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Thermal Decomposition and Glass Transition Temperature of Poly(isobutylene)

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ABSTRACT

The thermal decomposition and the glass transition temperature (T_g) of polyisobutylene (PIB) were studied with a differential scanning calorimeter (DSC). The undecomposed and the decomposed polymers were analyzed by gel permeation chromatography for molecular weight distributions and by DSC for changes in the thermal properties, e.g., T_g. In the isothermal decomposition of PIB, weight loss, α, is independent of the molecular weight (M) of the polymer. Random chain-scissions reduce $\overline{M}_w$ and $\overline{M}_n$ to average values of 10×10^3 and 5.0×10^3, respectively, after isothermal treatments for 50 min intervals at temperatures ranging from 250 to 375°C. The value of α is depolymerization controlled and the PIB is not quantitatively converted into monomer. Oligomers with a degree of polymerization of 12 are important products of the decomposition reactions. The activation energy of decomposition of PIB was found to be 184 kJ/mol, a value somewhat lower than that reported in the literature. T_{g_e}

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values (at q = 1 K/min) of undecomposed and decomposed PIB samples fall within ± 3.0° of 200 K in excellent agreement with reported values obtained by other means.

INTRODUCTION

Data on the thermal decomposition [1-7] and on the glass transition temperature (T_g) [8-16] of polyisobutylene (PIB) have been reported in the literature. The results of thermal decomposition studies showed that scissions of the main chains yield radicals which bring about depolymerization reactions leading to the formation of monomer [1, 3-5]. Furthermore, most of the PIB samples showed a decrease in the rate of volatilization [3] or decomposition [4] as a function of the percent degradation, and this irrespective of their initial molecular weights (M). It has also been suggested [6] that the secondary hydrogen atoms in PIB are less active than the primary ones due in all probability to steric effects of the methyl groups.

T_g values obtained from thermal expansion data [8], from refractometric measurements [9], from specific volume data [11], and from bulk viscosity determinations [13] were found to be in the vicinity of 200 K irrespective of the value of M.

With a vew to extending the study on the thermal decomposition and glass transition temperature of PIB to higher values of M, four samples with $\overline{M}_w$'s ranging from 4.0×10^5 to 4.0×10^6 were subjected to 50 min isothermal decompositions at various temperatures and the residual products were analyzed by gel permeation chromatography (GPC) and differential scanning calorimetry (DSC). A discussion of the principal results obtained in the study is the object of the present communication.

EXPERIMENTAL

PIB samples obtained from the Aldrich Chemical Co. were used as received. Viscosity-average molecular weights $\overline{M}_v$ of these polymers were calculated from intrinsic viscosity $[\eta]$ data obtained in toluene at 30°C using the relationship reported in the literature [17]. The molecular weight distributions of the PIB samples were obtained with a Waters Associates model 200 GPC [18-29]. Using the viscosity and the GPC data on the undecomposed PIB samples, a calibration curve was obtained for the GPC relating elution volume (V_e) and M; viz., $\log M = (14.1 - 0.051V_e)$. Calculated values of $\overline{M}_w$ and $\overline{M}_n$ of the undecomposed PIB samples are given in Table 1.

TABLE 1. Solution Properties of the Polyisobutylene Samples

Sample	$\overline{M}_w$ (GPC) $\times 10^{-4}$	$\overline{M}_n$ (GPC) $\times 10^{-4}$	$\overline{M}_w/\overline{M}_n$	$[\eta]$ (dL/g)[a]	$\overline{M}_v \times 10^{-4}$	Huggins coefficient,[b] k_H
PIB-A0	394.0	37.4	10.5	6.53	546	0.29
PIB-B0	344.0	36.8	9.35	4.63	327	0.34
PIB-C0	193.1	26.4	7.3	2.78	153	0.34
PIB-D0	42.5	13.7	3.2	1.18	37	0.28

[a]Viscosity measurements were carried out in toluene at 30° C.
[b]$(\eta_{sp}/c) = [\eta] + k_H[\eta]^2 c$.

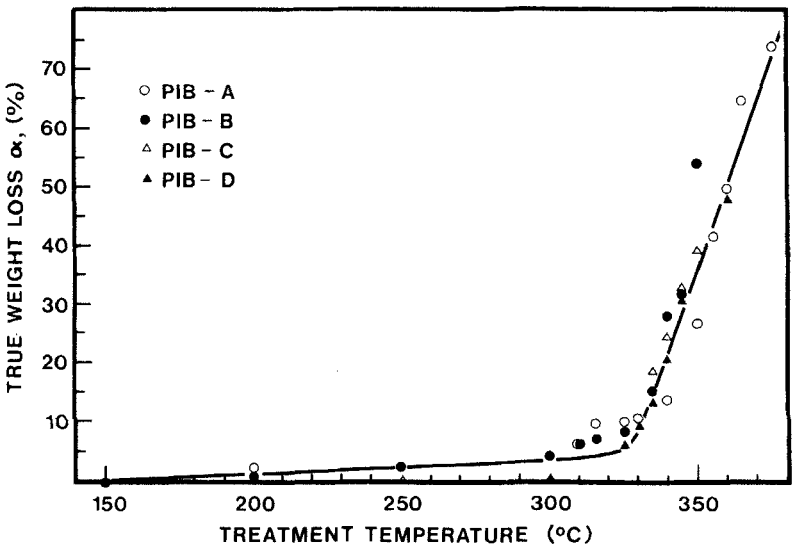

FIG. 1. Variation of weight-loss with treatment temperature for PIB samples from Series A, B, C, and D. See Tables 2 to 5 for other data.

A Perkin-Elmer model DSC-2B differential scanning calorimeter operating with an atmosphere of pure dry helium at the sample level was used for the isothermal decompositions of PIB whereas their model TGS-1 thermogravimetric scanning balance operating in an atmosphere of pure dry nitrogen was used for the dynamic decompositions of the same samples. The T_g values of the undecomposed and the decomposed samples of PIB were determined with the DSC apparatus [31-33].

RESULTS AND DISCUSSION

Thermal Decomposition of PIB

In Fig. 1 are presented values of the weight loss α in % obtained with PIB samples from Series A, B, C, and D (Tables 2, 3, 4, and 5, respectively) after isothermal treatments at various temperatures for 50 min periods. The data from PIB samples of different molecular weights fit a unique curve indicating that α is independent of molecular weight in the temperature range studied. In the temperature range

TABLE 2. Data on PIB Samples Subjected to Isothermal Treatment at Various Temperatures for 50 min Intervals. Series A

Sample	Decomposition temperature (°C)	Weight loss α (%)	$\overline{M}_w$ (GPC) $\times 10^{-4}$	$\overline{M}_n$ (GPC) $\times 10^{-4}$	$\overline{M}_w/\overline{M}_n$
PIB-A0	Undecomposed	0.0	394	37.4	10.5
PIB-A1	150	0.0	350	37.0	9.5
PIB-A2	200	2.4	316	36.0	8.8
PIB-A3	250	2.3	133	13.8	9.6
PIB-A4	310	6.3	5.8	2.1	2.7
PIB-A5	315	9.8	4.8	1.8	2.7
PIB-A6	325	9.9	3.4	1.3	2.6
PIB-A7	330	10.4	3.2	1.1	2.9
PIB-A8	340	13.7	3.8	0.76	5.0
PIB-A9	350	26.6	-	-	-
PIB-A10	355	41.6	1.6	0.48	3.3
PIB-A11	360	49.7	-	-	-
PIB-A12	365	64.7	1.1	0.40	2.8
PIB-A13	375	74.2	0.85	0.33	2.6

TABLE 3. Data on PIB Samples Subjected to Isothermal Treatment at Various Temperatues for 50 min Intervals. Series B

Sample	Decomposition temperature (°C)	Weight loss α (%)	$\overline{M}_w$ (GPC) $\times 10^{-4}$	$\overline{M}_n$ (GPC) $\times 10^{-4}$	$\overline{M}_w/\overline{M}_n$
PIB-B0	Undecomposed	0.0	344	36.8	9.4
PIB-B1	150	0.0	273	29.2	9.4
PIB-B2	200	0.9	245	19.9	12.3
PIB-B3	250	2.4	101	15.6	6.5
PIB-B4	300	4.2	10.0	3.2	3.1
PIB-B5	310	5.8	4.7	2.0	2.4
PIB-B6	315	7.0	4.1	1.9	2.2
PIB-B7	325	8.2	4.3	1.4	3.0
PIB-B8	330	12.6	3.0	1.3	2.4
PIB-B9	335	14.9	-	-	-
PIB-B10	340	28.2	1.7	0.8	2.1
PIB-B11	345	31.9	1.5	0.66	2.3
PIB-B12	350	54.1	1.1	0.55	2.0

TABLE 4. Data on PIB Samples Subjected to Isothermal Treatment at Various Temperatures for 50 min Intervals. Series C

Sample	Decomposition temperature (°C)	Weight loss α (%)	$\overline{M}_w$ (GPC) $\times 10^{-4}$	$\overline{M}_n$ (GPC) $\times 10^{-4}$	$\overline{M}_w/\overline{M}_n$
PIB-C0	Undecomposed	0.0	193	26.4	7.3
PIB-C1	200	0.0	131	23.0	5.7
PIB-C2	250	0.0	55.3	12.7	4.3
PIB-C3	325	8.1	3.1	1.4	2.2
PIB-C4	330	10.2	2.8	1.2	2.3
PIB-C5	335	18.4	1.6	0.75	2.1
PIB-C6	340	24.0	1.7	0.75	2.3
PIB-C7	345	32.3	1.3	0.61	2.1
PIB-C8	350	39.4	1.1	0.48	2.5

TABLE 5. Data on PIB Samples Subjected to Isothermal Treatment at Various Temperatures for 50 min Intervals. Series D

Sample	Decomposition temperature (°C)	Weight loss α (%)	$\overline{M}_w$ (GPC) $\times 10^{-4}$	$\overline{M}_n$ (GPC) $\times 10^{-4}$	$\overline{M}_w/\overline{M}_n$
PIB-D0	Undecomposed	0.0	42.5	13.7	3.2
PIB-D1	200	0.0	41.3	13.8	3.0
PIB-D2	250	0.4	35.8	11.0	3.2
PIB-D3	300	0.6	15.9	4.9	3.2
PIB-D4	325	5.8	4.1	1.8	2.3
PIB-D5	330	8.8	3.0	1.4	2.2
PIB-D6	335	13.5	-	-	-
PIB-D7	340	20.8	1.7	0.9	2.0
PIB-D8	345	31.2	1.4	0.7	2.0
PIB-D9	350	48.2	2.2	0.6	3.7

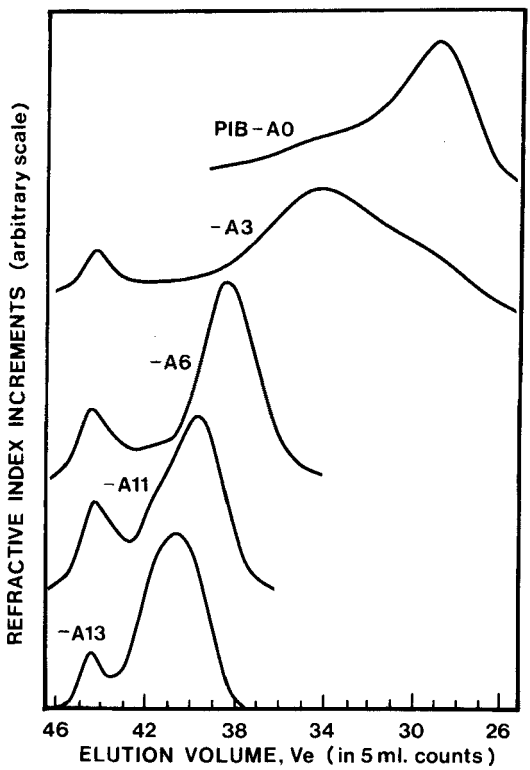

FIG. 2. GPC chromatograms of one undecomposed and four decomposed samples of PIB from Series A.

150 to 325°C, α increased slowly to a value of about 5 to 10%, whereas between 325 and 375°C the increase was rapid, attaining in one case a value of 74.2% (Table 2, PIB-A13).

In Figs. 2 and 3 (Series A and C, respectively) are shown raw GPC chromatograms of undecomposed and decomposed PIB samples. The maxima in the curves of the decomposed polymers move to higher elution volumes (i.e., lower molecular weights) and an additional peak appears at elution count 44 (molecular weight 675), corresponding to a degree of polymerization ($\overline{DP}$) of 12. The area of this peak accounts for approximately 10 to 20% of the total surface under a given GPC curve. As the proportion of polymer with a $\overline{DP}$ of 12 showed no decreasing or increasing trends as a function of treatment temperature, it was not thought necessary to attempt to isolate and characterize this component. It may be added that PIB samples from Series B and D yield relatively low proportions of this component.

To better understand the decomposition of PIB, the GPC chromatograms of the various samples were normalized and surface areas

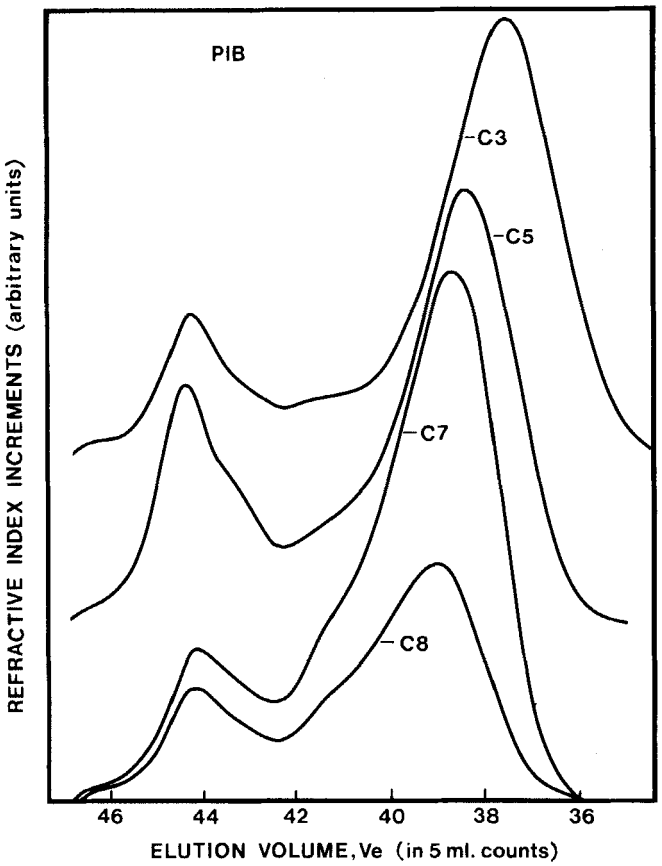

FIG. 3. GPC chromatograms of four decomposed samples of PIB from Series C.

under the GPC envelopes were corrected for weight losses suffered by the polymers during the thermal treatments. These are shown in Figs. 4, 5, 6, and 7 for Series A, B, C, and D, respectively. The normalized GPC distribution curves of polymers decomposed during 50 min periods at different temperatures were compared with the GPC curve of the undecomposed polymer in the same series. By subtracting from the distribution curve of the undecomposed polymer that of any subsequently decomposed polymer, the changes, both positive and negative, that take place as a result of the decomposition of the original higher molecular weight species can readily be visualized.

For the PIB samples of Series A, these changes are shown in

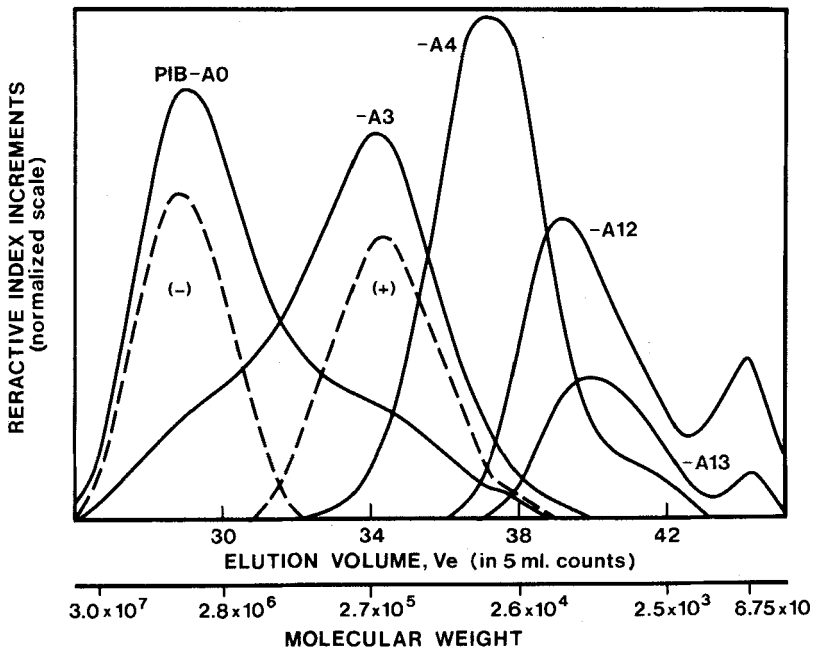

FIG. 4. Normalized GPC molecular weight distributions of undecomposed and decomposed samples of PIB from Series A. See Table 2 for other data.

Fig. 4. For 50 min isothermal decompositions, as the temperature is raised from 25 to 250°C (Samples no. PIB-A0 and A3), 46% of the PIB sample ($\overline{M}_w = 6.3 \times 10^6$ and $\overline{M}_n = 4.0 \times 10^6$) appearing between elution counts 26 and 32 in PIB-A0, breaks down (-) to yield (+) products (44%) of lower molecular weight ($\overline{M}_w = 2.66 \times 10^5$ and $\overline{M}_n = 1.34 \times 10^5$) eluting between counts 31 and 39. The polydispersity ratio 2.05 ($\overline{P}d = \overline{M}_w/\overline{M}_n$) of the decomposed product suggests that random scissions are the principal mechanism of chain degradation [34]. As the temperature is raised from 250 to 310°C and above, random chain scissions continue to lower $\overline{M}_w$ toward a lower limit of 1.0×10^4. However, weight loss between 25 and 375°C is believed to result mainly from depolymerization reactions for which the starting limit of $\overline{M}_w$ is something $< 1.0 \times 10^5$ (PIB-A4). The end products of the depolymerization reaction, however, are not only pure monomer but also oligomers appearing between elution counts 42 and 46 where the $\overline{DP}$ value is 12. These findings agree with those reported by Madorsky

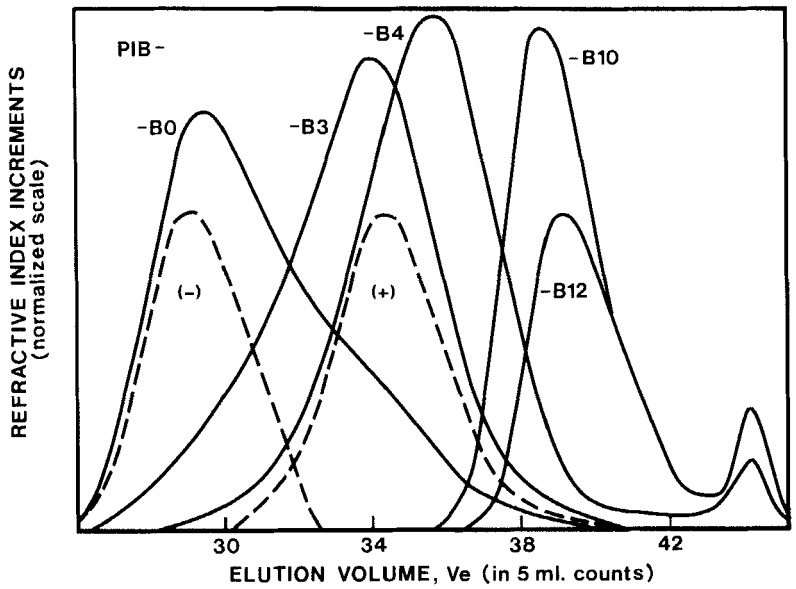

FIG. 5. Normalized GPC molecular weight distributions of undecomposed and decomposed samples of PIB from Series B. See Table 3 for other data.

et al. [1] and Matusevitch and Slobodin [2] who showed that a range of products from C_4 to C_{20} is evolved.

For the PIB samples of Series B (Fig. 5), as the temperature is raised from 25 to 250°C (PIB-B0 to PIB-B3), 44% of the polymer ($\overline{M}_w = 5.67 \times 10^6$ and $\overline{M}_n = 3.22 \times 10^6$) eluting between counts 26 and 33 breaks down (-) to yield (+) products (42%) of lower molecular weight ($\overline{M}_w = 2.89 \times 10^5$ and $\overline{M}_n = 1.45 \times 10^5$, with $\overline{Pd} = 2.0$), eluting between counts 30 and 41. As the temperature is raised from 250 to 300°C and yet higher, chain scissions continue to lower $\overline{M}_w$ toward the limit 1.0×10^4 with depolymerizations accounting for the subsequent weight loss. In this series, depolymerizations are believed to occur at $\overline{M}_w$ values even $> 1.0 \times 10^5$ while the quantity of oligomers formed during the degradation of the PIB samples of Series B is smaller than that noted for Series A. It is possible that the depolymerization reactions in Series B lead to greater monomer evolution.

For the PIB samples of Series C (Fig. 6), as the temperature is raised from 25 to 250°C (PIB-C0 to PIB-C2), 42% of the polymer ($\overline{M}_w = 3.51 \times 10^6$ and $\overline{M}_n = 1.67 \times 10^6$) eluting between counts 26 and

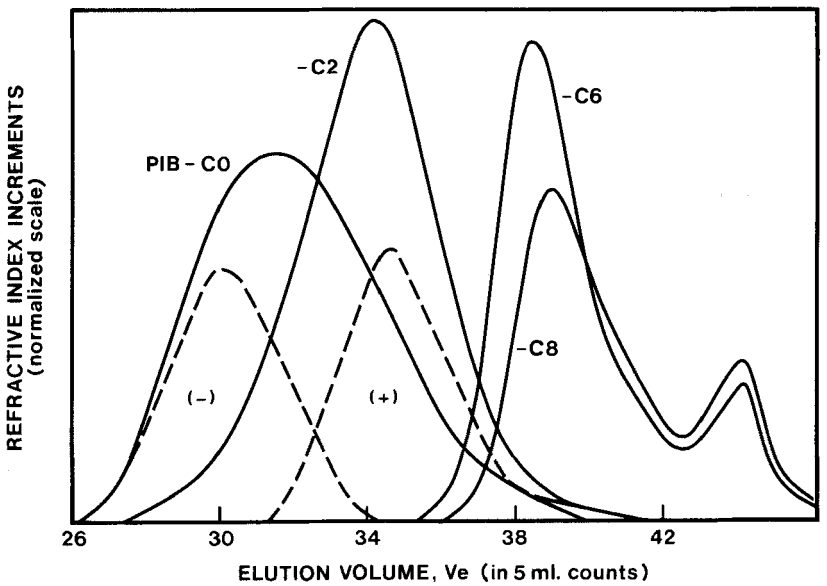

FIG. 6. Normalized GPC molecular weight distributions of undecomposed and decomposed samples of PIB from Series C. See Table 4 for other data.

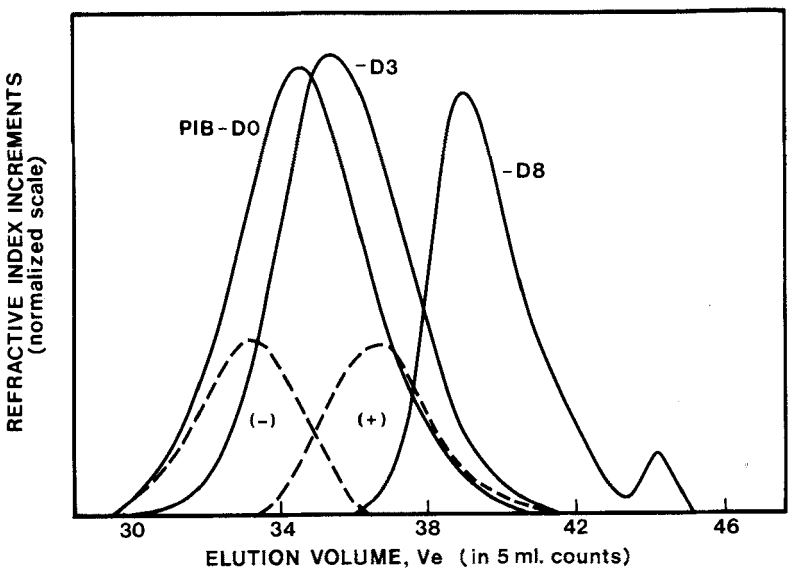

FIG. 7. Normalized GPC molecular weight distributions of undecomposed and decomposed samples of PIB from Series D. See Table 5 for other data.

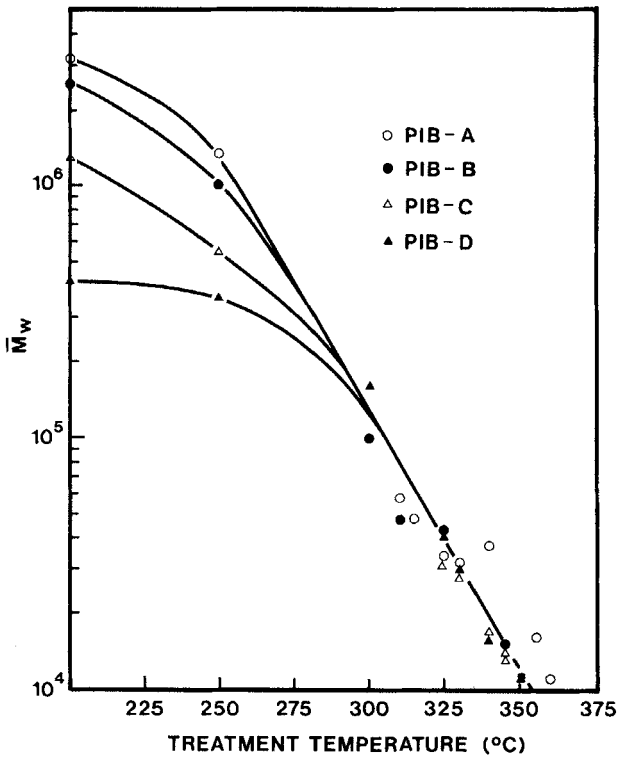

FIG. 8. Variation of molecular weight $\overline{M}_w$, with treatment temperature for samples of PIB from Series A, B, C, and D.

34, breaks down (-) to yield (+) products (42%) of lower molecular weight ($\overline{M}_w = 2.14 \times 10^5$ and $\overline{M}_n = 1.0 \times 10^5$, with $\overline{Pd} = 2.1$) which appear at elution counts lying between 31.5 and 41.5. As the temperature is raised from 250 to 325°C and higher, random chain scissions lower $\overline{M}_w$ to the limit 1.0×10^4 while depolymerization yields quantities of oligomers (with a $\overline{DP}$ of 12) which are comparable to those obtained in Series A but considerably higher than those obtained in Series B where more monomer evolution must be taking place.

For the PIB samples of Series D (Fig. 7), as the temperature is raised from 25 to 300°C (PIB-D0 to PIB-D3), 30% of the polymer ($\overline{M}_w = 6.0 \times 10^5$ and $\overline{M}_n = 3.53 \times 10^5$) eluting between counts 29 and 36, breaks down (-) to yield (+) products (30%) of lower molecular weight ($\overline{M}_w = 7.1 \times 10^4$ and $\overline{M}_n = 3.6 \times 10^4$, with $\overline{Pd} = 2.0$), eluting

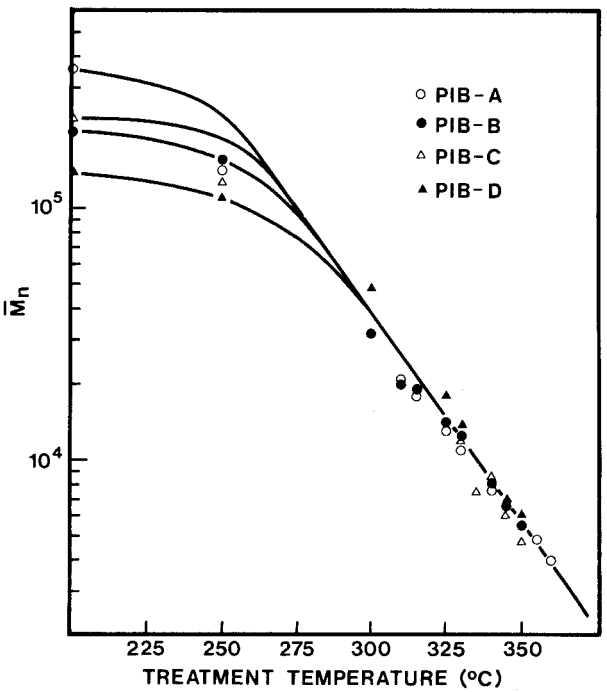

FIG. 9. Variation of molecular weight $\overline{M}_n$ with treatment temperature for samples of PIB from Series A, B, C, and D.

between counts 33 and 41. As the temperature is raised from 300 to 325°C and higher, chain scissions continue to operate, thus lowering $\overline{M}_w$ to the 1.0×10^4 limit.

Depolymerization yields quantities of oligomers which are comparable to those obtained in Series B but smaller than those in either Series A or C. It would appear that more monomer is formed in Series B and D, while more oligomers (with DP of 12) are formed in PIB samples of Series A and C. It should be mentioned here that the NMR spectra of all of the undecomposed PIB samples were identical. It is thought that the cause for the differences in the thermal behavior of these samples must reside in the synthesis route adopted for their production.

Based on the GPC data, $\overline{M}_w$ and $\overline{M}_n$ values were computed for both the undecomposed and the decomposed PIB samples of Series A (Table 2), B (Table 3), C (Table 4), and D (Table 5). Making use of the data, curves exhibiting variation of $\overline{M}_w$ and $\overline{M}_n$ as a function of

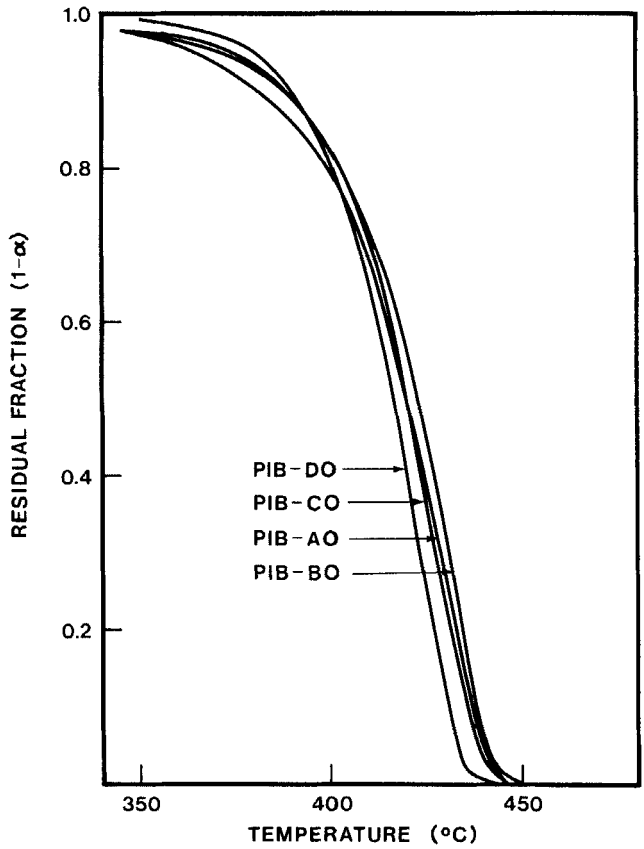

FIG. 10. Dynamic thermogravimetric decompositions of four PIB samples from Series A, B, C, and D at a heating rate of 20 K/min. See Table 6 for other data.

temperature were prepared and are shown in Figs. 8 ($\overline{M}_w$ data) and 9 ($\overline{M}_n$ data). One notes that around 290°C the PIB samples of different molecular weights, viz., PIB-A0 ($\overline{M}_w = 39.4 \times 10^5$, $\overline{M}_n = 3.74 \times 10^5$), PIB-B0 ($\overline{M}_w = 34.4 \times 10^5$, $\overline{M}_n = 3.68 \times 10^5$), PIB-C0 ($\overline{M}_w = 19.3 \times 10^5$, $\overline{M}_n = 2.64 \times 10^5$), and PIB-D0 ($\overline{M}_w = 4.25 \times 10^5$, $\overline{M}_n = 1.37 \times 10^5$), all attain $\overline{M}_w$ and $\overline{M}_n$ values of about 1.0×10^5 and 0.5×10^5, respectively. Between 290 and 375°C, the $\overline{M}_w$ and $\overline{M}_n$ data obtained with the PIB samples of the four series fit a single curve.

TABLE 6. Activation Energy Values Calculated by the Method of Coats and Redfern for the Thermal Decomposition of PIB Samples of Different Molecular Weights

Sample	$\overline{M}_n \times 10^{-4}$	Activation energy (kJ/mol)	
		n = 0	n = 1
PIB-A0	37.4	142.4	-
PIB-B0	36.8	188.0	-
PIB-C0	26.4	183.0	-
PIB-D0	13.7	-	278.0

In Fig. 10 are shown curves representing the dynamic thermogravimetric decomposition (at a heating rate of 20 K/min) of the four PIB samples. Using the method of Coats and Redfern [35], activation energy values were calculated, assuming, successively, orders of reaction of zero and one. The values obtained with the better fit are presented in Table 6. With the exception of PIB-D0, all of PIB samples yielded better fits for zero-order kinetics. An average activation energy of 184 kJ/mol agrees reasonably well with the 205 kJ/mol reported in the literature [3].

Glass Transition Temperature of PIB

The value of the glass transition temperature (T_g) of a polymer is often known to be heating-rate dependent [24-32] and sometimes, though more rarely, cooling-rate dependent [36, 37]. Recent work on substituted polystyrenes using the same techniques has shown that the cooling rate has no effect on T_g [24-32]. Therefore, in the present study, a single cooling rate of 320 K/min was used throughout for the T_g measurements. In Fig. 11 are shown typical DSC thermograms obtained with the undecomposed PIB-A0 sample recorded in the glass transition range at various heating rates. As expected, T_g was found to increase with increasing heating rate. T_g data obtained with a sample cooling rate of 320 K/min and heating rates of 80, 40, 20 and 10 K/min for the undecomposed and a number of decomposed PIB samples are summarized in Table 7. T_{g_e} values for PIB sample of $\overline{M}_n$ ranging from 4.8×10^3 to 374.0×10^3 remained constant within $\pm 3^\circ$

TABLE 7. Variation of T_g as a Function of Heating Rate for Undecomposed and Decomposed Samples of PIB

Sample no.	$\overline{M}_n$ (GPC) $\times 10^{-3}$	T_g at various heating rates				T_{g_e} [a]
		80 K/min	40 K/min	20 K/min	10 K/min	1 K/min
PIB-A0	374.0	213.5	210.5	209.5	207.5	201.5
PIB-A8	7.6	211.5	209.5	209.0	205.0	200.0
PIB-A10	4.8	210.0	207.0	205.5	204.5	198.5
PIB-B12	5.5	209.0	205.5	204.5	203.0	197.0
PIB-C0	264.0	213.0	211.0	210.0	206.5	200.5
PIB-D0	137.0	213.5	211.0	210.0	208.5	203.0
PIB-D8	14.0	210.0	207.5	205.5	204.0	197.5

[a]Extrapolated value at a heating rate (q) of 1 K/min using the equation $\log q = a - b/T_g$ [24-32].

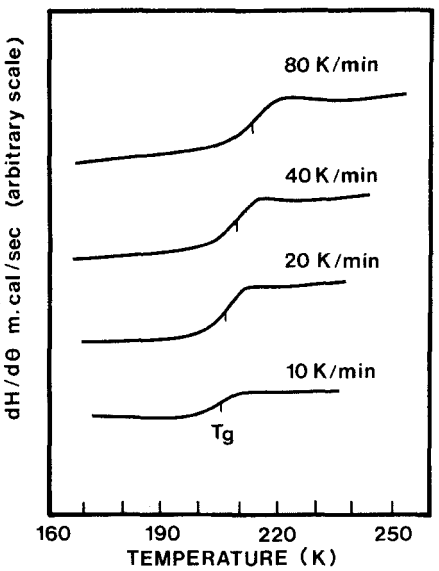

FIG. 11. Typical DSC thermograms of undecomposed PIB-A0 samples recorded in the glass transition region at various heating rates. Cooling rate was constant at 320 K/min. See Table 7 for other data.

of 200 K. These agree well with the value (200 K) reported in the literature [8-16].

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

1. In the isothermal decomposition of PIB, weight-loss is independent of the molecular weight of the polymer.
2. Random chain scissions in PIB samples with $\overline{M}_w$ as high as 6.0×10^6 reduce the molecular weight to an $\overline{M}_w$ of 1.0×10^4 and an $\overline{M}_n$ of 5.0×10^3 after isothermal treatments for 50 min at temperatures ranging from 250 to 375°C. Weight loss is depolymerization controlled. Polymer is not quantitatively converted into monomer; oligomers with a $\overline{DP}$ of 12 are also important products of the decomposition reactions.
3. Activation energy for the decomposition of PIB was evaluated at 184 kJ/mol, a value in reasonable agreement with that reported in the literature.

4. T_{g_e} values of undecomposed and decomposed PIB samples fall with ± 3.0 of 200 K which is in excellent agreement with the value reported in the literature.

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