

TABLE 7. GPC Analysis of Poly-α-methylstyrene Prepared at 25°C[a]

No.	[M]$_o$ (mole/liter)	[P]$_e$ (base-mole/liter)				[LE] (GPC) (mole/liter)				[LE] from Eq. (2) (mole/liter)
		A + D	B	C	Total [P]$_e$	A + D	B	C	Total [LE]	
L-106	2.00	0.18	0.08	0.12	0.38	0.03	0.005	0.001	0.04	0.004
L-101	3.00	0.16	0.46	0.30	0.92	0.03	0.02	0.004	0.05	0.010
L-65	4.48	0.14	0.81	2.55	3.50	0.03	0.03	0.014	0.07	0.010
L-81	5.55	0.58	1.98	2.99	5.55	0.06	0.02	0.006	0.09	0.009
L-86[b]	6.00	0.67	1.14	4.84	6.65	0.13	0.02	0.01	0.16	0.010
L-83	6.00	0.68	1.43	4.14	6.25	0.12	0.01	0.005	0.14	0.005
L-52[b]	7.00	1.08	1.12	5.80	8.00	0.21	0.02	0.03	0.26	0.010
L-53[b]	7.00	2.12	1.29	4.59	8.00	0.43	0.05	0.05	0.53	0.050
L-78[b]	7.00	7.00	(1.00)		8.00	0.92	(0.01)		0.93	0.400

[a]Time of initiation is 2 to 5 min for [M]$_o$ between 2 and 4.5 mole/liter. For higher [M]$_o$, time varies depending upon the desired [LE].
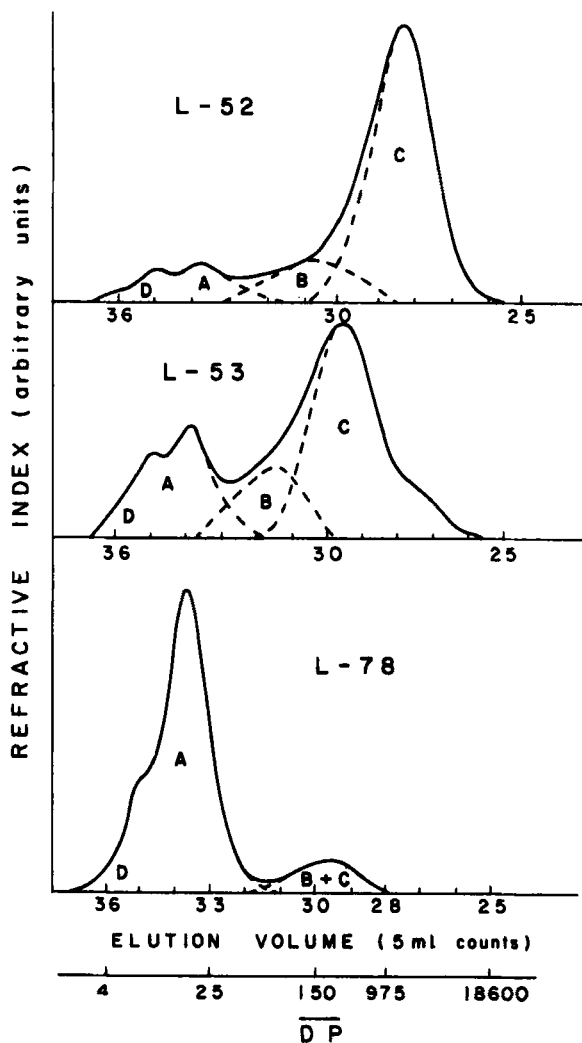[b]Initiated at 50°C.

FIG. 10. GPC chromatograms of poly-α-methylstyrene (samples L-52, L-53, and L-78) initiated at 50°C and polymerized at 25°C from 7.0 mole/liter solutions of α-methylstyrene. (See Table 7 for other data.)
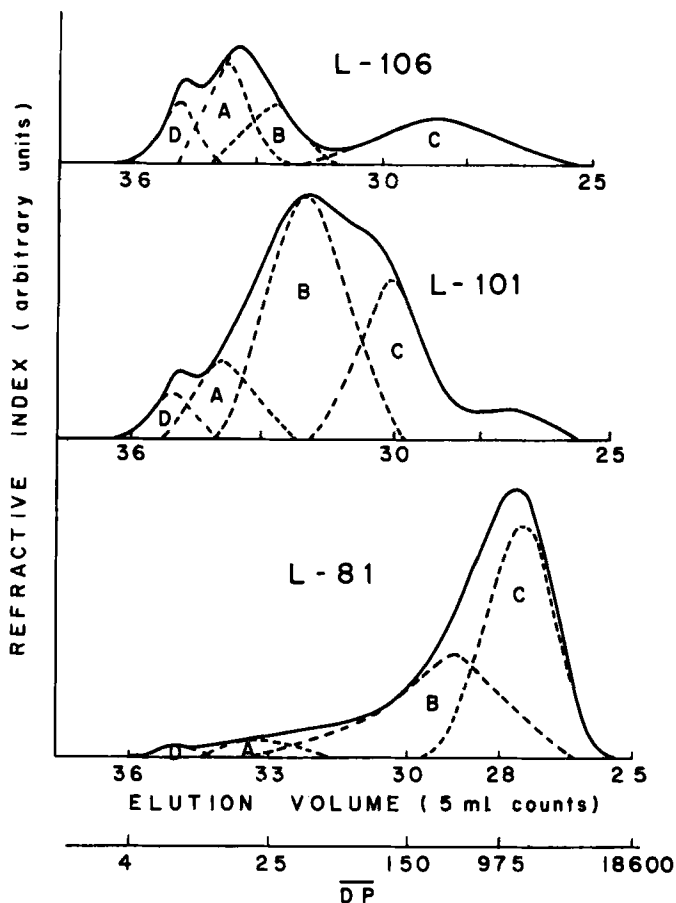
FIG. 11. GPC chromatograms of poly-α-methylstyrene initiated and polymerized at 25° C from solutions of α-methylstyrene with [M]₀ values of 2.0 (sample L-106), 3.0 (sample L-101), and 5.5 (sample L-81) mole/liter, (See Table 7 for other data.)

as initiator and THF as solvent, initiation being carried out at 25° C, the probability for the presence of multimodal distributions is high when the [LE] concentration is of the order of 10^{-2} or 10^{-1} mole/liter.

After having established that multimodal distributions are not the

result of an artefact of the initiation process, the causes for such a result remain to be found. The presence of a high molecular peak after the reacting mixture has been kept at high temperature may be explained in two different ways: (a) the species responsible for the formation of polymer associated with components B and C are deactivated at high temperature before they could depropagate; (b) these species (or one of these) undergo irreversible propagation.

In order to determine the extent of deactivation occurring at high temperatures, a 6.0 $\underline{M}$ solution of α-methylstyrene in tetrahydrofuran initiated at 25°C with potassium mirror was divided into two parts. The living end concentration in the two ampoules was about the same. One of these ampoules was polymerized at 25°C (L-19) for 2 hr and yielded 5.1 base-mole/liter of the polymer. The other ampoule was kept at 60°C for 5 days immediately after initiation. Five days later this ampoule was removed from the 60°C bath and polymerized (L-21) at 25°C for 2 hr. It was observed that during that period of time the meniscus of the solution decreased showing that polymerization was going on. This time, the yield of the polymer was 4.1 base-mole/liter. The GPC chromatograms of the two polymers (Fig. 12) show two similar distributions. A complete deactivation of the living ends at 60°C would certainly not bring about polymerization at 25°C. On the other hand, although it seems from the results of Table 8 that the concentration of chains is the same in both cases, it is obvious that deactivation has occurred, since identical concentrations of living ends would have yielded the same amounts of polymer for the same time of polymerization. However, it may be concluded that a large proportion of chains are still active.

In a similar experiment a 6.5 $\underline{M}$ solution of α-methylstyrene in THF initiated at 25°C with potassium was divided into two parts. Both of these ampoules were polymerized for 1 hr at 25°C. After 1 hr one of these (L-63) was opened and it yielded 2.85 base-mole/liter of polymer. The other was kept for 5 days in a bath set at 60°C. After this period the ampoule was removed from the bath and further polymerized at -25°C (L-64) instead of +25°C as was done earlier. The GPC chromatograms of these two polymers are shown in Fig. 13 and the results of their analysis are listed in Table 8. The main feature of Fig. 13 is the appearance of peak E at lower elution volume. From Table 8 it can be seen that [LE] associated with component E is very small and the polymer produced is large, leading to the formation of very high molecular weight species ($\overline{M}_w$(GPC) = 7.1 × 10^6). At this point it is impossible to determine from which of the four components D, A, B, and C these species originate. However one may safely conclude that species E propagate much more rapidly than all others and are probably different in nature.
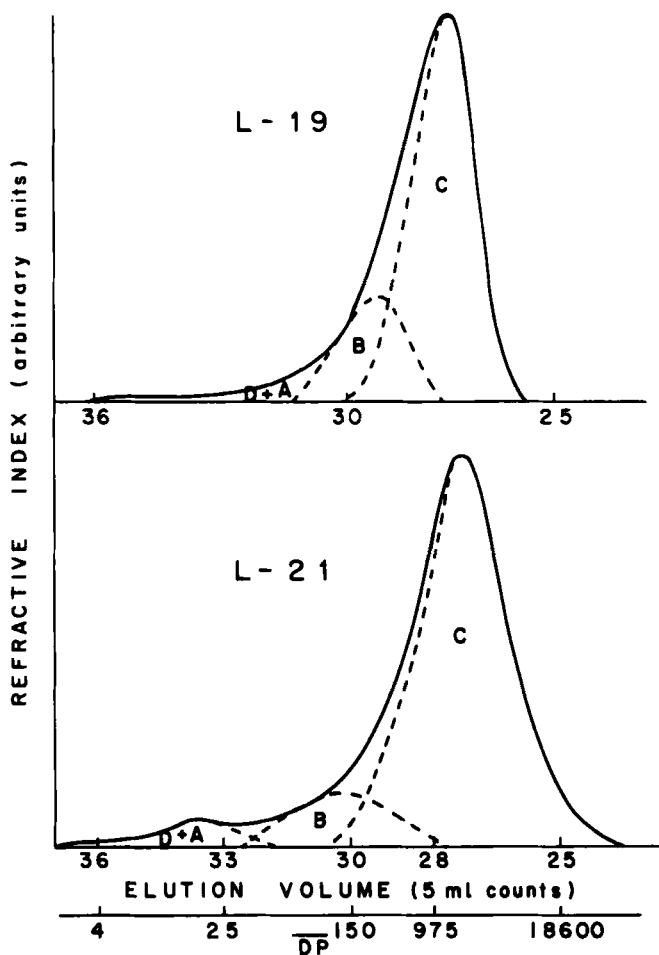
FIG. 12. GPC chromatograms of poly-α-methylstyrene initiated at 25° C; sample L-19 polymerized at 25° C for 2 hr, sample L-21 polymerized at 60° C for 5 days and further polymerized at 25° C for 2 hr. (See Table 8 for more data.)

In most of the cases we have considered up to now, initiation was carried out at 25° C and polymerization at higher temperature. It may be thought that the existence of multimodal distributions simply arises from the deactivation of active species at high temperature. In order to overcome this objection, a 4.5 $\underline{M}$ solution of α-methylstyrene

TABLE 8. GPC Analysis of Poly-α-methylstyrene Prepared under Various Conditions[a]

Series	No.	$[M]_0$ (mole/liter)	$[P]_e$ (base-mole/liter)				$[LE]$ (GPC) (mole/liter)				$\overline{M}_w \times 10^{-5}$ (GPC)	
			A+D	B	C	Total $[P]_e$	A+D	B	C	Total $[LE]$	B	C
X	L-19	6.0	0.31	1.09	3.70	5.10	0.03	0.01	0.008	0.05	0.35	1.8
	L-21	6.0	0.23	0.52	3.35	4.10	0.04	0.01	0.007	0.05	0.30	4.4
Y	L-63	6.5	0.92	0.42	1.51	2.85	0.13	0.005	0.003	0.14	0.30	1.9
	L-64	6.5	1.32	0.67 E=2.24	2.27	6.50	0.17	0.007 E=0.0001	0.003	0.18	0.40 71 (E)	3.2
Z	L-11	4.5	1.55	0.09	0.46	2.10	0.22	0.003	0.005	0.23	0.08	0.31
	L-12	4.5	1.73	0.42	0.55	2.70	0.26	0.01	0.005	0.28	0.10	0.33
	L-26	4.5	1.68		(1.32)	3.00	0.24		(0.01)	0.25	0.40	0.33
	L-27	4.5	1.52		(1.91)	3.43	0.23		(0.01)	0.24	0.80	0.33

[a]Series X: L-19, initiated at 25°C, polymerized at 25°C, polymerized at 25°C for 2 hr; L-21, initiated at 25°C, kept at 60°C for 5 days, polymerized at 25°C for 2 hr. Series Y: L-63, initiated at 25°C, polymerized at 25°C for 1 hr; L-64, initiated at 25°C, polymerized at 25°C for 1 hr, kept at 60°C for 5 days, polymerized at 25°C for 2 hr. Series Z: L-11, L-12, L-26, and L-27, initiated and polymerized at 40°C for 24 hr; L-11 opened at 40°C; L-12, L-26, and L-27 further polymerized at -25°C for 15, 30, and 60 min, respectively.
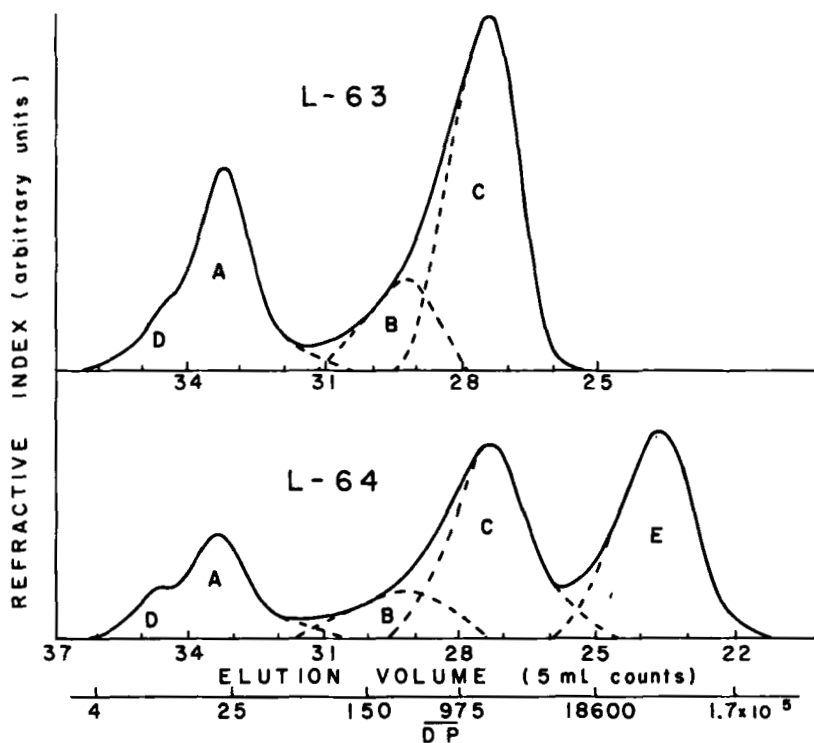
FIG. 13. GPC chromatograms of poly-α-methylstyrene initiated and polymerized at 25°C for 1 hr. One reaction was then terminated (sample L-63) and the other one (sample L-64) was kept at 60°C for 5 days and further polymerized at -25°C for 2 hr. (See Table 8 for more data.)

was initiated at 40°C and distributed in four ampoules. All of these were polymerized at 40°C. After 24 hr one of these (L-11) was opened at 40°C and the other three (L-12, L-26 and L-27) were further polymerized at -25°C for periods of 15, 30, and 60 min, respectively. The GPC chromatograms of these polymers are shown in Fig. 14. The analysis of these chromatograms with other relevant data is also presented in Table 8. One can see that, while the presence of a peak B in L-11 can be questioned, there is no doubt about the appearance of such a peak in L-12. This species
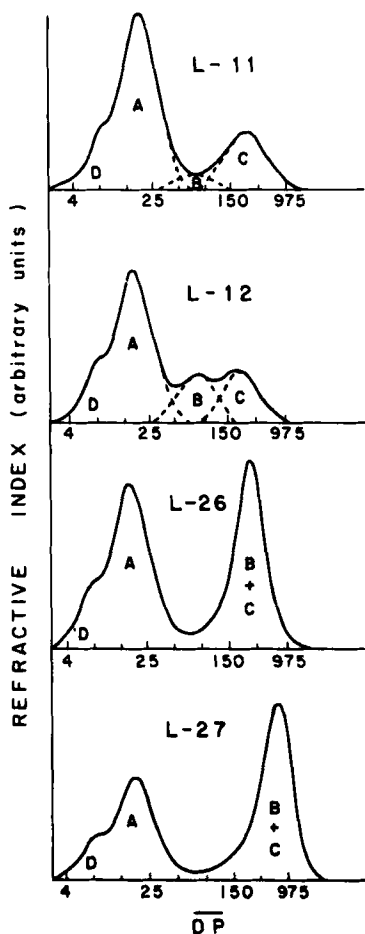
FIG. 14. GPC chromatograms of poly-α-methylstyrene initiated
and polymerized at 40°C; sample L-11 terminated at 40°C after 24
hr; samples L-12, L-26, and L-27 were further polymerized at -25°C
for 15, 30, and 60 min, respectively. (See Table 8 for other data.)

can originate only from the (D) and (A) species and grows much more
rapidly than all other species. In L-26 and L-27 component B has
merged with component C. If it is assumed that molecular weight of
component C remains practically unchanged at 3.3×10^4, then B varies
from 1.0×10^4 (L-12) to 8.0×10^4 (L-27) within 45 min.

CONCLUSION

Gel-permeation chromatograms show that, generally speaking, the anionic polymerization of α-methylstyrene in tetrahydrofuran at relative high temperature at high concentrations of living ends and monomer lead to multimodal distributions in the polymer. Such distributions can also be obtained at low temperature under certain experimental conditions (Figs. 13 and 14). Possible artefacts in the initiation stage cannot be invoked in order to explain multimodal distributions nor deactivation at high temperature although it occurs to a certain extent.

It is shown that low molecular weight polymer formed is not inactive. Part of this species is reactivated upon decreasing the temperature to yield high molecular weight polymer (Figs. 13 and 14). A thermodynamic treatment of this polymerization system also shows that the observed short chain effect is possible only if the short-chain polymer is active. This result is analogous to the one obtained by Glusker, Lysloff, and Stiles [22] for the anionic polymerization of methyl methacrylate. They found that 90% of the "living" species had an average molecular weight of 2000 and the remaining 10% a molecular weight of 27,000. This process was termed helical polymerization and was associated with the slow polymerization of oligomers retaining their cyclic structure.

Multimodal distribution may be explained through the presence of different species. In an attempt to identify these various species, component D may be associated with "dead" tetramer deactivated at the early stage of the polymerization. Component A always appears at the same elution volume corresponding to a $\overline{DP}$ of about 15 and reminds one of species sometimes encountered in living polymerization and described as dormant polymer [23].

Components B, C, and E might be correlated with various types of ion pairs. Recently bimodal distributions in polystyrene prepared in 3-methyltetrahydrofuran have been found and have been attributed to the presence of different ion pairs [24]. The rapid build-up of a high molecular weight peak at -25 C could be related to the presence of dissociated ions at low temperature.

Although the present data apply to polymerizations where the initial monomer concentration is high, the conclusion may not be extended to anionic bulk polymerization and more studies dealing with bulk and solution polymerizations are in progress in this laboratory.

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