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Thermal Decomposition of Poly-α-methylstyrene

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ABSTRACT

Kinetic studies on the decomposition of poly-α-methylstyrene samples with molecular weights ranging from 3.7×10^3 to to 2.0×10^5 have been carried out with the differential thermogravimetric technique. Changes in molecular weight distributions with decomposition, at different temperatures, have been studied by gel-permeation chromatography. A depolymerization mechanism was shown to be responsible for the decomposition phenomenon. The order of reaction for this depolymerization reaction was found to be one. The values of the activation energy for samples of different molecular weights showed no specific trends; however, it would appear that polymers with relatively higher molecular weights have lower activation energies of decomposition. The proportions of the three steric forms, viz., isotactic, heterotactic, and syndiotactic, in the polymer before and after thermal treatments did not change, suggesting that stereoregularity has no apparent effect on the decomposition of poly-α-methylstyrene.

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INTRODUCTION

The thermal decomposition of polystyrene [1-17], poly-α-methylstyrene [18-20], and a few other ring-substituted styrenes [21-27] has been the subject of many studies. The reaction mechanism leading to such decompositions is believed to involve two steps. In the first, random thermal scissions break the polymer chains at their weak points [1, 2, 5, 8, 9]. In the second, the shorter chain segments thus formed depolymerize into volatile products. The activation energies for these two steps were found to be different [3, 4, 6, 15-17]. Studies covering the effect of chain lengths and their distributions on thermal decompositions are also reported in the literature [17, 28-31] and have been related to the reaction mechanisms involved. The process whereby the decomposition of a high molecular weight polymer leads to products having a most probable distribution, has been attributed to random scissions [31]. In reactions involving depolymerizations, however, the disappearance of polymer molecules is independent of their chain length [17, 31].

In an earlier study from this laboratory [17], the changes in the molecular weight distributions during the decomposition of polystyrene were studied by using gel-permeation chromatography (GPC). It was pointed out that if one followed only the overall changes in the polydispersity index, before and after decompositions, it may not be possible to point out the exact moment at which the scission step ends and the depolymerization step begins. This led to suggestions that the changes in the molecular weight distribution should be studied exclusively on the decomposed component of the polymer (GPC technique [17]), which helps to separate the individual contributions of random scissions and depolymerizations during a decomposition, especially when these two proceed simultaneously. In this study, it was also speculated that the various components of a polymer which decompose at different temperatures may have different steric structures. This could not be supported experimentally, since the tacticity measurements on polystyrene by nuclear magnetic resonance (NMR) spectroscopy are difficult to make. With a view to elaborating on this aspect and to confirm a few other observations, decomposition studies were carried out on poly-α-methylstyrene. The results obtained are discussed in the present communication.

EXPERIMENTAL

Materials

Anionically prepared [32, 33] poly-α-methylstyrene samples [34] showing unimodal gel-permeation chromatographic (GPC) molecular weight distributions and having weight-average molecular weights $\overline{M}_w$

ranging from 3.7×10^3 to 2.0×10^5 were used in the present study. The calibration of the GPC instrument was performed with a few monodispersed poly-α-methylstyrene samples whose $\overline{M}_w$ were calculated from intrinsic viscosity data obtained at 30° C in toluene by using the relation reported in the literature [35].

Apparatus

A Perkin-Elmer model TGS-1 thermogravimetric scanning balance, operating with a pure dry nitrogen atmosphere and a heating rate of 20° C/min, was used to follow the decomposition of 2 mg samples of the polymer selected. A Perkin-Elmer model DSC-2 differential scanning calorimeter operating in this case with a pure dry helium atmosphere and a heating rate of 20° C/min were also used.

Analyses of the poly-α-methylstyrene samples both before and after the decomposition were carried out with a Waters Associates Model 200 gel permeation chromatograph operated in a constant temperature (25 ± 0.5° C) room. The separating system consisted of five 1.2-m-long columns connected in series, each packed with cross-linked polystyrene gel having (by the Waters method) pore sizes of 1×10^6, 1.5×10^5, 3×10^3, 250, and 60 Å, respectively. The flow of solvent, tetrahydrofuran degassed with nitrogen, was maintained at 1 ml/min while the concentration of polymer in the samples was limited to 0.125 wt % in order to render negligible the "concentration effects" on the peak position in the chromatograms. Molecular weights were then computed by the summation method suggested in the Waters Associate instruction manual [36].

Nuclear magnetic resonance (NMR) analyses of poly-α-methylstyrene samples were carried out with a 220 MHz NMR spectrophotometer by using 10 wt % solutions of the polymers in o-dichlorobenzene at 100° C, tetramethylsilane was the internal standard used.

RESULTS AND DISCUSSION

In Table 1 are summarized values of percent weight loss, α, molecular weight $\overline{M}_w$, and polydispersity $\overline{P}_d$ ($\overline{M}_w/\overline{M}_n$) obtained before and after the 50 min isothermal decomposition of various poly-α-methylstyrene samples. It may be noted that for all the polymers studied ($\overline{M}_w$ ranging from 3.7×10^3 to 2.0×10^5), the values of $\overline{M}_w$ and $\overline{P}_d$ do not change by much, even when the polymers were subjected to isothermal treatments at temperatures between 300 and 315° C, where α attained a magnitude of 40 to 60%. The variation of molecular

TABLE 1. Results of 50 min Isothermal Decompositions of Poly-α-methylstyrene at Various Temperatures: GPC Molecular Weight, $\overline{M}_w$ Polydispersities P_d, and Weight Losses α

		Temperature of decomposition										
Sample	Characterization index	25°C (Run 0)	230°C (Run 1)	250°C (Run 2)	275°C (Run 3)	285°C (Run 4)	290°C (Run 5)	295°C (Run 6)	300°C (Run 7)	305°C (Run 8)	310°C (Run 9)	315°C (Run 10)
3	$\overline{M}_w \times 10^{-3}$	198	-	194	184	-	178	-	150	141	-	-
	$\overline{P}_d$	2.8	-	2.8	2.6	-	2.9	-	3.0	3.0	-	-
	α (%)	0	-	1.3	5.7	-	18.4	-	31.2	59.4	-	-
5	$\overline{M}_w \times 10^{-3}$	163	-	158	145	-	148	-	135	123	-	-
	$\overline{P}_d$	2.5	-	2.6	2.5	-	2.8	-	2.8	2.8	-	-
	α (%)	0	-	2.8	6.9	-	15.9	-	41.3	53.8	-	-
4	$\overline{M}_w \times 10^{-3}$	143	-	139	135	121	118	-	103	-	-	-
	$\overline{P}_d$	2.4	-	2.1	2.2	2.2	2.5	-	3.3	-	-	-
	α (%)	0	-	3.5	7.5	18.0	30.8	-	52.0	-	-	-
L-19	$\overline{M}_w \times 10^{-3}$	127	121	118	107	-	-	100	-	84	-	-
	$\overline{P}_d$	3.2	2.7	2.8	2.5	-	-	2.8	-	2.9	-	-
	α (%)	0	2.4	5.2	12.0	-	-	35.0	-	58.0	-	-
L-22	$\overline{M}_w \times 10^{-3}$	88	-	79	75	72	64	58	-	-	-	-
	$\overline{P}_d$	1.9	-	1.8	1.8	1.7	2.0	2.0	-	-	-	-
	α (%)	0	-	3.3	5.8	11.9	25.2	40.0	-	-	-	-

L-45	$\overline{M}_w \times 10^{-3}$	60	-	59	63	-	59	-	50	43	-	-
	$\overline{P}_d$	2.0	-	2.0	2.0	-	1.9	-	2.0	2.0	-	-
	α (%)	0	-	2.9	4.8	-	17	-	33.8	47.6	-	-
M-9	$\overline{M}_w \times 10^{-3}$	45	-	44	44	-	-	42	-	39	39	-
	$\overline{P}_d$	2.5	-	2.2	2.2	-	-	2.1	-	1.9	1.9	-
	α (%)	0	-	8.4	12.4	-	-	20.2	-	34.2	43.7	-
M-3	$\overline{M}_w \times 10^{-3}$	41	-	41	39	-	-	39	-	36	34	-
	$\overline{P}_d$	2.1	-	1.9	2.2	-	-	2.1	-	2.3	2.4	-
	α (%)	0	-	3.4	8.7	-	-	17.0	-	35.2	44.2	-
M-10	$\overline{M}_w \times 10^{-3}$	21	21	19	19	-	-	-	-	18	-	17
	$\overline{P}_d$	1.7	1.7	1.8	1.8	-	-	-	-	2.0	-	2.0
	α (%)	0	3.6	7.0	9.5	-	-	-	-	20.0	-	36.0
L-17	$\overline{M}_w \times 10^{-3}$	10	-	-	10	-	10	-	9	-	8	6
	$\overline{P}_d$	1.6	-	-	1.6	-	1.6	-	1.6	-	1.5	1.4
	α (%)	0	-	-	2.9	-	10.8	-	19.4	-	41.9	59.9
L-15	$\overline{M}_w \times 10^{-3}$	6.1	-	5.6	5.6	-	-	5.5	-	5.5	-	5.0
	$\overline{P}_d$	1.3	-	1.3	1.2	-	-	1.2	-	1.2	-	1.2
	α (%)	0	-	8.0	10.1	-	-	18.4	-	27.3	-	44.5
L-16	$\overline{M}_w \times 10^{-3}$	4.7	-	4.6	4.6	-	4.5	-	-	4.3	-	4.1
	$\overline{P}_d$	1.3	-	1.3	1.25	-	1.25	-	-	1.2	-	1.2
	α (%)	0	-	4.4	7.2	-	11.0	-	-	23.6	-	40.0

(continued)

TABLE 1 (continued)

		Temperature of decomposition										
Sample	Characterization index	25°C (Run 0)	230°C (Run 1)	250°C (Run 2)	275°C (Run 3)	285°C (Run 4)	290°C (Run 5)	295°C (Run 6)	300°C (Run 7)	305°C (Run 8)	310°C (Run 9)	315°C (Run 10)
B	$\overline{M}_w \times 10^{-3}$	4.0	-	4.2	4.3	-	-	4.2	-	3.9	-	3.5
	$\overline{P}_d$	1.4	-	1.4	1.4	-	-	1.3	-	1.3	-	1.2
	α (%)	0	-	4.6	8.0	-	-	19.6	-	31.2	-	51.7
M-14	$\overline{M}_w \times 10^{-3}$	3.7	-	3.7	3.7	3.8	-	-	3.8	-	-	3.6
	$\overline{P}_d$	1.2	-	1.2	1.2	1.2	-	-	1.2	-	-	1.2
	α (%)	0	-	2.9	5.3	6.8	-	-	14.0	-	-	36.0

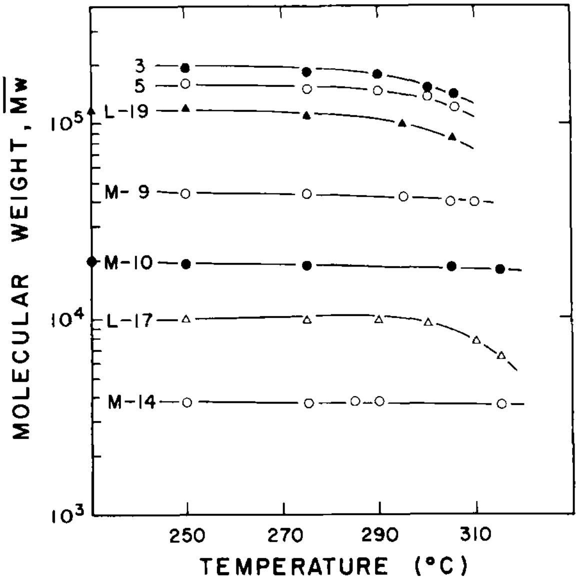

FIG. 1. Variation of molecular weight $\overline{M}_w$ with temperature for several poly-α-methylstyrene samples. See Table 1 for other data.

weights with temperature, for some of the polymers, is presented in Fig. 1. On heating samples for 50 min at temperatures ranging up to 290°C, the $\overline{M}_w$ of the polymers decreased very little. On heating beyond 290°C, however, some of the polymers, viz., samples 3, 5, L-19, and L-17 did show a noticeable decrease in $\overline{M}_w$.

In Fig. 2 are presented the variation of molecular weights as a function of the volatilized fraction a, defined as the ratio of polymer mass decomposed at a temperature T to its initial mass. It may be seen that even for a values of 0.6, $\overline{M}_w$ decreases very little in comparison to that noticed in the case of the decomposition of polystyrene [17]. Furthermore, the $\overline{P}_d$ values in the present study changed little as a result of decompositions in almost all of the polymer samples studied.

In order to be able to carry out a precise comparison between the decomposition of polystyrene ($\overline{M}_w = 1.6 \times 10^5$ [17]) and that of poly-α-methylstyrene (sample 5), the data obtained with the two polymers were analyzed (molecular weights and polydispersities). The results

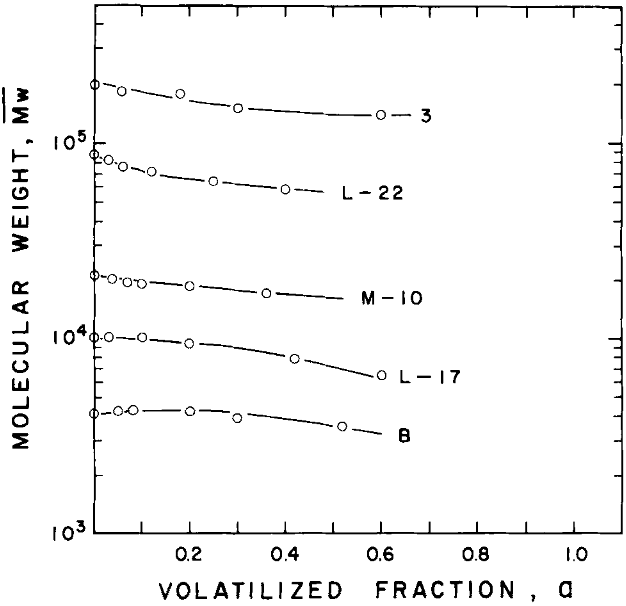

FIG. 2. Variation of molecular weight $\overline{M}_w$ with volatilized fraction a for several poly-α-methylstyrene samples. See Table 1 for other data.

of the variation of $\overline{M}_w$ with a obtained during the 50 min isothermal decompositions in the two cases may be divided into three parts: (1), a $<$ 0.05, (2), a between 0.05 and 0.20, and (3) a $>$ 0.20.

In the case of the decomposition of polystyrene, yielding a values of 0.03, 0.16, and 0.54, isothermal heating was required at 330, 355, and 377° C, respectively. The overall $\overline{M}_w$ of the polymer decreased from an initial value of 1.66×10^5 to 1.56×10^5, 6.5×10^4, and 3.9×10^4, respectively while the overall polydispersity values did not change.

In the case of the decomposition of poly-α-methylstyrene yielding a values of 0.03, 0.16, and 0.54, isothermal heating was carried out at 250, 290, and 305° C, respectively. The $\overline{M}_w$ of polymer sample 5 decreased only slightly from its initial value of 1.63×10^5 to 1.58×10^5, 1.48×10^5, and 1.23×10^5, respectively. Like in the earlier study the overall polydispersity values did not change.

A comparison of these results reveals two interesting facts: (1) for identical weight losses occurring during thermal decompositions, relatively lower temperatures are required for poly-α-methylstyrene than is the case for polystyrene; (2) during the decomposition of polystyrene [17], where "random scissions" was established as the mechanism responsible for the phenomenon at a values of 0.10 or less and "random scissions plus depolymerization" at a values greater than 0.10, the overall $\overline{M}_w$ as well as the $\overline{M}_w$ values of the individual components decreased significantly. For instance, for an a value of 0.03, a component P (33%) of the polymer having an $\overline{M}_w$ of 1.76×10^5 ($\overline{P}_d = 1.1$) decomposed to yield a lower molecular weight component P' with an $\overline{M}_w$ of 8.73×10^4 ($\overline{P}_d = 1.5$). For an a value of 0.16, another component Q with an $\overline{M}_w$ of 1.73×10^5 ($\overline{P}_d = 1.3$) decomposed to yield yet another component Q' with an $\overline{M}_w$ of 3.3×10^4 ($\overline{P}_d = 1.5$). Thus, the random scissions cut down the chain length of the polymer ($\overline{M}_w$ going from 1.76×10^5 to 8.73×10^4 or to 3.3×10^4 and P_d from 1.1 to 1.5) and when this reaches a $\overline{DP}$ (degree of polymerization) of about 300 ($\overline{M}_w = 3.5 \times 10^4$), depolymerization becomes the principal mode of decomposition. This suggested that in the decomposition of a polystyrene standard, $\overline{M}_w = 1.6 \times 10^5$, the two mechanisms operate simultaneously.

In the decomposition of poly-α-methylstyrene, the overall molecular weight of the polymer decreases only slightly from 1.63×10^5 to 1.23×10^5 even for an a value as high as 0.54, and the overall polydispersity value varies from 2.5 to 2.8. This suggests that the mechanism responsible for the decomposition of poly-α-methylstyrene (sample 5) may be that of depolymerization alone.

In the earlier work [17], it was noticed on occasion that when the molecular weight and polydispersity changes were followed solely from overall results, erroneous conclusions were drawn. To avoid such conclusions and to obtain a better understanding of the decomposition process, it was decided to compare normalized GPC molecular weight distributions where the areas under the GPC curves correspond to the weight of the undecomposed polymer.

In Figs. 3, 4, and 5 are presented normalized molecular weight distributions of undecomposed and decomposed polymer samples: 3 ($\overline{M}_w = 1.98 \times 10^5$); M-10 ($\overline{M}_w = 2.1 \times 10^4$); and B ($\overline{M}_w = 4.0 \times 10^3$), respectively. In all three cases the GPC maxima of the undecomposed and the decomposed polymers appear at the same elution volume. Furthermore, their overall GPC molecular weight distributions before and after decomposition do not change. The curves in Figs. 3-5 resemble those obtained with the polystyrene standard ($\overline{M}_w = 1.03 \times 10^4$) reported earlier [17], where such behavior was attributed to a depolymerization mechanism leading to the rapid and complete

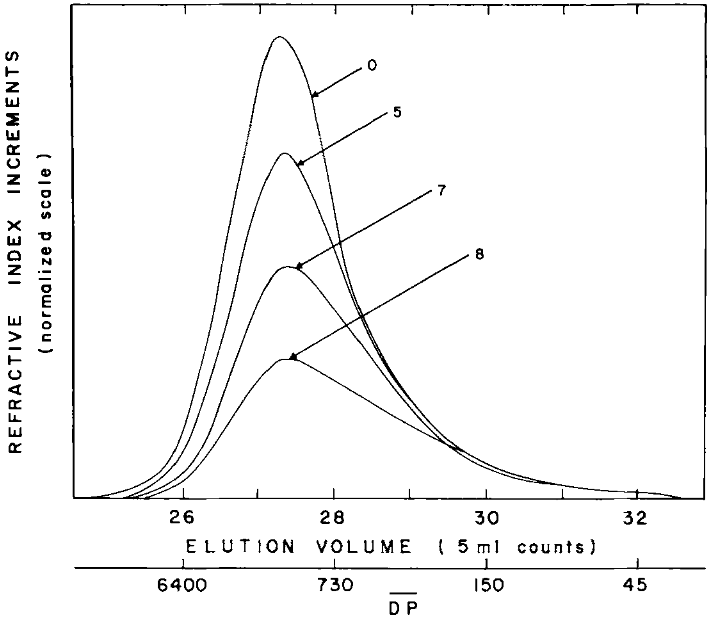

FIG. 3. GPC distributions of poly-α-methylstyrene (sample 3) subjected to 50 min isothermal treatments at various temperatures: (0) undecomposed; (5) 290°C; (7) 300°C; (8) 305°C. See Table 1 for other data.

depropagation of radical bearing chains. Berlin and Yenikolopyan [31] had predicted that this mechanism was independent of the chain length. Based on the above arguments and on the results obtained in the present study one is led to conclude that depolymerization is the sole mechanism responsible for the decomposition of poly-α-methylstyrene samples having molecular weights ($\overline{M}_w$) of 2.0×10^5 or lower.

Effect of Polymer Stereoregularity on Decomposition

In the case of polystyrene, the stereoregularity of the polymer was not found to have any influence on its decomposition [37]. In the earlier work [17] from this laboratory, however, it was speculated that three components of polystyrene, having similar $\overline{M}_w$ values but decomposing at different temperatures, might have different structures,

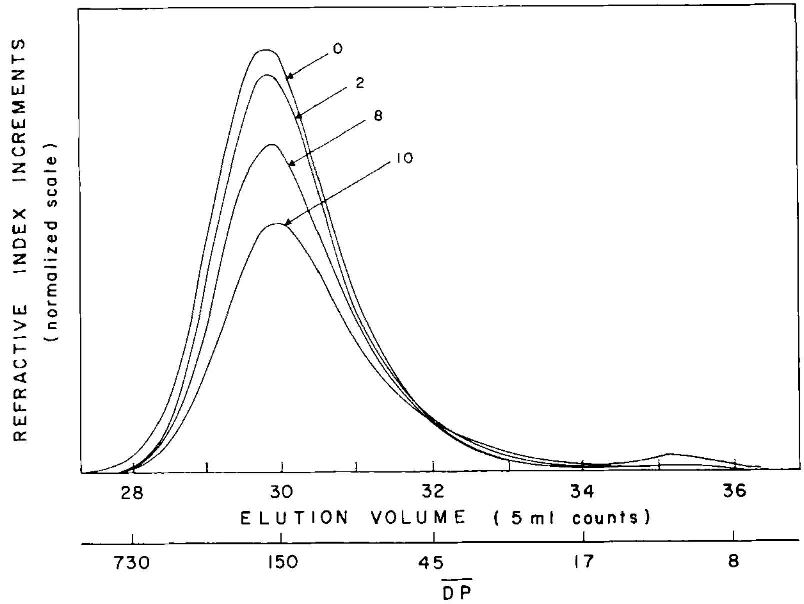

FIG. 4. GPC distributions of poly-α-methylstyrene (sample M-10) subjected to 50 min isothermal treatments at various temperatures: (0) undecomposed; (2) 250°C; (8) 305°C; and (10) 315°C. See Table 1 for other data.

i.e., isotactic, heterotactic, and syndiotactic. This, however, could not be proved experimentally at the time, since the benzene rings of polystyrene are not sufficiently sensitive to proton spectra. To justify the above speculation, it was decided to reinvestigate this question with poly-α-methylstyrene, as it is very easy to calculate the proportions of the three different steric forms of this polymer by NMR [38], where the triads corresponding to isotactic, heterotactic, and syndiotactic structures appear at τ values of 9.0, 9.45, and 9.7, respectively.

In Fig. 6 are shown the NMR spectra of decomposed poly-α-methylstyrene (L-19-1 to L-19-6) and in Fig. 7 are presented the NMR spectra of undecomposed (M-10-0) and decomposed (M-10-1 to M-10-10) poly-α-methylstyrene samples. The NMR analyses of these polymers showed that they carry different proportions of the three steric configurations and are not 100% of one or the other. The polymers (undecomposed) used in the present study are nevertheless predominantly syndiotactic (P_m = 0.22-0.24) as shown in Table 2, where are

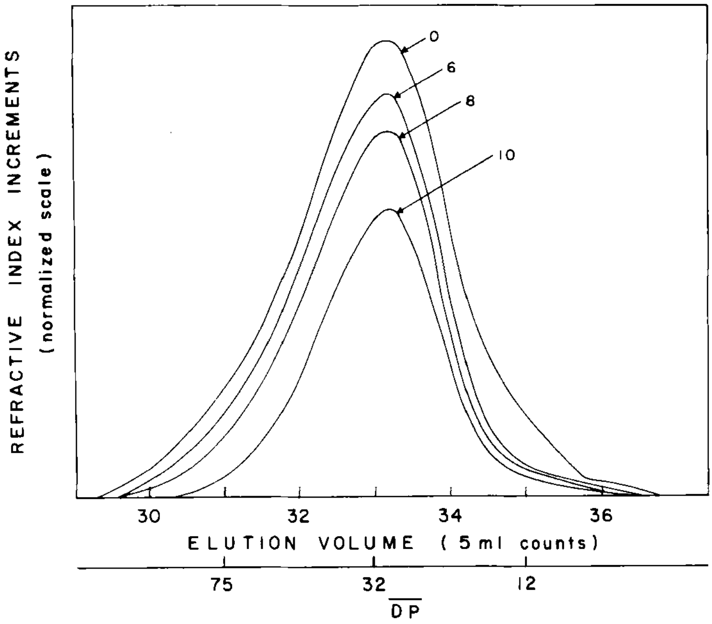

FIG. 5. GPC distributions of poly-α-methylstyrene (sample B) subjected to 50 min isothermal treatments at various temperatures: (0) undecomposed; (6) 295°C; (8) 305°C; (10) 315°C. See Table 1 for other data.

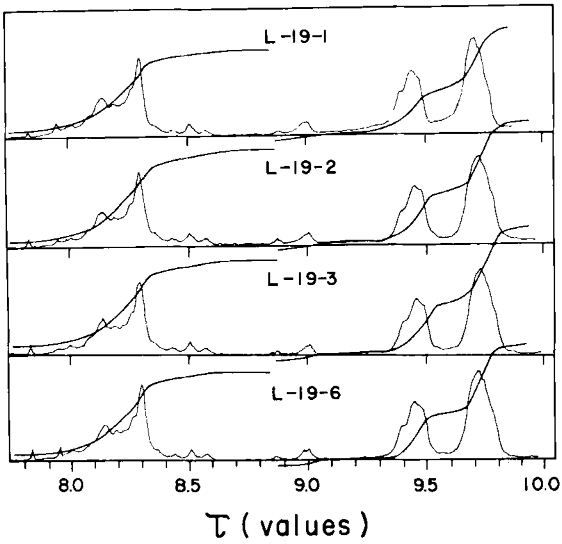

FIG. 6. NMR spectra of decomposed poly-α-methylstyrene samples (L-19-1 to L-19-6). See Table 2 for other data.

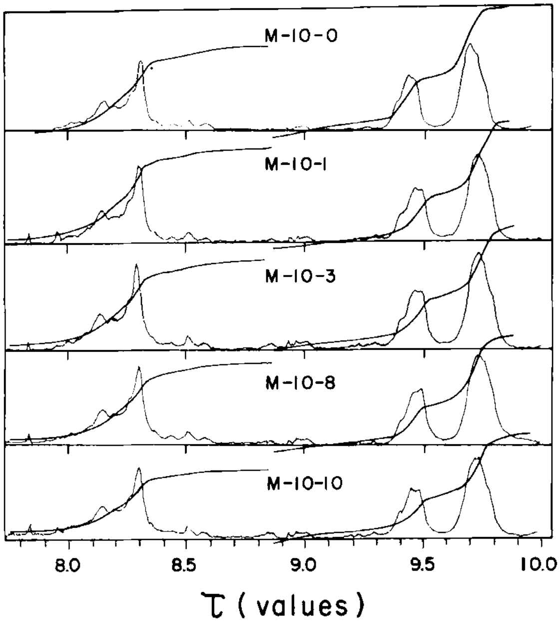

FIG. 7. NMR spectra of undecomposed (M-10-0) and decomposed (M-10-1 to M-10-10) poly-α-methylstyrene samples. See Table 2 for other data.

presented data on the intensities associated with the triad configurations of both undecomposed and decomposed polymers. One notes that polymer samples L-19 (mm = 0.05, mr = 0.37, rr = 0.58) and M-10 (mm = 0.03, mr = 0.36, rr = 0.61) show more or less the same triad intensities before and after thermal decomposition. This suggests that in the case of poly-α-methylstyrene the influence of stereoregularity on decomposition is negligible.

Decomposition Kinetics

In dynamic thermogravimetry, the rate law for the decomposition of polymer may be written as:

$$da/dT = (k/q)f(a) \qquad (1)$$

where a is that fraction of the polymer which is volatilized; f(a) is a function of a; q is the heating rate (in °C/min); and k, the rate constant

TABLE 2. Intensity Associated with the Triad Configurations before and after Thermal Decomposition of Poly-α-methylstyrene Samples M-10 and L-19[a]

Sample	Temperature of decomposition (°C)	True weight loss α (%)	Molecular weights (GPC) × 10^{-3}		Intensity associated with various triad configurations			Bernoullian statistics
			$\overline{M}_w$	$\overline{M}_n$	mm	mr	rr	P_m
M-10-0	25	0.0	20.7	11.9	0.03	0.36	0.61	0.22
M-10-1	230	3.6	19.9	11.5	0.04	0.35	0.61	0.22
M-10-3	275	9.5	19.1	10.9	0.05	0.36	0.59	0.23
M-10-8	305	20.0	18.5	9.4	0.06	0.35	0.59	0.23
M-10-10	325	36.0	17.2	8.4	0.05	0.36	0.59	0.23
L-19-0	25	0.0	127.0	39.7	0.05	0.37	0.58	0.24
L-19-1	230	2.4	121.0	44.5	0.05	0.37	0.58	0.24
L-19-2	250	5.2	118.0	42.3	0.05	0.37	0.58	0.24
L-19-3	275	12.0	107.0	42.8	0.05	0.37	0.58	0.24
L-19-6	295	35.0	100.0	36.2	0.05	0.37	0.58	0.24

[a] A 10-mg portion of polymer was taken for each decomposition run.

said to obey the Arrhenius law written in the form: $k = Z \exp\{-E/RT\}$. Here Z is the pre-exponential factor (in min^{-1}) and E is the energy of activation (in kcal/mole).

For decompositions where weight loss is due primarily to a depolymerization reaction, as in the present case, Audebert and Aubineau [39] have shown that f(a) has the following form:

$$f(a) = (1 - a)^n \tag{2}$$

n being the order of reaction. Substituting this in Eq. (1), one obtains:

$$da/dT = (Z/q) \exp\{-E/RT\}(1 - a)^n \tag{3}$$

To compute activation energies, Flynn and Wall [40] have suggested the integration of Eq. (3) between the limits 0 and a.

Therefore:

$$\int_0^a \frac{da}{(1 - a)^n} = \frac{Z}{q} \int_0^T \exp\{-E/RT\}dT \tag{4}$$

Coats and Redfern [41, 42] have shown that the integral $\int_0^T \exp\{-E/RT\}dT$ is equal to $(RT^2/E) \exp\{-E/RT\}$. Thus Eq. (4) can be written as:

$$\int_0^a \frac{da}{(1 - a)^n} = \frac{ZRT^2}{qE} \exp\{-E/RT\} \tag{5}$$

The left hand side of Eq. (5) is equal to

$1 - (1 - a)^{1-n}/(1 - n)$ for values of n other than 1 and $-\ln(1 - a)$ for $n = 1$.

If $\int_0^a [da/(1 - a)^n]/T^2$ is plotted as a function of 1/T for different values of n, that value of n which yields a straight line may be used to compute the value of the activation energy.

Figure 8 shows dynamic thermogravimetric curves for poly-α-methylstyrene samples having molecular weights ranging from 3.7×10^3 to 2.0×10^5 and decomposed at a heating rate of 20°C/min, the initial mass of polymer being, in all cases, 2 mg. The curves indicate that the higher the molecular weight of the polymer the lower is the temperature to achieve 100% decomposition. By using the

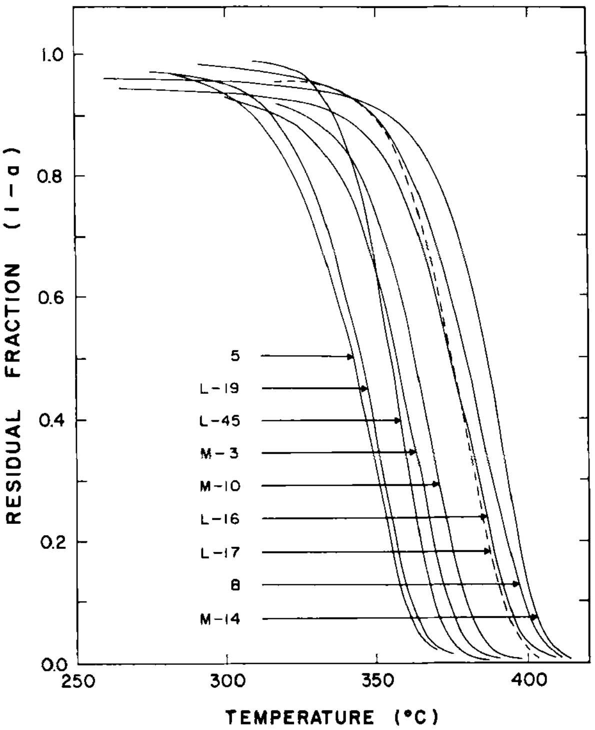

FIG. 8. Influence of molecular weight on the dynamic thermogravimetric decomposition of poly-α-methylstyrene samples heated at a rate of 20°C/min.

method of Coats and Redfern [41, 42], activation energies have been calculated and are presented in Table 3. For most of the polymers studied, an order of reaction of one was found to yield straight lines with the method of Coats and Redfern [41, 42]. This is in agreement with what had been observed earlier in the case of the decomposition of polystyrene where the depolymerization mechanism also followed first-order kinetics. As it was not always possible to choose which of zero or one as order of reaction gave the best straight line, activation energies were calculated using both values of n. The results in Table 3 indicate that the values of the activation energy do not show any specific trends with molecular weight, though in a few cases lower activation energies seem to be associated with the decomposition of higher molecular weight polymers. A comparison of the results obtained in the present study with those published earlier for

TABLE 3. Activation Energy as a Function of Molecular Weight[a]

Sample	Molecular weight $\overline{M}_n \times 10^{-3}$	$\overline{M}_w / \overline{M}_n$	Activation energy (kcal/mole) n = 0[b]	Activation energy (kcal/mole) n = 1[b]
B	2.9	1.4	39.0	50.0
M-14	3.0	1.2	45.0	70.0
L-13	3.2	1.3	36.0	47.0
L-16	3.6	1.3	42.0	51.5
L-15	4.7	1.3	34.6	51.7
L-17	6.5	1.6	-	59.7
M-10	12.2	1.7	27.4	51.5
M-9	18.1	2.5	30.7	57.6
M-3	19.3	2.1	33.1	47.7
L-45	30.2	2.0	51.0	66.0
L-19	39.7	3.2	30.0	52.0
L-22	46.4	1.9	56.1	62.3
4	59.6	2.4	27.2	37.4
5	65.2	2.5	31.3	38.6
3	70.3	2.8	28.3	52.1

[a] Method of Coats and Redfern [41, 42].
[b] n is the order of reaction.

polystyrene [17] clearly show that the energy of activation for the decomposition of poly-α-methylstyrene is lower. It is possible that the introduction of a methyl group in the α position of polystyrene facilitates the formation of radicals and in the consequent depolymerization reaction, a lower activation energy is therefore involved.

The principal conclusions to be drawn from this study, keeping in mind the data published earlier on polystyrene, may be summed up as follows. To obtain identical weight losses during the thermal decomposition of equimolecular weight polystyrene and poly-α-methylstyrene, lower temperatures are required for the latter. Depolymerization is the mechanism responsible for the decomposition of poly-α-methylstyrene, whereas random scissions and depolymerization jointly play a role in the case of polystyrene. The depolymerization reaction in the decomposition of poly-α-methylstyrene follows first-order kinetics, in agreement with the results obtained in the case of polystyrene. The activation energy for the decomposition of poly-α-methylstyrene decomposition is lower than that for polystyrene. The stereoregularity of the polymer has no apparent effect on the decomposition of poly-α-methylstyrene.

Further studies are in progress on the decomposition of poly-p-isopropyl-α-methylstyrene and will be reported in due course.

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