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Polymerization of α-Methylstyrene with Potassium as Initiator. VII. Thermal Decomposition of the Reaction Products

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Polymerization of α-Methylstyrene with Potassium as Initiator. VII. Thermal Decomposition of the Reaction Products

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ABSTRACT

The polymerization of α-methylstyrene, initiated with high concentrations of potassium in tetrahydrofuran and in p-dioxane or with a butyllithium-tetramethylethylenediamine complex in bulk, was carried out at temperatures above 25°C. The resulting products comprising varying proportions of both low (D + A of $\overline{M}w = 2.0$ to 4.0×10^3) and high (B + C of $\overline{M}w > 20.0 \times 10^3$) molecular weight components were subjected to 50 min isothermal treatments at different temperatures. The poly-α-methylstyrene samples, prepared under the above mentioned solvent-conditions, which had similar proportions of components D + A and B + C, as characterized by gel permeation chromatography and nuclear magnetic resonance showed that their thermal stability decreased with the following order of solvent-conditions: Bulk > p-dioxane > THF. A comparison of the decomposition results obtained with polymers made up of

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components D + A and B + C and those made up exclusively of component B + C showed that the percent weight-loss and the decrease in molecular weight associated with the latter component B + C is more pronounced when the low molecular weight component D + A is present.

INTRODUCTION

The molecular weight distributions determined by gel-permeation chromatography (GPC) of poly-α-methylstyrene prepared from reactions initiated with potassium in tetrahydrofuran (THF) [1, 2], in p-dioxane [3], and in cyclohexane [4] were reported earlier. It was shown that, irrespective of the solvent used, the polymers prepared at temperatures above 25°C and with high concentrations of "living" ends [LE] have multimodal molecular weight distributions, which include all of the four components: D, A, B, and C where D denotes a dead polymer; A, a dormant polymer; and B and C, polymers which are due to different ion-pair mechanisms.

Nuclear magnetic resonance (NMR) studies [5, 6] of polymers made up of both low (D + A) and high (B + C) molecular weight components showed that the methyl and methylene protons associated with component D + A have lower τ values than those associated with component B + C. Furthermore, the propagation reactions responsible for the formation of components D + A and B + C obeyed Bernoullian statistics, the P_m value being somewhat higher for component D + A. Based on these studies [5, 6], it was concluded that though the reaction steps leading to the formation of component D + A in THF, in p-dioxane, and in cyclohexane were of a similar nature, they were none the less different from those responsible for the formation of component B + C.

With a view to exploring further the nature of component D + A, a study was undertaken on the thermal decomposition of polymers prepared under different solvent conditions and having varying proportions of this component. The principal results of this study are outlined in the following paragraphs.

EXPERIMENTAL

The data on the origin and purification of materials, mode of initiation and procedure of polymerization have been presented in detail elsewhere [1-4]. The characterization of the products by GPC [1-4], NMR [5, 6], and thermogravimetry [7] was carried out

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as previously reported, with the exception that 10-mg samples of polymer were taken for each thermal treatment. The intensity of the triads mm, mr, and rr associated with components B + C, were made on the basis of their τ values presented in the literature [8-10].

RESULTS AND DISCUSSION

Decomposition of Poly-α-methylstyrene with Similar Contents of Component D + A

Polymers Prepared under Identical Initiator but Different Solvent Conditions

In Fig. 1 are shown normalized GPC molecular weight distributions of a poly-α-methylstyrene (sample L-11), prepared at 40°C in THF from a 4.5 M solution of monomer with potassium as the initiator, subjected to 50 min isothermal treatments at various temperatures. The analytical data obtained from the curves shown in Fig. 1 are summarized in Table 1, which also includes data on the percent total weight loss of the samples at various temperatures. The data on the residual weight associated with the GPC-characterized components D + A and B + C show that on subsequent thermal treatments the two components of the original polymer (L-11-0) appear to decompose independently of each other. These results agree well with those reported by Roestamsjah et al. [11] in their degradation study of mixtures of quasi-monodisperse poly-α-methylstyrenes. The molecular weights, $\overline{M}_w$ and $\overline{M}_n$, of component D + A remain unchanged, while those of component B + C decrease in a general manner with the treatment temperature. The polydispersity ratio $\overline{M}_w/\overline{M}_n$ remains constant at 1.2 for component D + A and within ± 0.1 of 1.2 for component B + C.

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In Fig. 2 are shown NMR spectra (L-11-3 to L-11-7) of decomposed poly-α-methylstyrene. A summary of the analytical data obtained from these spectra, in terms of the methyl proton intensity of the low (D + A) and the high (B + C) molecular weight components as well as the associated changes in their P_m values following thermal treatment at different temperatures is presented in Table 2. The P_m values of component D + A calculated from mm (8.6-8.75 τ), mr (8.75-9.05 τ) and rr (9.05-9.3 τ) triads decrease, whereas those of component B + C calculated from the mm (9.0 τ), mr (9.45 τ), and rr (9.69 τ) triads remain constant following thermal treatment at successively higher temperatures. This indicates that parts of component D + A, having higher initial P_m values, decompose earlier

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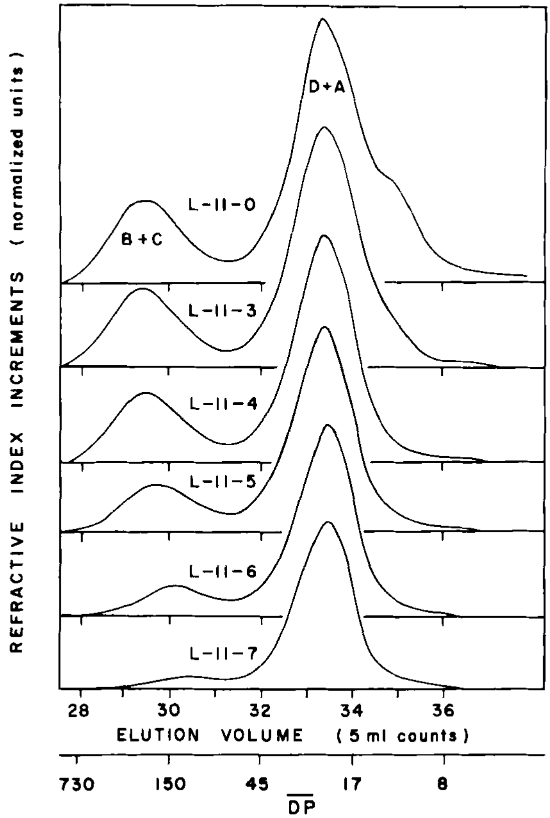

FIG. 1. GPC molecular weight distributions of poly-α-methylstyrene (sample L-11) subjected to 50 min isothermal treatments at various temperatures. See Table 1 for other data.

than those with lower P_m values. The residual weights associated with the NMR characterized components D + A and B + C, both before and after the thermal treatments, also decrease regularly with increasing temperature.

In Fig. 3 are shown normalized molecular weight distributions of poly-α-methylstyrene (sample L-6), prepared at 40°C in p-dioxane from a 4.2 M solution of monomer with potassium as the initiator, subjected to 50 min isothermal treatments at various temperatures. In Table 3 are presented the analytical data derived from the curves presented in Fig. 3. The data on the residual weight associated with

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TABLE 1. Isothermal Decomposition of Poly-α-methylstyrene at Various Temperatures: Sample L-11 Initiated with Potassium in THF and Polymerized at 40°C

Sample	Temperature of decomposition (°C)	True weight loss (%)	Residual weight (mg)		Molecular weight × 10^{-3} (GPC)					
					D + A			B + C		
			D + A	B + C	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
L-11-0	25	0	7.7	2.3	2.5	2.1	1.2	26.8	19.5	1.4
L-11-1	150	4.7	7.3	2.2	2.6	2.2	1.2	27.2	19.4	1.4
L-11-2	210	11.0	6.7	2.2	2.7	2.3	1.2	27.4	19.9	1.4
L-11-3	230	15.0	6.4	2.1	2.8	2.4	1.2	28.4	20.5	1.4
L-11-4	275	25.5	5.5	1.9	2.9	2.5	1.2	26.5	18.7	1.4
L-11-5	290	38.5	4.9	1.3	2.9	2.5	1.2	23.2	17.1	1.3
L-11-6	300	48.0	4.4	0.8	2.9	2.5	1.2	17.2	13.2	1.3
L-11-7	307	59.0	3.8	0.3	2.9	2.5	1.2	14.1	11.5	1.2

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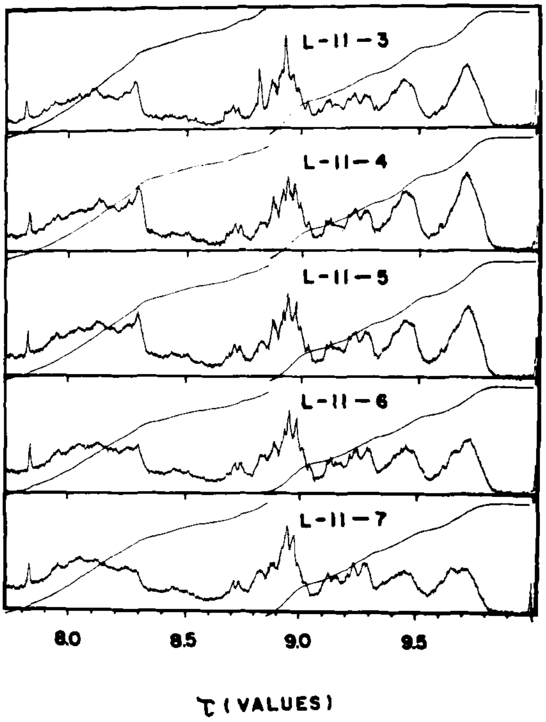

FIG. 2. NMR spectra of decomposed poly-α-methylstyrene (samples L-11-3 to L-11-7). See Tables 1 and 2 for other data.

the GPC-characterized components D + A and B + C show that on subsequent thermal treatments of the original polymer (L-6-0), the two components, as in the case of sample L-11-0, decompose independently of each other. Once again, the polydispersity of component D + A remains unchanged at 1.2, regardless of the treatment temperature; that for the component B + C remains within ± 0.1 of 1.2.

In Fig. 4 are shown NMR spectra (L-6-1 to L-6-5) of decomposed poly-α-methylstyrene. Analytical data, reported in terms of the methyl proton intensity of components D + A and B + C as well as the P_m value changes after thermal treatment at increasing temperatures, are presented in Table 4. The P_m values of component D + A

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TABLE 2. Intensity of the Methyl Protons of Low (D + A) and High (B + C) Molecular Weight Components of Sample L-11 and Associated Changes in P_m values on Thermal Decomposition at Various Temperatures[a]

	D + A					B + C				
	Intensity associated with various configurations					Intensity associated with various configurations				
Sample	mm (8.6-(8.75 τ)	mr (8.75-9.05 τ)	rr (9.05-9.3 τ)	$\sim P_m$	Residual weight (mg)	mm (9.0 τ)	mr (9.45 τ)	rr (9.69 τ)	$\sim P_m$	Residual weight (mg)
L-11-0	0.14	0.51	0.35	0.39	5.5	0.07	0.40	0.53	0.27	4.5
L-11-3	0.14	0.52	0.34	0.39	4.6	0.07	0.40	0.53	0.27	3.9
L-11-4	0.13	0.49	0.38	0.38	3.7	0.07	0.40	0.53	0.27	3.8
L-11-5	0.13	0.49	0.38	0.38	3.1	0.08	0.41	0.51	0.28	3.0
L-11-6	0.11	0.51	0.38	0.36	2.9	0.08	0.40	0.52	0.28	2.3
L-11-7	0.11	0.50	0.39	0.35	2.5	0.08	0.42	0.50	0.28	1.6

[a] See Table 1 for other data.

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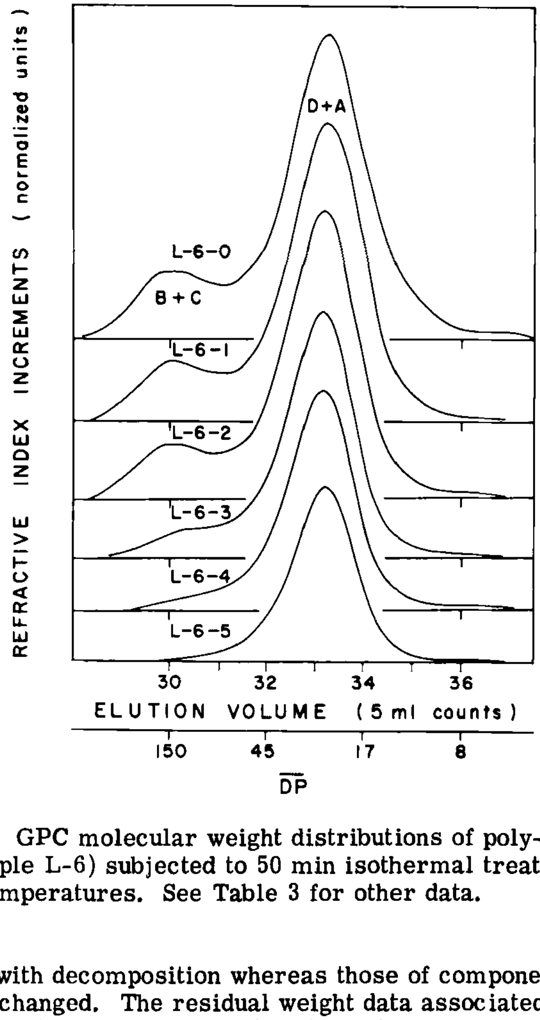

FIG. 3. GPC molecular weight distributions of poly-α-methylstyrene (sample L-6) subjected to 50 min isothermal treatments at various temperatures. See Table 3 for other data.

decrease with decomposition whereas those of component B + C remain unchanged. The residual weight data associated with the NMR characterized components D + A and B + C show regularly decreasing trends with increasing temperature.

Polymers Prepared under Different Solvent and Initiator Conditions

In an earlier publication related to the decomposition of poly-α-methylstyrene [7], it was observed that two polymer samples, viz., M-14 ($\overline{M}_w = 3.7 \times 10^3$, $\overline{M}_n = 1.2 \times 10^3$) and B ($\overline{M}_w = 4.0 \times 10^3$, $\overline{M}_n = 1.4 \times 10^3$) having similar molecular weights, yielded different

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TABLE 3. Isothermal Decomposition of Poly-α-methylstyrene at Various Temperatures: Sample L-6 Initiated with Potassium in p-Dioxane and Polymerized at 40°C

Sample	Temperature of decomposition (°C)	True weight loss (%)	Residual weight (mg)		Molecular weight × 10^{-3} (GPC)					
					D + A			B + C		
			D + A	B + C	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
L-6-0	25	0	8.3	1.7	3.2	2.6	1.2	18.7	14.6	1.3
L-6-1	250	9.7	7.6	1.5	3.3	2.7	1.2	18.0	14.4	1.3
L-6-2	275	15.7	7.1	1.3	3.5	2.9	1.2	18.1	14.3	1.3
L-6-3	300	36.1	5.7	0.7	3.5	2.9	1.2	14.1	11.5	1.2
L-6-4	308	46.7	5.0	0.3	3.5	2.9	1.2	12.3	10.6	1.2
L-6-5	316	60.0	4.0	0.0	3.4	2.8	1.2	-	-	-

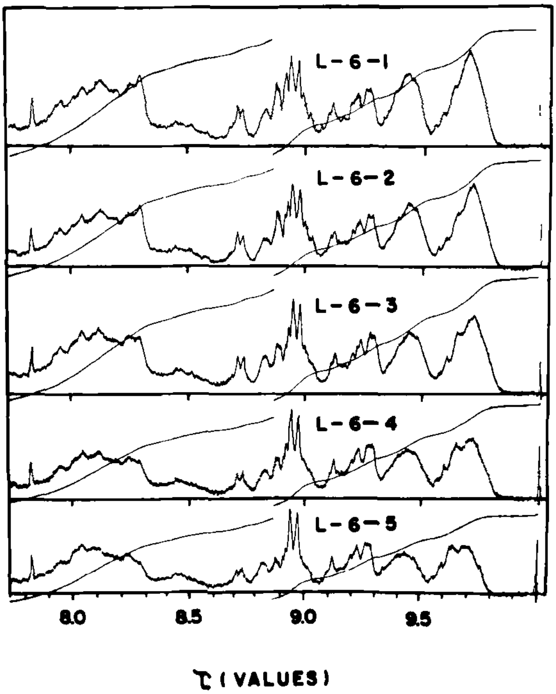

FIG. 4. NMR spectra of decomposed poly-α-methylstyrene (samples L-6-1 to L-6-5). See Tables 3 and 4 for other data.

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weight losses on thermal decomposition at identical temperatures and periods of exposure, the former polymer being more stable than the latter. The mechanism of decomposition in both polymers was that of depolymerization as was indicated by the constant molecular weight data obtained both before and after decomposition [7]. The normalized molecular weight distributions of M-14 are shown in Fig. 5 where, after each thermal treatment, the GPC maxima lie at more or less the same elution volumes, thus supporting the mechanism of decomposition proposed in the earlier work [7]. Polymer M-14 was prepared at 50°C in bulk with a butyllithium-tetramethylethylenediamine complex (BuLi-TMEDA) as initiator. The reaction yielded a product with a P_m value of 0.29 for the NMR characterized component D + A and 0.22 for component B + C. Sample B, on the other hand, was prepared at 25°C in p-dioxane with potassium as the initiator. The polymer product showed a P_m value of 0.34 for the

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TABLE 4. Intensity of Methyl Protons of Components (D + A) and (B + C) of Sample L-6 and Associated Changes in P_m Values on Thermal Decomposition at Various Temperatures[a]

	D + A					B + C				
	Intensity of various configurations				Residual weight (mg)	Intensity of various configurations				Residual weight (mg)
Sample	mm	mr	rr	$\sim P_m$		mm	mr	rr	$\sim P_m$	
L-6-0	0.13	0.51	0.36	0.38	5.3	0.08	0.39	0.53	0.27	4.7
L-6-1	0.14	0.46	0.40	0.37	4.3	0.07	0.39	0.54	0.27	4.7
L-6-2	0.14	0.45	0.41	0.37	3.9	0.08	0.39	0.53	0.27	4.5
L-6-3	0.13	0.43	0.44	0.34	3.0	0.07	0.40	0.53	0.27	3.4
L-6-4	0.11	0.46	0.43	0.34	2.6	0.08	0.40	0.52	0.28	2.7
L-6-5	0.12	0.45	0.43	0.34	2.2	0.08	0.40	0.52	0.28	1.8

[a] See Table 3 for other data.

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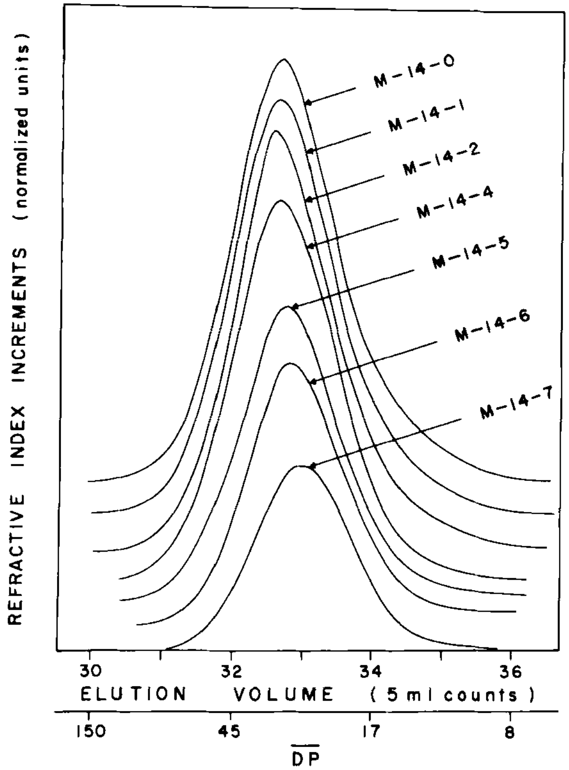

FIG. 5. GPC molecular weight distributions of poly-α-methylstyrene (sample M-14) subjected to 50 min isothermal treatments at various temperatures. See Table 5 for other data.

NMR-characterized component D + A and 0.26 for component B + C. Based on these observations one is tempted to conclude that because of the difference in the P_m values of components D + A and B + C in polymers M-14 and B these decompose differently. This, however, may not be entirely true as is shown by the P_m value data obtained on the decomposition of sample M-14 (Fig. 6 and Table 5). Components D + A (P_m = 0.29) and B + C (P_m = 0.22) of sample M-14 would appear to decompose in a more or less similar fashion.

Another hypothesis which may be put forth to explain the differences in the decomposition of the M-14 and B polymers could have its origin in the different initiators used for the preparation of these

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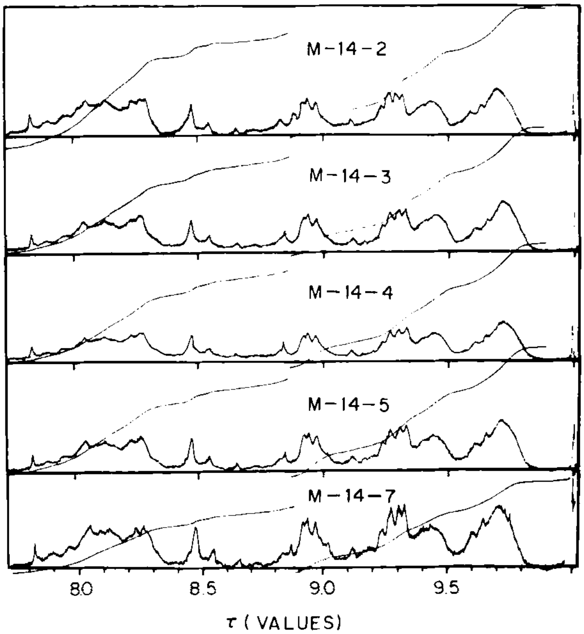

FIG. 6. NMR spectra of decomposed poly-α-methylstyrene (samples M-14-2 to M-14-7). See Table 5 for other data.

polymers. Cowie and Bywater [12] demonstrated, however, that during the thermal breakdown of poly-α-methylstyrene, samples prepared with BuLi or sodium naphthalene yielded similar results, indicating that the nature of the catalyst did not influence the decomposition process. It would appear then that it is the nature of the solvent in which a polymer is prepared which has some influence on its thermal decomposition.

Figure 7, obtained by using the data listed in Tables 1 to 5, shows the percent weight loss in polymers L-11, L-6, M-14 and B as a function of the treatment temperature. If one defines the stability of polymers solely on the basis of the total weight loss, the polymers prepared in different solvents, in the present study, obey the following order of thermal stability: polymers prepared in bulk are more stable than those prepared in p-dioxane, which in turn are more stable (bulk > p-dioxane > THF) than those prepared in THF.

In Fig. 8 are shown the residual weights of NMR-characterized components D + A and B + C of samples M-14, L-6, and L-11 as a function of the treatment temperature. The order of stability

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TABLE 5. Intensity of Methyl Protons of Components (D + A) and (B + C) of Sample M-14 and Associated Changes in P_m Values on Thermal Decomposition at Various Temperatures

		D + A					B + C				
		Intensity associated with various configurations					Intensity associated with various configurations				
Sample	Temperature of decomposition (°C)	mm	mr	rr	$\sim P_m$	Residual weight (mg)	mm	mr	rr	$\sim P_m$	Residual weight (mg)
M-14-0	25	0.08	0.41	0.51	0.29	4.9	0.05	0.34	0.61	0.22	5.1
M-14-2	275	0.06	0.39	0.55	0.26	4.4	0.05	0.35	0.60	0.23	5.0
M-14-3	285	0.07	0.39	0.54	0.26	4.3	0.05	0.36	0.59	0.23	5.0
M-14-4	300	0.08	0.40	0.52	0.28	3.9	0.05	0.36	0.59	0.23	4.7
M-14-5	315	0.07	0.40	0.53	0.26	3.0	0.05	0.36	0.59	0.23	3.4
M-14-7	325	0.08	0.37	0.55	0.26	1.9	0.05	0.36	0.59	0.23	2.0

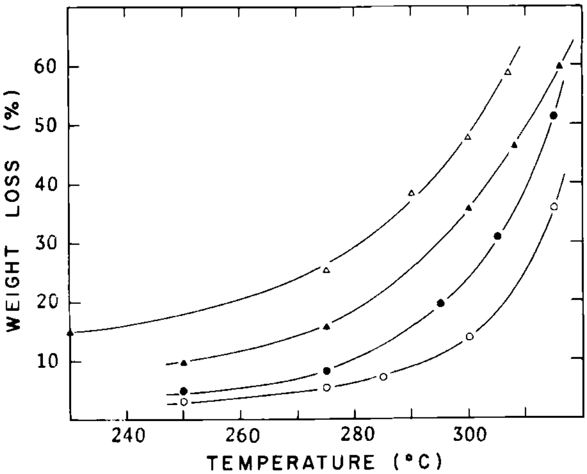

FIG. 7. Weight loss as a function of decomposition temperature for four samples of poly-α-methylstyrene: (△) L-11; (▲) L-6, (●) B; (O) M-14. See Tables 1 to 5 for other data.

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for component D + A in samples M-14, L-6, and L-11 is: bulk > p-dioxane = THF, whereas that for component B + C is: bulk ≫ p-dioxane ≫ THF.

Decomposition of Polymers with Different Contents of Component D + A

In an earlier study on the decomposition of a high molecular weight polystyrene in the presence of low molecular weight poly glycols [13], it was observed that weight losses as well as changes in the molecular weight distributions of the polystyrene were very pronounced when compared to the results obtained in the absence of polyglycols. This was attributed to the presence of large amounts of low molecular weight active fragments arising out of the decomposition of polyglycols. Thus, it was thought of interest to study the influence of low molecular weight component D + A on the decomposition of the high molecular weight component B + C in polymers prepared in THF with varying proportions of the two components. It should be mentioned immediately that in the work of Roestamsjah et al. [11] on the thermal decomposition of mixtures of high molecular weight ($\overline{M}_w = 10^5$-10^6) poly-α-methylstyrenes, it was shown that

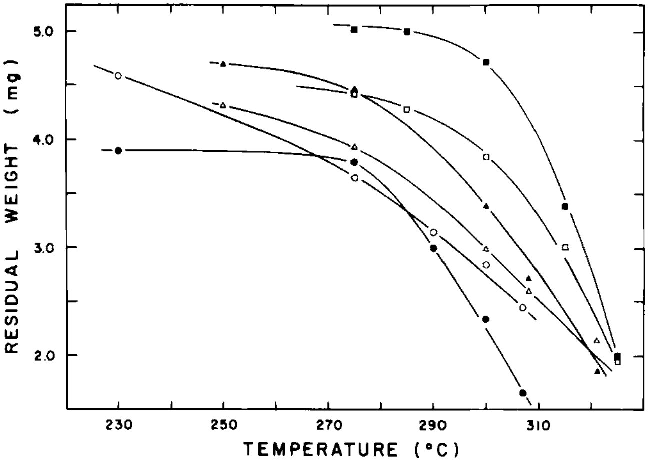

FIG. 8. Residual weight associated with the NMR characterized components D + A and B + C of three poly-α-methylstyrene samples, as a function of the temperature of decomposition: (■) M-14 (B + C); (□) M-14 (D + A); (▲) L-6 (B + C); (△) L-6 (D + A); (●) L-11 (B + C); ( ) L-11 (D + A). See Tables 1 to 5 for other data.

the lower molecular weight component ($\overline{M}_w = 10^5$) of the mixture had no influence on the decomposition of the higher molecular weight component ($\overline{M}_w = 10^6$).

Four poly-α-methylstyrene samples: 65-B, 67, 68, and 66 were subjected to 50-min isothermal treatments at various temperatures, and the residual decomposed products were analyzed by GPC (see Figs. 9, 11, 13, 15, and 17 and Tables 6, 8, 10, and 12) and NMR (see Figs. 10, 12, 14, 16, and 18 and Tables 7, 9, 11, and 13).

In Fig. 9 are shown normalized GPC molecular weight distributions of a poly-α-methylstyrene (sample 65-B), composed of 63% of component D + A ($\overline{M}_w = 2.2 \times 10^3$) and 37% of component B + C ($\overline{M}_w = 64.4 \times 10^3$), which was subjected to 50-min isothermal treatments carried out at various temperatures. The analyses of the curves shown in Fig. 9 and expressed in terms of true weight loss, residual weights, and molecular weights of GPC-characterized components D + A and B + C, are presented in Table 6. A comparison of these results with those obtained during the decomposition of poly-α-methylstyrene (sample L-45; $\overline{M}_w = 60 \times 10^3$) [7] revealed that, following thermal treatments at 235, 275, 288, 294 and 301°C

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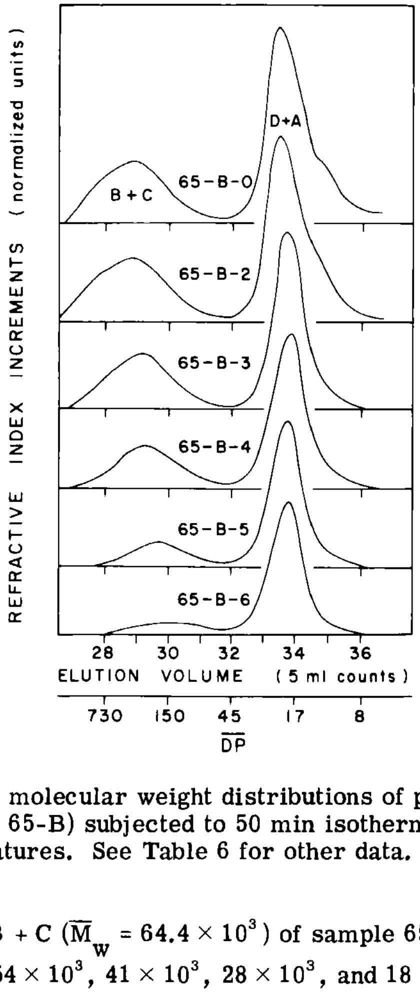

FIG. 9. GPC molecular weight distributions of poly-α-methylstyrene (sample 65-B) subjected to 50 min isothermal treatments at various temperatures. See Table 6 for other data.

for component B + C ($\overline{M}_w = 64.4 \times 10^3$) of sample 65-B, the $\overline{M}_w$ values were 67×10^3, 54×10^3, 41×10^3, 28×10^3, and 18×10^3, respectively, whereas for the same five temperatures in the case of sample L-45 the corresponding $\overline{M}_w$ values were 63×10^3, 63×10^3, 53×10^3, 51×10^3, and 47×10^3, respectively. The $\overline{M}_w/\overline{M}_n$ values of component B + C of sample 65-B decreased from 2.2 (curve 65-B-0) to 1.4 (curve 65-B-6).

In Fig. 10 are shown NMR spectra (65-B-2 to 65-B-6) of decomposed poly-α-methylstyrene, and in Table 7 the analytical data derived from these spectra are summarized. The residual weight data associated with components D + A and B + C show that these components decompose regularly, the P_m values of the former (D + A) decreasing

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TABLE 6. Isothermal Decomposition of Poly-α-methylstyrene at Various Temperatures: Sample 65-B Initiated with Potassium in THF and Polymerized at 55°C

Sample	Temperature of decomposition (°C)	True weight loss (%)	Residual weight (mg)		Molecular weight × 10^{-3} (GPC)					
					D + A			B + C		
			D + A	B + C	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
65-B-0	25	0	6.3	3.7	2.2	1.9	1.1	64.4	29.5	2.2
65-B-1	150	2.2	6.0	3.7	2.2	2.0	1.1	61.7	27.9	2.2
65-B-2	235	8.6	5.5	3.6	2.4	2.1	1.1	67.2	29.5	2.3
65-B-3	275	22.3	4.8	3.0	2.4	2.2	1.1	54.3	27.0	2.0
65-B-4	288	34.0	4.6	2.0	2.4	2.2	1.1	41.3	23.3	1.8
65-B-5	294	47.8	4.1	1.1	2.5	2.2	1.1	27.5	18.3	1.5
65-B-6	301	59.0	3.4	0.7	2.6	2.3	1.1	18.1	12.9	1.4

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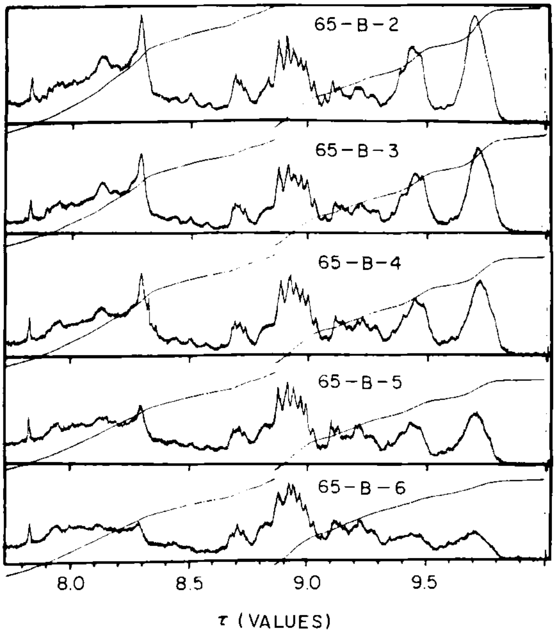

FIG. 10. NMR spectra of decomposed poly-α-methylstyrene (samples 65-B-2 to 65-B-6). See Tables 6 and 7 for other data.

and that of the latter (B + C) increasing with increasing treatment temperature.

In Fig. 11 are shown normalized GPC molecular weight distributions of a poly-α-methylstyrene (sample 67), composed of 58% of component D + A ($\overline{M}_w = 2.8 \times 10^3$) and 42% of component B + C ($\overline{M}_w = 44.2 \times 10^3$), subjected to 50-min isothermal treatments carried out at various temperatures. The analyses of the curves shown in Fig. 11 and expressed in terms of true weight loss, residual weights, and molecular weights of GPC-characterized components D + A and B + C are presented in Table 8. A comparison of these results with those obtained during the decomposition of poly-α-methylstyrene (sample M-3; $\overline{M}_w = 41 \times 10^3$) [7] reveals that on thermal treatment at 200, 250, 275, 288, and 295°C for component B + C ($\overline{M}_w = 44 \times 10^3$) of sample 67, the $\overline{M}_w$ values were 43×10^3, 42×10^3, 39×10^3, 30×10^3, and 24×10^3, respectively, whereas for the same five temperatures in the case of M-3 the $\overline{M}_w$ values were 41×10^3, 41×10^3,

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TABLE 7. Intensity of Methyl Protons of Components (D + A) and (B + C) of Sample 65-B and Associated Changes in P_m Values on Thermal Decomposition at Various Temperatures[a]

	D + A					B + C				
	Intensity of various configurations					Intensity of various configurations				
Sample	mm	mr	rr	$\sim P_m$	Residual weight (mg)	mm	mr	rr	$\sim P_m$	Residual weight (mg)
65-B-0	0.19	0.51	0.30	0.45	5.2	0.08	0.40	0.52	0.28	4.8
65-B-2	0.17	0.53	0.30	0.43	4.5	0.07	0.40	0.53	0.27	4.7
65-B-3	0.18	0.50	0.32	0.43	3.9	0.07	0.39	0.54	0.26	3.9
65-B-4	0.16	0.54	0.30	0.42	3.6	0.08	0.40	0.52	0.28	3.0
65-B-5	0.16	0.52	0.32	0.42	3.2	0.09	0.42	0.49	0.30	2.0
65-B-6	0.16	0.52	0.32	0.42	2.8	0.10	0.43	0.47	0.32	1.3

[a] *See Table 6 for other data.*

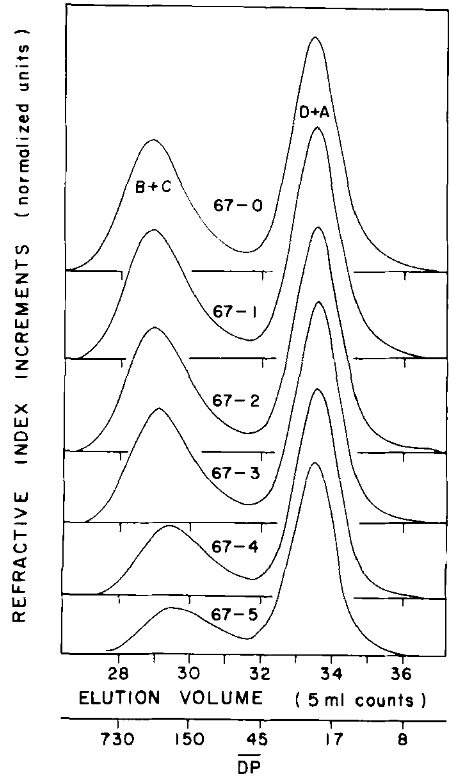

FIG. 11. GPC molecular weight distributions of poly-α-methylstyrene (sample 67) subjected to 50 min isothermal treatments at various temperatures. See Table 8 for other data.

39×10^3, 39×10^3, and 39×10^3, respectively. The $\overline{M}_w/\overline{M}_n$ values of component B + C in sample 67 remained within ± 0.1 of 1.7.

In Fig. 12 are shown NMR spectra (67-2 to 67-5) of decomposed poly-α-methylstyrene. Their analyses in terms of residual weights of NMR-characterized components D + A and B + C and the P_m values associated with these are presented in Table 9. A comparison of the results of 65-B (52% of NMR characterized D + A component) with those of sample 67 (44% of NMR characterized D + A component) shows that component D + A is relatively more stable in sample 67. The P_m values of components D + A and B + C in sample 67 remained constant at all temperatures of decomposition.

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TABLE 8. Isothermal Decomposition of Poly-α-methylstyrene at Various Temperatures: Sample 67 Initiated with Potassium in THF and Polymerized at 55°C

Sample	Temperature of decomposition (°C)	True weight loss (%)	Residual weight (mg)		Molecular weight × 10^{-3} (GPC)					
					D + A			B + C		
			D + A	B + C	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
67-0	25	0	5.8	4.2	2.8	2.4	1.1	44.2	24.9	1.8
67-1	200	5.7	5.4	4.0	2.8	2.4	1.1	42.5	24.9	1.7
67-2	250	9.3	5.1	3.9	2.8	2.4	1.1	41.8	24.0	1.7
67-3	275	15.5	4.9	3.6	2.8	2.5	1.1	38.9	22.9	1.7
67-4	288	31.0	4.6	2.3	2.8	2.5	1.1	29.5	18.0	1.6
67-5	295	42.0	4.2	1.6	2.9	2.6	1.1	24.2	15.0	1.6

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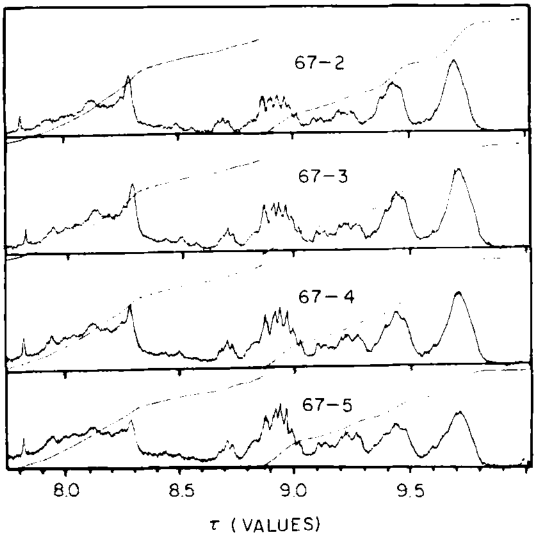

FIG. 12. NMR spectra of decomposed poly-α-methylstyrene (samples 67-2 to 67-5). See Tables 8 and 9 for other data.

In Fig. 13 are shown normalized GPC molecular weight distributions of a poly-α-methylstyrene (sample 68), composed of 36% of component D + A ($\overline{M}_w = 2.8 \times 10^3$) and 64% of component B + C ($\overline{M}_w = 131.6 \times 10^3$), subjected to isothermal treatments at different temperatures. The analyses of the curves shown in Fig. 13 is summarized in Table 10. A comparision of these results with those obtained in the case of poly-α-methylstyrene (sample L-19; $\overline{M}_w = 1.27 \times 10^3$) [7] shows that, on thermal treatments at 250, 275, 282, 288, and 295°C for component B + C of sample 68, the $\overline{M}_w$ values were 129×10^3, 103×10^3, 72×10^3, 49×10^3, and 31×10^3, respectively, whereas in sample L-19 for the same five temperatures the corresponding $\overline{M}_w$ values were 118×10^3, 107×10^3, 105×10^3, 103×10^3, and 100×10^3, respectively. The $\overline{M}_w/\overline{M}_n$ values of component B + C of sample 68 drop from 2.7 (curve 68-0) to 1.5 (curve 68-6).

In Fig. 14 are shown NMR spectra (68-2 to 68-6) of decomposed poly-α-methylstyrene. The analysis of these spectra expressed in terms of residual weights of NMR characterized components D + A and B + C and the P_m values associated with these components are summarized in Table 11. The results reveal that the high molecular weight component B + C contributes a major proportion of the weight

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TABLE 9. Intensity of Methyl Protons of Components (D + A) and (B + C) of Sample 67 and Associated Changes in P_m Values on Thermal Decomposition at Various Temperatures[a]

	D + A					B + C				
	Intensity of various configurations					Intensity of various configurations				
Sample	mm	mr	rr	$\sim P_m$	Residual weight (mg)	mm	mr	rr	$\sim P_m$	Residual weight (mg)
67-0	0.17	0.47	0.36	0.40	4.4	0.07	0.39	0.54	0.27	5.6
67-2	0.16	0.49	0.35	0.40	3.7	0.07	0.38	0.55	0.26	5.3
67-3	0.15	0.51	0.34	0.40	3.7	0.07	0.38	0.55	0.26	4.7
67-4	0.16	0.49	0.35	0.40	3.3	0.07	0.39	0.54	0.26	3.6
67-5	0.14	0.50	0.36	0.40	3.1	0.07	0.40	0.53	0.27	2.7

[a] See Table 8 for other data.

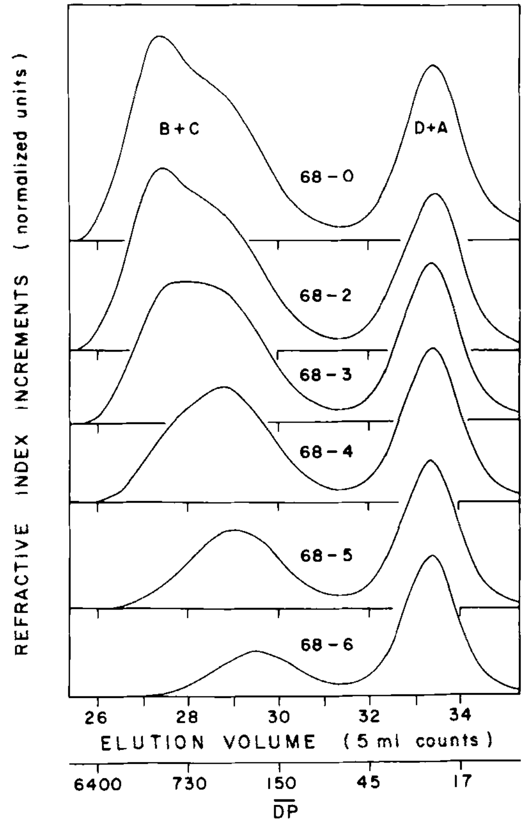

FIG. 13. GPC molecular weight distributions of poly-α-methylstyrene (sample 68) subjected to 50 min isothermal treatments at various temperatures. See Table 10 for other data.

loss and the P_m values of the two components do not change on decomposition.

In Fig. 15 are shown normalized GPC molecular weight distributions of a poly-α-methylstyrene (sample 66), composed of 26% of component D + A ($\overline{M}_w = 2.4 \times 10^3$) and 74% of component B + C ($\overline{M}_w = 214 \times 10^3$), subjected to 50-min isothermal treatments at various temperatures. The analyses of the curves shown in Fig. 15 and expressed in terms of true weight loss, residual weights, and molecular weights of GPC characterized components D + A and B + C are summarized in Table 12. A comparison of these results with

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TABLE 10. Isothermal Decomposition of Poly-α-methylstyrene at Various Temperatures: Sample 68 Initiated with Potassium in THF and Polymerized at 55°C

Sample	Temperature of decomposition (°C)	True weight loss (%)	Residual weight (mg)		Molecular weight × 10^{-3} (GPC)					
					D + A			B + C		
			D + A	B + C	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
68-0	25	0	3.6	6.4	2.8	2.4	1.1	131.6	48.6	2.7
68-1	170	6.8	3.3	6.0	2.7	2.4	1.1	130.0	49.0	2.6
68-2	250	9.8	3.1	5.9	2.8	2.5	1.1	128.8	49.4	2.6
68-3	275	21.0	3.0	4.9	2.9	2.6	1.1	103.3	42.0	2.5
68-4	282	35.5	2.9	3.6	2.8	2.5	1.1	72.0	33.2	2.2
68-5	288	49.0	2.8	2.3	2.9	2.6	1.1	49.4	25.8	1.9
68-6	295	64.0	2.5	1.1	2.9	2.6	1.1	30.7	20.0	1.5

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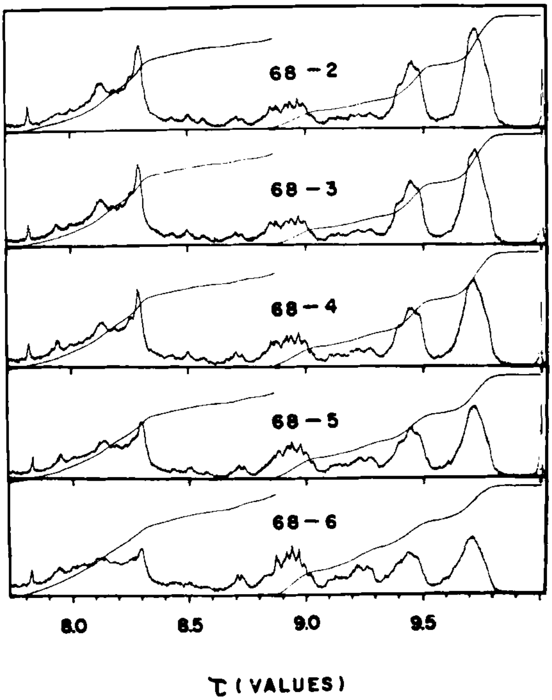

FIG. 14. NMR spectra of decomposed poly-α-methylstyrene (samples 68-2 to 68-6). See Tables 10 and 11 for other data.

those obtained in the case of poly-α-methylstyrene (sample 3; $\overline{M}_w$ = 198 × 10^3) [7] reveals that, on thermal treatment at 250, 265, 278, 285, and 292°C, the $\overline{M}_w$ values for component B + C were 197 × 10^3, 203 × 10^3, 172 × 10^3, 146 × 10^3, and 97 × 10^3, respectively, whereas in the case of sample 3 for the same five temperatures the $\overline{M}_w$ values were 194 × 10^3, 190 × 10^3, 185 × 10^3, 180 × 10^3, and 170 × 10^3, respectively. The $\overline{M}_w/\overline{M}_n$ values of component B + C of sample 66 remain within ± 0.1 of 2.9.

From the results of the data derived from Figs. 9-15 and listed in Tables 6-12 a few very interesting observations can be made. The decrease in $\overline{M}_w$ and $\overline{M}_n$ of component B + C is very pronounced in the presence of component D + A. Furthermore, the $\overline{M}_w/\overline{M}_n$ values of component B + C decrease in general with increasing temperature of decomposition. The values, however, do not show a clear tendency

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TABLE 11. Intensity of Methyl Protons of Components (D + A) and (B + C) of Sample 68 and Associated Changes in P_m Values on Thermal Decomposition at Various Temperatures[a]

	D + A					B + C				
	Intensity of various configurations					Intensity of various configurations				
Sample	mm	mr	rr	$\sim P_m$	Residual weight (mg)	mm	mr	rr	$\sim P_m$	Residual weight (mg)
68-0	0.15	0.47	0.38	0.38	2.6	0.07	0.39	0.54	0.26	7.4
68-2	0.12	0.51	0.37	0.38	2.3	0.06	0.38	0.56	0.25	6.8
68-3	0.15	0.48	0.38	0.38	2.2	0.06	0.38	0.56	0.25	5.7
68-4	0.15	0.47	0.38	0.38	2.1	0.06	0.38	0.56	0.25	4.4
68-5	0.14	0.48	0.38	0.38	1.9	0.07	0.38	0.55	0.26	3.2
68-6	0.14	0.48	0.38	0.38	1.7	0.07	0.39	0.54	0.26	1.9

[a] See Table 10 for other data.

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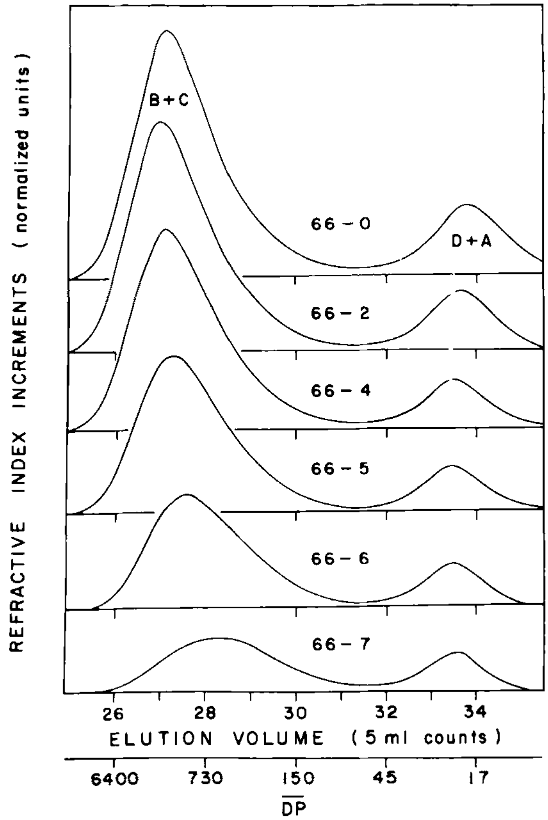

FIG. 15. GPC molecular weight distributions of poly-α-methylstyrene (sample 66) subjected to 50 min isothermal treatments at various temperatures. See Table 12 for other data.

towards approaching an $\overline{M}_w/\overline{M}_n$ value of 2, which is the theoretically calculated value for decompositions involving free-radical chain depropagation and termination (by disproportionation) [14, 15]. Roestamsjah et al. [11] have shown that the approach to $\overline{M}_w/\overline{M}_n$ values of 2 is not always monotonic and that values as low as 1.37 are reached before the ratio begins to rise towards 2. In the present study, the $\overline{M}_w/\overline{M}_n$ ratios in the case of polymers 67 and 68 did indeed approach the critical value of 1.37, but they never rose to a value of 2 thereafter. It must be mentioned here that the theoretical calculations of Boyd et al. [13] and the experimental data of Roestamsjah

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TABLE 12. Isothermal Decomposition of Poly-α-methylstyrene at Various Temperatures: Sample 66 Initiated with Potassium in THF and Polymerized at 55° C

Sample	Temperature of decomposition (°C)	True weight loss (%)	Residual weight (mg)		Molecular weight × 10^{-3} (GPC)					
					D + A			B + C		
			D + A	B + C	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
66-0	25	0	2.6	7.4	2.4	2.0	1.2	214.0	71.8	3.0
66-1	170	6.8	1.8	7.4	2.4	2.1	1.15	215.4	74.0	2.9
66-2	210	10.0	1.6	7.4	2.4	2.1	1.1	208.2	74.0	2.8
66-3	250	16.3	1.4	6.9	2.4	2.2	1.1	197.4	76.0	2.6
66-4	265	20.2	1.3	6.8	2.6	2.3	1.1	203.0	70.2	2.9
66-5	278	31.2	1.3	5.6	2.7	2.4	1.1	171.8	61.2	2.8
66-6	285	44.0	1.1	4.5	2.7	2.4	1.1	146.3	49.7	2.9
66-7	292	66.5	1.0	2.4	2.7	2.4	1.1	97.2	34.4	2.8

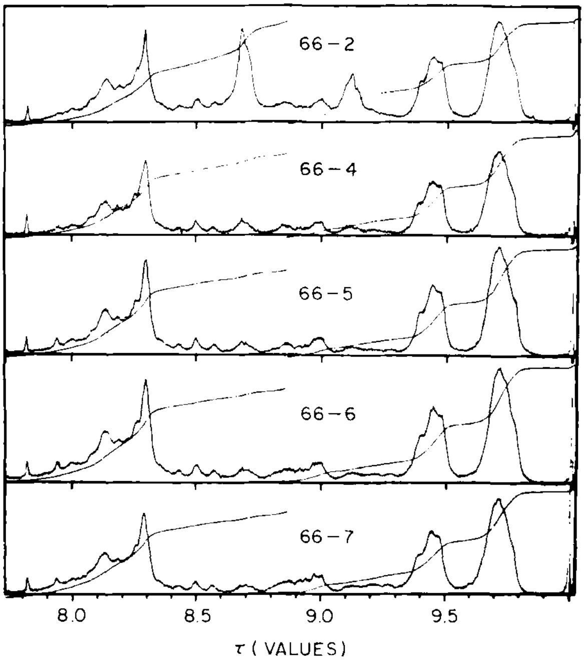

FIG. 16. NMR spectra of decomposed poly-α-methylstyrene (samples 66-2 to 66-7). See Tables 12 and 13 for other data.

et al. [11] were collected from quasi-monodisperse polymers where $\overline{M}_w/\overline{M}_n = 1.1$, and thus it is possible that because of the higher $\overline{M}_w/\overline{M}_n$ ratio of component B + C the results of the present experiments are different.

In the case of the polymers used in the present study, the $\overline{M}_w$ and $\overline{M}_n$ values both decrease, whereas the $\overline{M}_w/\overline{M}_n$ decrease does not follow any specific trend. These results can also be explained by invoking the presence of both the random scission and depolymerization mechanisms proposed by Berlin and Yenikolopyan [16]. In the case of poly-α-methylstyrene comprised exclusively of component B + C, the mechanism of decomposition is solely that of depolymerization [7]. It would appear that due to the presence of the low molecular weight component D + A, scission of the polymer chains precedes the depolymerization reaction.

In Fig. 16 are shown NMR spectra (66-2 to 66-7) of decomposed poly-α-methylstyrene. Their analyses in terms of residual weights

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TABLE 13. Intensity of Methyl Protons of Components (D + A) and (B + C) of Sample 66 and Associated Changes in P_m Values on Thermal Decomposition at Various Temperatures[a]

	D + A					B + C				
	Intensity of various configurations					Intensity of various configurations				
Sample	mm[b]	mr	rr	$\sim P_m$	Residual weight (mg)	mm	mr	rr	$\sim P_m$	Residual weight (mg)
66-0	-	-	-	-	-	-	-	-	-	-
66-2	-	-	-	-	3.3	0.06	0.38	0.56	0.25	5.7
66-4	0.32	0.30	0.38	-	1.9	0.06	0.38	0.56	0.25	6.1
66-5	0.26	0.33	0.41	-	1.3	0.06	0.38	0.56	0.25	5.6
66-6	0.20	0.40	0.40	-	1.1	0.06	0.38	0.56	0.25	4.5
66-7	0.18	0.43	0.39	-	0.7	0.06	0.38	0.56	0.25	2.6

[a] See Table 12 for other data.

[b] The values of mm listed here have side contributions from other methyls.

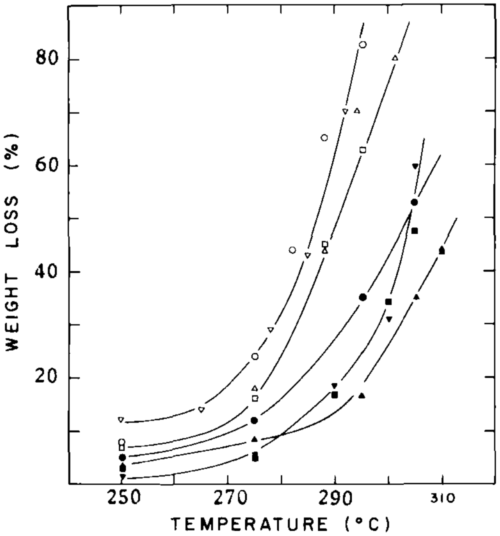

FIG. 17. Weight loss, associated with the GPC characterized component B + C of various poly-α-methylstyrene samples, as a function of the temperature of decomposition: (▽) 66; (▼) 3; (○) 68; (●) L-19; (△) 67; (▲) M-3; (□) 65-B; (■) L-45. See Tables 8, 10, and 12 for other data.

of NMR characterized components D + A and B + C and P_m values associated with component B + C only are presented in Table 13. The P_m analyses of component D + A in the undecomposed and decomposed samples of 66 were not made because of the presence of certain unassigned peaks at 8.7 and 9.13 τ which fall in the zone assigned to the triads mm and rr of component D + A and thus interfere with the analyses. These two peaks, however, disappear on heating the sample between 210 and 250°C where a major portion (> 66%) of the weight loss occurs due to decomposition of some parts of component D + A (see Table 12). It would appear that these peaks at 8.7 and 9.13 τ are due to the methylene and methyl protons, respectively, of certain components other than D + A and B + C.

It may be added here that of all of the bimodal poly-α-methylstyrene samples studied by NMR [5-6], polymer 66 was the only example in which these two peaks appeared at 8.7 and 9.13 τ. All of the other polymer samples (L-11, L-6, M-14, 65-B, 67, and 68) whose methyl protons due to component D + A appear between 8.6 and 8.75, 8.75 and 9.05, and 9.05 and 9.3 τ and which have been assigned to mm, mr, and rr

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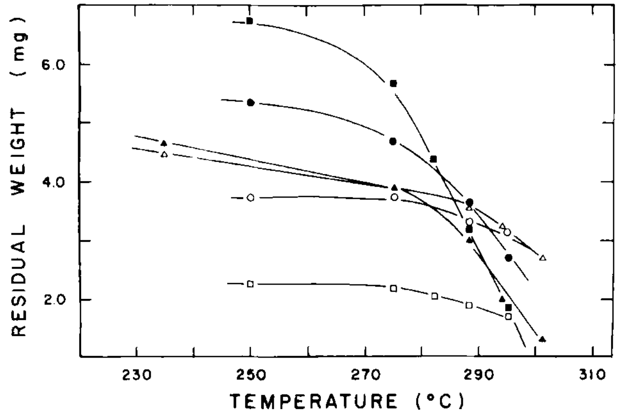

FIG. 18. Residual weights associated with the NMR characterized components D + A and B + C of three poly-α-methylstyrene samples: (■) 68 (B + C); (□) 68 (D + A); (●) 67 (B + C); (○) 67 (D + A); (▲) 65-B (B + C); (△) 65-B (D + A). See Tables 6 to 11 for other data.

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triads, respectively [5, 6], retain these peaks on heating at temperatures as high as 300°C. The calculated values of P_m at such elevated temperatures agree reasonably well with those of the undecomposed polymer. These results resemble those obtained during the decomposition of poly-α-methylstyrene samples [7] comprised only of component B + C whose triad assignments [8-10] are well known. This is additional support in favor of the triad assignments [5, 6] of the methyls due to component D + A.

In Fig. 17 are shown curves representing the percent weight loss associated with the GPC-characterized component B + C as a function of the temperature of decomposition and this for various poly-α-methylstyrene samples. It may be noted that for equimolecular weight samples the percent weight loss of component B + C in the presence of component D + A (samples 66, 68, 67, and 65-B) is far more pronounced than when this component is absent (samples 3, L-19, M-3, and L-45).

In Fig. 18 are presented the residual weights associated with the NMR-characterized components D + A and B + C of three poly-α-methylstyrene samples viz., 68, 67, and 65-B. One notes that component D + A is more stable than its B + C counterpart. The order of stability for component B + C in the three samples is 65-B > 67 > 68 which would mean that the higher the molecular weight the lower the stability. These results agree well with those reported earlier [7, 11, 12].

The principal conclusions to be drawn from this study may be summed up as follows.

(1) Poly-α-methylstyrene samples prepared with potassium in THF and in p-dioxane but having similar proportions of GPC- and NMR-characterized components D + A and B + C decompose differently, the true weight loss in the case of polymer prepared in the former solvent being higher at all temperatures. Poly-α-methylstyrene samples prepared with potassium in p-dioxane and with BuLi-TMEDA but having identical proportions of GPC- and NMR-characterized components D + A and B + C also decompose in a different fashion, the polymer prepared in the former case showing a higher weight loss at all temperatures. The order of stability based on weight loss in the present polymers prepared in the three solvents is: bulk > p-dioxane > THF.

(2) A comparison of the decomposition results obtained with poly-α-methylstyrenes comprised of components D + A and B + C and those comprised exclusively of component B + C show that the percentage weight loss associated with the latter component (B + C) is greater when the low molecular weight component D + A is present. For two polymers, both involving equimolecular weight component B + C, the decrease in molecular weight is far more pronounced when component D + A is present than when it is not. Furthermore, in the case of the higher molecular weight component B + C, the $\overline{M}_w/\overline{M}_n$ values decrease considerably on decomposition. It is quite likely that the presence of component D + A introduces random scissions in the polymer prior to its depolymerization. Component D + A, in general, is more stable than component B + C.

Further studies are in progress on the glass transition temperatures of poly-α-methylstyrenes rich in component D + A. The results of this study will be reported on in due course.

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