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Thermal Decomposition and Glass Transition Temperature of Poly(methyl Methacrylate) and Poly(isobutyl Methacrylate)

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ABSTRACT

The thermal decomposition and the glass transition temperatures of poly(methyl methacrylate) (PMMA) and poly(isobutyl methacrylate) (PiBuMA) were studied with a differential scanning calorimeter (DSC). The undecomposed and decomposed polymers were analyzed by gel permeation chromatography (GPC) for molecular weight distributions and by DSC for changes in the thermal properties and glass transition temperatures, T_g. In the isothermal decomposition of PMMA and PiBuMA, depolymerization reactions exclusively are operative. During low temperature decompositions, longer PMMA chains depolymerize first. These are followed by the shorter chains. In the case of PiBuMA, the shorter chains depolymerize first. Some of these undergo chain recombinations to yield very high molecular weight products. For identical values of weight loss, the respective decomposition temperatures for PiBuMA are 40 to 70 K lower than those for PMMA. The activation energies of decomposition (42 kJ/mol for PMMA

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and 67 kJ/mol for PiBuMA) have been found to be lower than those reported in the literature. Although Tg_∞ of PiBuMA (331 K) agrees well with the literature value (326 K), Tg_∞ of atactic PMMA (394 K) is higher than the reported value (378 K).

INTRODUCTION

The thermal degradation [1-14] and the glass transition temperature (T_g) [15-55] of poly(methyl methacrylate) (PMMA) have been studied extensively; however, limited data are available on the thermal degradation [56] and the T_g of poly(isobutyl methacrylate) (PiBuMA) [29, 42, 57, 58]. The degradation behavior of PMMA is characterized by high monomer yields on thermal volatilization [6]. At temperatures below 270°C, chain depolymerization reactions are initiated at the chain-ends where double bonds were formed by radical disproportionation during polymerization [1, 2]. Above 270°C, chain-end decomposition and random scissions occur simultaneously. At temperatures above 300°C, labile chain-end carrying molecules are rapidly removed and random scission degradation can then be followed quantitatively [8]. With PiBuMA [56], the energy of abstraction of monomer molecules from the chain ends is lower than the energy of breaking a carbon-carbon bond in the chain. Consequently, depolymerization processes predominate.

In the glass transition temperature region, the values of Tg_∞ (the glass transition temperature at infinite molecular weight) for isotactic PMMA (311 K) [15, 21, 27, 48] and isotactic PiBuMA (281 K) [42, 58] are considerably higher than their atactic counter parts, i.e., atactic PMMA (378 K) [29, 35, 46] and atactic PiBuMA (326 K) [29, 57].

Thus it was thought of interest to monitor the thermal decomposition of atactic samples of PMMA and of PiBuMA with a T_g and a GPC molecular weight distribution study of the decomposed residues, and then to compare the data with those obtained with PiBuMA [59]. The principal results obtained are summarized in the present article.

EXPERIMENTAL

PMMA and PiBuMA were both obtained from the Aldrich Chemical Co. and used as received. Precise viscosity-average molecular weights, $\overline{M}_v$, of three PMMA samples of different molecular weights were calculated from the intrinsic viscosity data obtained in toluene

TABLE 1. Molecular Characteristics of the Polymers Used for GPC Calibration

Sample	Tacticity P_m	T_{g_e} (K)	$[\eta]^a$ (dL/g)	$\overline{M}_v \times 10^{-4}$	Huggins coefficient k_H	THF elution volume V_e (mL)	$\overline{M}_w \times 10^{-4}$ (GPC)	$\overline{M}_n \times 10^{-4}$ (GPC)	$\overline{M}_w/\overline{M}_n$
PMMA-1	0.30	385	0.136	4.2	0.86	145.0	4.3	0.7	6.1
PMMA-2	0.30	375	0.284	12.0	0.46	140.0	13.0	4.1	3.2
PMMA-0	0.25	394	0.822	54.0	0.48	134.5	66.3	22.2	3.0
PiBuMA	0.23	328	0.515	57.0	0.37	136.5	58.2	22.2	2.6

[a] Data for PMMA were obtained in toluene at 30°C and those for PiBuMA were obtained in acetone at 25°C.

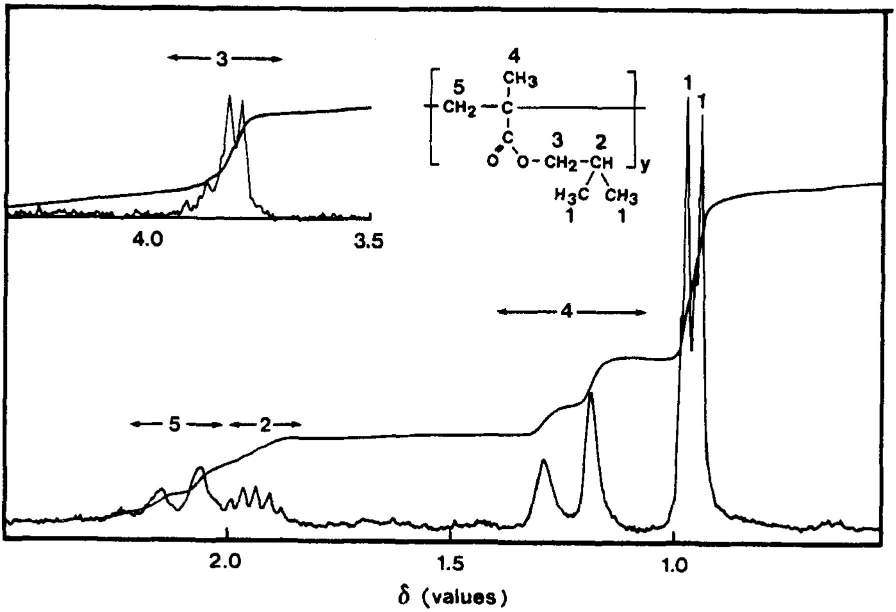


FIG. 1. 220 MHz NMR proton spectrum of PiBuMA-0.

at 30° C using the relation reported in the literature [60]. Molecular weight distributions of the PMMA samples were obtained with a Waters Associates Model 200 gel permeation chromatograph [61-70]. Making use of the viscosity data and the molecular weight distributions of the PMMA samples, a calibration curve relating elution volume V_e (in mL) and molecular weight M yielded the expression

$$\log M = 15.96 - 0.078\ V_e.$$

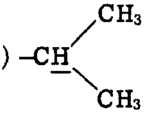
Similarly, an $\overline{M}_v$ value of a PiBuMA sample was calculated from the intrinsic viscosity data obtained in acetone [71-73] at 25°C. Making use of the viscosity and GPC molecular weight distribution data, V_e was related to M as follows: $\log M = 16.27 - 0.078\ V_e$. Calculated values of $\overline{M}_w$ and $\overline{M}_n$ for PMMA and PiBuMA are presented in Table 1.

Nuclear magnetic resonance (NMR) analyses of the polymer used for the decomposition studies (PMMA-0) were carried out with a Varian 220 MHz NMR spectrometer using o-dichlorobenzene as solvent at 110°C and tetramethylsilane (TMS) as internal standard. Making use of the chemical shift assignments for isotactic, heterotactic, and syndiotactic triads of PMMA reported in the literature [74], a Pm value of 0.25 was calculated for PMMA-0.

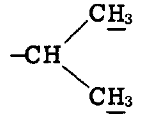
The NMR spectrum of PiBuMA-0 (Fig. 1) was also recorded as described above. The highlights of the spectrum are as follows:

(a) $-OC\underline{H}_2-$ at $\delta = 3.78,\ 3.81,\ 3.86$ (triplet)

(b) $-C\underline{H}_2-$ at $\delta = 2.05,\ 2.14,\ 2.23$ (triplet)

(c)  at $\delta = 1.84,\ 1.87,\ 1.90,\ 1.93,\ 1.96,\ 1.99,\ 2.02$ (heptet)

(d) $-C\underline{H}_3$ at $\delta = 1.17,\ 1.29,\ 1.41$ (triplet)

(e)  at $\delta = 0.96$ and 0.99 (doublet)

PiBuMA-0 is an atactic polymer with a Pm of 0.23.

A Perkin-Elmer model 2B differential scanning calorimeter (DSC) operating with an atmosphere of pure dry helium was used for the isothermal decomposition of PMMA and PiBuMA, while a Perkin-Elmer model 1 thermogravimetric scanning balance (TGS) operating in a pure dry nitrogen atmosphere was used for the dynamic decomposition of the polymers. The T_g values of the undecomposed and decomposed samples of PMMA and PiBuMA were determined with the DSC apparatus [7-77].

RESULTS AND DISCUSSION

Thermal Decomposition of PMMA and PiBuMA

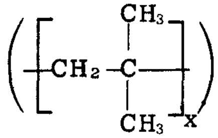
In Tables 2 and 3 are summarized the values of the weight loss (α in %), the molecular weights ($\overline{M}_w$ and $\overline{M}_n$), and the polydispersity ratios ($\overline{M}_w/\overline{M}_n$) obtained with PMMA (Table 2) and PiBuMA (Table 3) both before and after their isothermal treatment at various temperatures for a fixed period of 50 min each. Using these data, curves showing the variation of α with temperature are given in Fig. 2. For comparison purposes, data for 50 min isothermal treatments of polyisobutylene (PIB) [59] are also plotted in this figure. For all values of α, the thermal stability of the three polymers follows the order PIB > PMMA > PiBuMA. It is interesting to note that replacing one of the CH_3 groups on PIB  $\left(\left[-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-\right]_x\right)$ by a - COO CH_3 group to

TABLE 2. Data on PMMA Samples Subjected to Isothermal Treatment at Various Temperatures for 50 min Periods

		Volatilized fraction				Residue			
Sample	Treatment temperature (°C)	α (%)	$\overline{M}_w \times 10^{-3}$ (GPC)	$\overline{M}_n \times 10^{-3}$ (GPC)	$\overline{M}_w/\overline{M}_n$	Weight (%)	$\overline{M}_w \times 10^{-3}$ (GPC)	$\overline{M}_n \times 10^{-3}$ (GPC)	$\overline{M}_w/\overline{M}_n$
PMMA-0	25	0.0	-	-	-	100.0	663	222	3.0
PMMA-1	235	10.0	1340	708	1.9	90.0	516	182	2.8
PMMA-2	250	16.6	1160	554	2.1	83.4	474	166	2.9
PMMA-3	265	23.9	1060	497	2.1	76.1	461	162	2.9
PMMA-4	290	31.4	1130	521	2.2	69.6	458	157	2.9
PMMA-5	305	37.4	1021	432	2.4	62.6	376	133	2.8
PMMA-6	325	50.5	872	450	1.9	49.5	318	120	2.7

TABLE 3. Data on PiBuMA Samples Subjected to Isothermal Treatment at Various Temperatures for 50 min Periods

		Volatilized fraction				Residue			
Sample	Treatment temperature (°C)	α (%)	$\overline{M}_w \times 10^{-3}$ (GPC)	$\overline{M}_n \times 10^{-3}$ (GPC)	$\overline{M}_w/\overline{M}_n$	Weight (%)	$\overline{M}_w \times 10^{-3}$ (GPC)	$\overline{M}_n \times 10^{-3}$ (GPC)	$\overline{M}_w/\overline{M}_n$
PiBuMA-0	25	0.0	-	-	-	100.0	582	222	2.6
PiBuMA-1	185	12.3	337	269	1.3	87.7	754	250	3.0
PiBuMA-2	200	13.3	361	288	1.3	86.7	677	203	3.3
PiBuMA-3	210	16.3	390	304	1.3	83.7	692	197	3.5
PiBuMA-4	220	24.0	414	306	1.4	76.0	659	212	3.1
PiBuMA-5	230	27.3	552	348	1.6	72.7	599	188	3.2
PiBuMA-6	235	30.4	615	372	1.7	69.6	571	179	3.2
PiBuMA-7	240	43.2	746	459	1.6	56.8	427	162	2.6

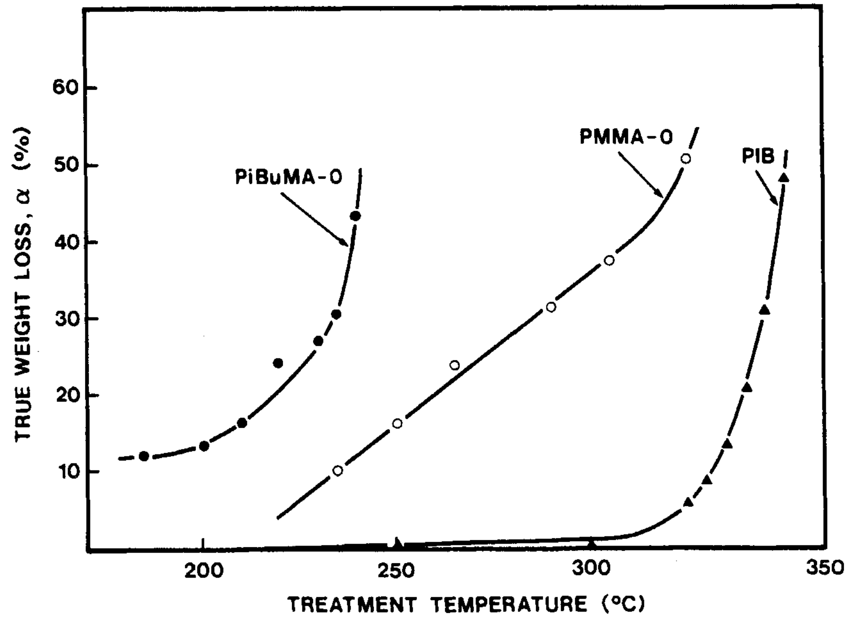
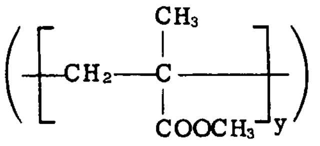
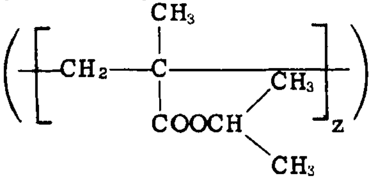


FIG. 2. Variation of α with treatment temperature for PMMA-0, PiBuMA-0, and PIB (see Tables 2 and 3 for other data).

form PMMA  $\left(\left[-CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}-\right]_y\right)$ leads to a decrease in the thermal stability of the polymer. Further replacements in PMMA to form PiBuMA  $\left(\left[-CH_2-\overset{CH_3}{\underset{COOCH(CH_3)_2}{C}}-\right]_z\right)$ leads to an additional decrease in thermal stability. This means that the presence of a $-COO_x$ group on the polymer chain favors an increase in the formation of radicals which bring about the depolymerization reactions [1, 2, 6, 8, 56].

In Fig. 3 are shown normalized GPC molecular weight distribution curves of undecomposed and decomposed samples of PMMA. The maximum at elution count 26.75 (133.75 mL) in the GPC molecular weight distribution of PMMA-0 moves to 27.0 (135 mL) after a 50-min

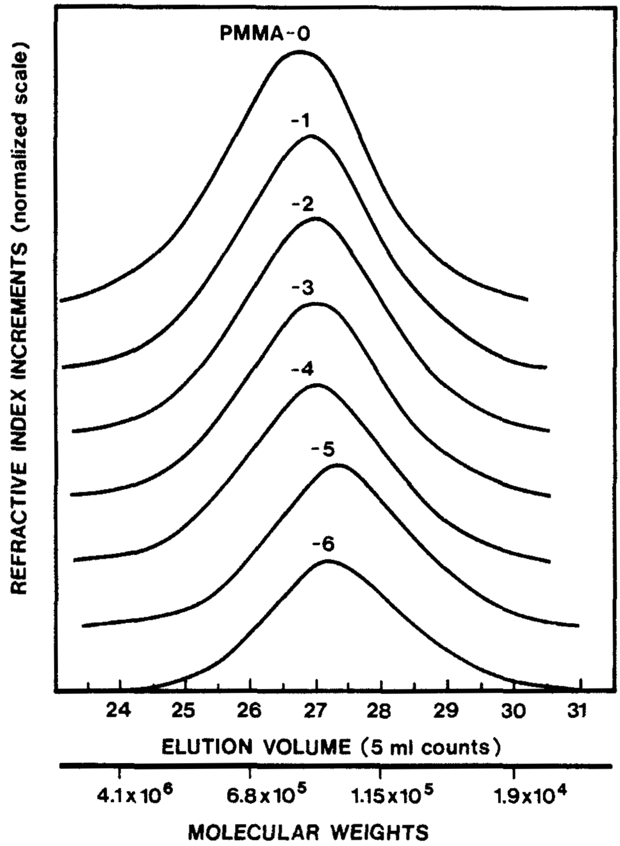


FIG. 3. Normalized GPC molecular weight distributions of undecomposed and decomposed samples of PMMA (see Table 2 for other data).

isothermal treatment at 250° C (PMMA-2). In the temperature range 250 to 290° C, the position of the maximum remains unchanged at an elution count of 27.0 (135 mL). On raising the temperature above 290° C, the maximum shifts to a slightly higher elution count, 27.25 (136.25 mL). The overall values of $\overline{M}_w$ and $\overline{M}_n$ (Table 2 and Fig. 4) show a regular but slight decrease with thermal treatments; however, the decreases do not arise from random chain-scissions. The depolymerization of the longer chains in the higher molecular weight fractions of PMMA appears to have a lower activation energy. As a consequence, these chains depolymerize first as is shown in Fig. 5, where the normalized GPC molecular weight distribution of the

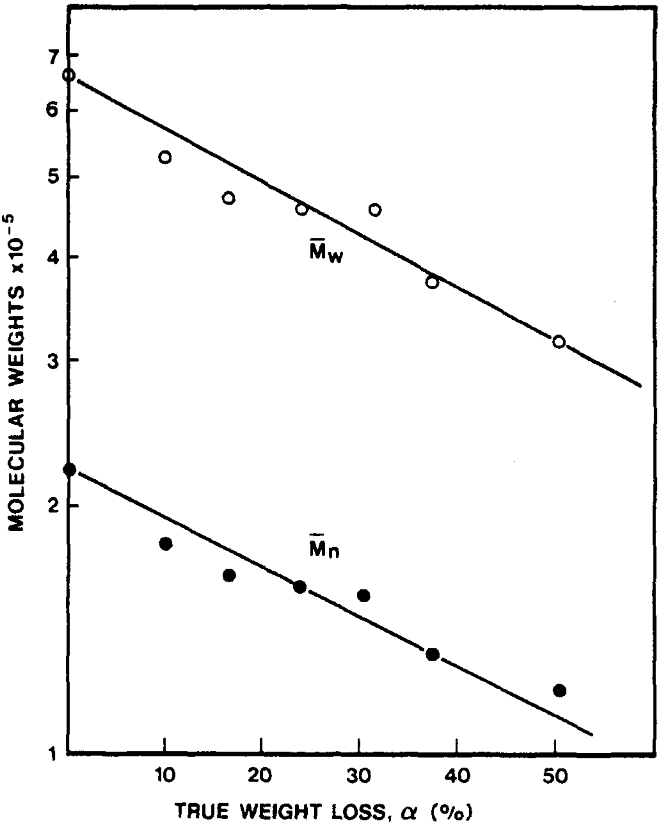


FIG. 4. Variation of PMMA molecular weights ($\overline{M}_w$ and $\overline{M}_n$) as a function of α.

decomposed polymers PMMA-1, PMMA-2, PMMA-4, and PMMA-6 are successively subtracted from that of PMMA-0. The volatilized fraction (-) of the polymer is represented by the hashed lines. The hashed area for the case PMMA-0/PMMA-6 has been converted into a molecular weight distribution, as is shown in the lower part of Fig. 5. Values of $\overline{M}_w$ and $\overline{M}_n$ of the volatilized fractions were then calculated from these. The results are presented in Table 2. The data clearly show that the higher molecular weight fractions having a most probable distribution ($\overline{M}_w/\overline{M}_n$ = 2.0) decompose earlier at temperatures ranging from 235 to 300°C, followed, as the temperature is raised, by the decomposition of the lower molecular weight fractions.

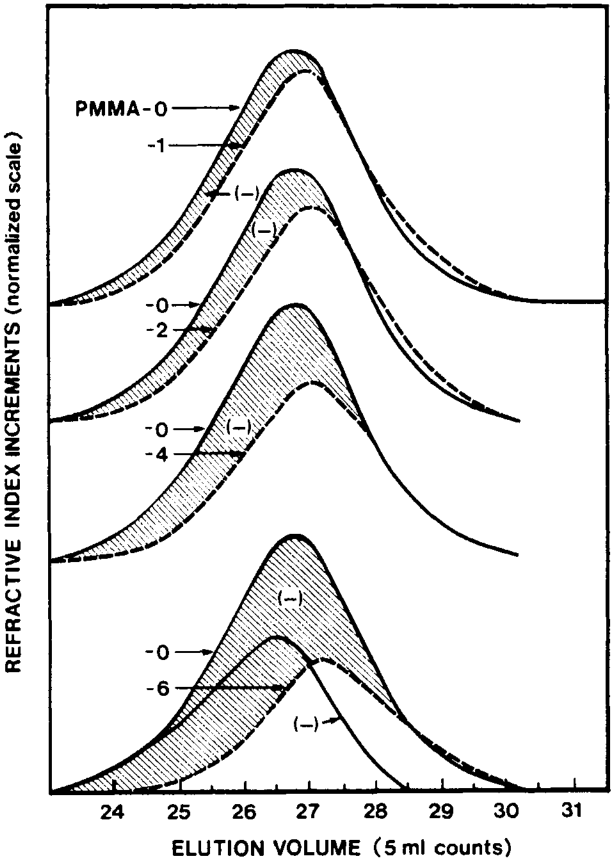


FIG. 5. Graphical method of analysis whereby GPC molecular weight distribution curves are broken down into components. The case of PMMA-0 subjected to 50 min decomposition periods at 235° (PMMA-1), 250° (PMMA-2), 290° (PMMA-4), and 325°C (PMMA-6) (see Table 2 for other data).

In Fig. 6 are shown the normalized GPC molecular weight distributions of undecomposed and decomposed samples of PiBuMA. The maximum, at elution count 27.25 (136.25 mL) in the GPC molecular weight distribution of PiBuMA-0, moves to a lower value–27 (135 mL) in the higher molecular weight region–following 50 min isothermal treatments between 185 and 220°C. The maximum at elution count 27 (135 mL) then shifts back to 27.25 on heating the PiBuMA-0 sample at 230°C. It continues to shift toward yet higher values (in the lower molecular weight region) as isothermal treatments are

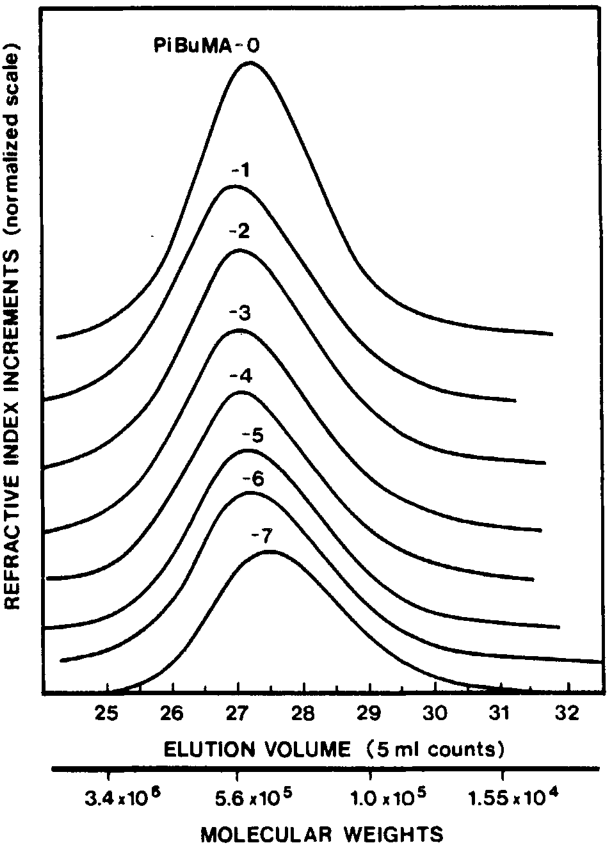


FIG. 6. Normalized GPC molecular weight distributions of undecomposed and decomposed samples of PiBuMA (see Table 3 for other data).

carried out at temperatures higher than 230° C. The overall values of $\overline{M}_w$ and $\overline{M}_n$ (Table 3) for the decomposed polymers, however, do not show any definite trends. The increase in the $\overline{M}_w$ values following isothermal treatments at 185° C (PiBuMA-1), 200° C (PiBuMA-2), 210° C (PiBuMA-3), and 220° C (PiBuMA-2) may originate from two sources, viz., a) chain recombination and b) preferential depolymerization of lower molecular weight fractions of the polymer.

To better understand the decomposition reactions, the normalized distributions of PiBuMA-1, PiBuMA-3, PiBuMA-4, and PiBuMA-6 were successively subtracted from that of PiBuMA-0 (Fig. 7). The

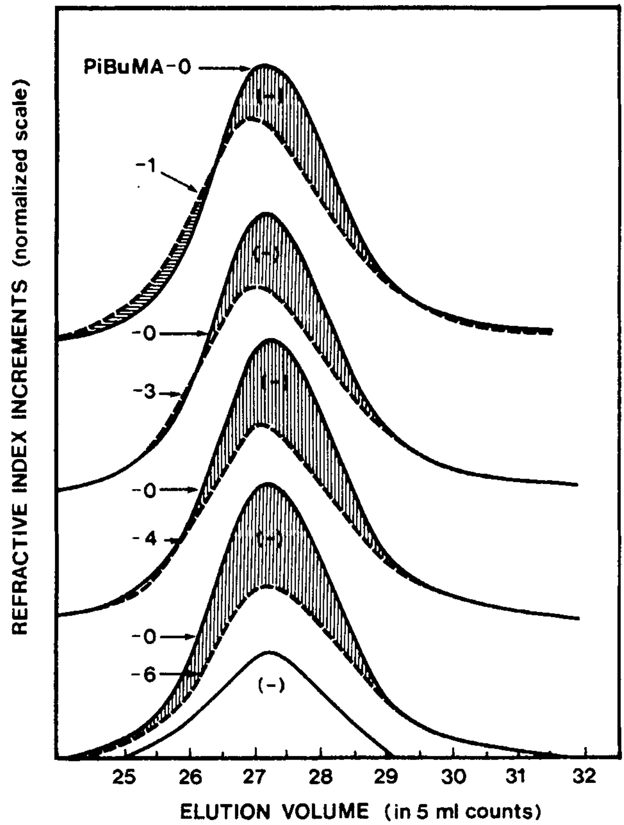


FIG. 7. Graphical method of analysis whereby GPC molecular weight distribution curves are broken down into components. The case of PiBuMA subjected to 50 min decomposition periods at 185° (PiBuMA-1), 210° (PiBuMA-3), 220° (PiBuMA-4), and 235°C (PiBuMA-6) (see Table 3 for other data).

volatilized fraction (-) of the polymer is represented by vertical hash lines. As with PMMA, the hashed areas were converted to molecular weight distributions (one is shown in Fig. 7: PiBuMA-0/PiBuMA-6). From these, values of $\overline{M}_w$ and $\overline{M}_n$ for the volatilized fractions were calculated. These are listed in Table 3. The higher molecular weight fraction (+) (horizontal hash lines) in some of the residues were also converted into molecular weight distributions (not shown here) and their $\overline{M}_w$ and $\overline{M}_n$ values calculated. One notes that the molecular weights of the volatilized fractions increase consistently with increasing treatment temperature. Furthermore, at lower temperatures

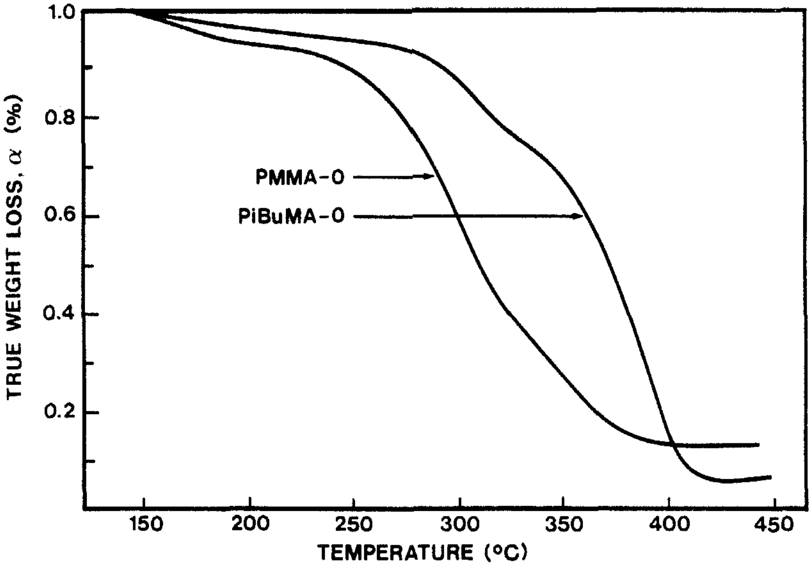


FIG. 8. Dynamic thermogravimetric decomposition of PMMA-0 and PiBuMA-0 at a heating rate of 20 K/min (see Table 4 for other data).

(185 to 210°C), unexpected high molecular weight polymers are formed. On 50 min isothermal treatment of PiBuMA-0 at 185° C, 11.0% (GPC weight) of the low molecular weight fraction ($\overline{M}_w = 3.37 \times 10^5$ and $\overline{M}_n = 2.69 \times 10^5$) volatilizes yielding monomer, whereas 5.5% of this material recombines to yield products with an $\overline{M}_w$ of 2.57×10^6 and an $\overline{M}_n$ of 1.8×10^6. At 200° C, 12.0% of the low molecular weight fraction ($\overline{M}_w = 3.61 \times 10^5$ and $\overline{M}_n = 2.88 \times 10^5$) volatilizes with 3.0% of this material recombining to form products with an $\overline{M}_w$ of 2.26×10^6 and an $\overline{M}_n$ of 1.68×10^6. At 210° C, 16.6% of the low molecular weight fraction ($\overline{M}_w = 3.90 \times 10^6$ and $\overline{M}_n = 3.04 \times 10^5$) volatilize with 2.4% of the material recombining to form products with an $\overline{M}_w$ of 2.71×10^6 and an $\overline{M}_n$ of 2.18×10^6. In the temperature range 210 to 240° C, no unusual reaction products are observed and volatilization via depolymerization yields monomer. The preferential depolymerization of the lower molecular weight fractions (shorter chains) to yield monomer at low temperature combined with the formation of higher molecular weight products (by chain-chain recombination) leads to overall high values of $\overline{M}_w$

TABLE 4. Activation Energy Values Calculated by the Method of Coats and Redfern for the Thermal Decomposition of PMMA and PiBuMA

Sample	$\overline{M}_n \times 10^{-4}$ (GPC)	Activation energy (kJ/mol)[a] n = 0	Activation energy (kJ/mol)[a] n = 1
PMMA-0	22.2	42.0	-
PiBuMA-0	22.2	-	67.0
PIB-0[b]	26.4	183.0	-

[a] n is the order of reaction.
[b] See Ref. 59.

and $\overline{M}_n$ for PiBuMA-1, PiBuMA-2, and PiBuMA-3. In this aspect, the thermal behavior of PiBuMA is very much different from that of PMMA, where, at low temperatures, the preferential depolymerization involves the high molecular weight fractions of the polymer.

In Fig. 8 are shown curves representing the dynamic thermogravimetric decomposition, at a heating rate of 20 K/min, of PMMA-0 and PiBuMA-0. By using the method of Coats and Redfern [78], activation energy values were calculated assuming successively zero- and first-order kinetics. The values obtained with the better fit are presented in Table 4. PMMA-0 follows zero-order kinetics whereas the PiBuMA-0 data best fit first-order kinetics. Values of 42.0 kJ/mol for PMMA-0 and 67 kJ/mol for PiBuMA are, however, lower than the values reported in the literature [3]. The differences are believed to arise from the method used in the activation energy calculations.

Glass Transitions of PMMA and PiBuMA

The glass transition temperature (T_g) of a polymer is usually heating-rate dependent [61-70] and often cooling-rate dependent [79-80] although recent work on substituted polystyrenes showed that the cooling rates used had no significant effect on their T_g's [61-70].

In the present study a cooling rate of 320 K/min was used for the measurements. In Figs. 9 (PMMA-5) and 10 (PiBuMA-2) are shown typical DSC thermograms recorded at various heating rates and, as expected, T_g's increase with increasing heating rate. The T_g data obtained with a sample cooling rate of 320 K/min and heating rates

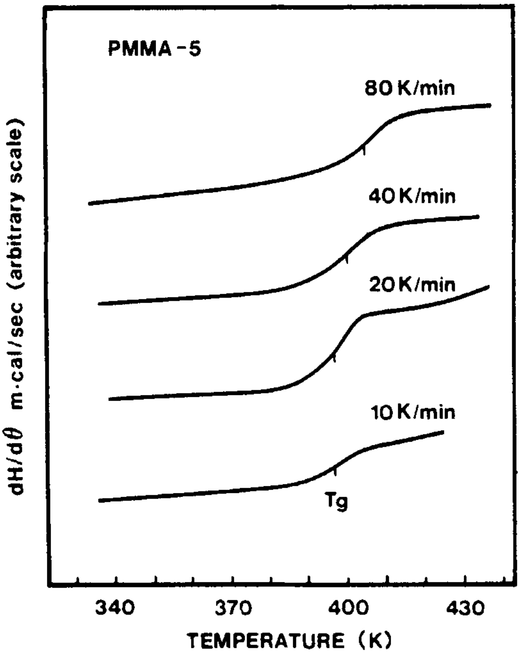


FIG. 9. Typical DSC thermograms of PMMA-5, recorded in the glass transition region at various heating rates. Cooling rate was constant at 320 K/min (see Table 5 for other data).

of 80, 40, 20, and 10 K/min for undecomposed and decomposed polymer samples are summarized in Tables 5 (PMMA) and 6 (PiBuMA). T_{g_e} values of undecomposed and decomposed samples of PMMA remain constant within ±1 of 394 K (Table 5). Because of the high $\overline{M}_n$ ($> 1.0 \times 10^5$) values of the PMMA samples, the T_{g_e} value of 394 K may be considered as a T_{g_∞} value, but this value is about 16 K higher than the reported value 378 K [29, 35, 46]. T_{g_e} values of undecomposed and decomposed samples of PiBuMA remain within ±5 of 331 K (Table 6). In this case as well, T_{g_e} and T_{g_∞} are considered to be the same because of the high $\overline{M}_n$ ($> 1.6 \times 10^5$) values of all of the PiBuMA samples studied. A T_{g_∞} of 331 K for atactic PiBuMA is close to the value of 326 K reported in the literature [29, 57].

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

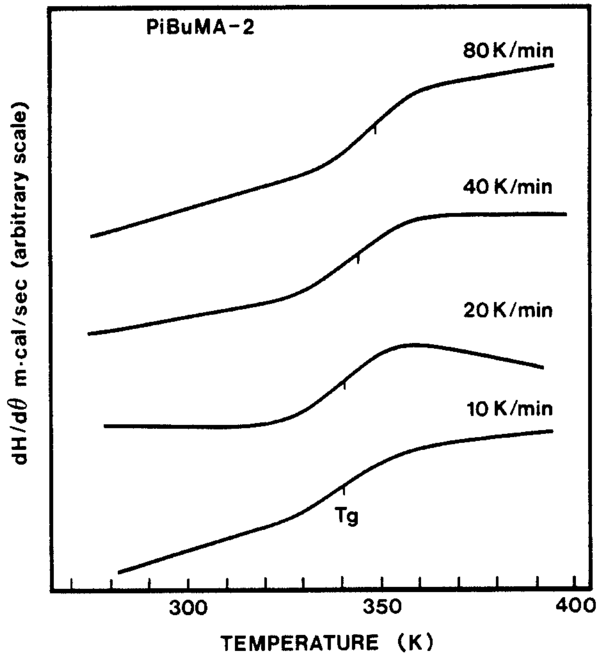


FIG. 10. Typical DSC thermograms of PiBuMA-2, recorded in the glass transition region at various heating rates. Cooling rate was constant at 320 K/min (see Table 6 for other data).

1. For identical values of α, the respective decomposition temperatures for PiBuMA-0 are 40 to 70°C lower than those for PMMA-0, indicating the importance of the substituent in controlling the thermal stability of the polymer;
2. In the isothermal decomposition of PMMA-0 and PiBuMA-0, depolymerization reactions account for the weight loss. Thermal treatment of PMMA-0 at the lower temperatures results in the depolymerization of the longer polymer chains at first, then the shorter polymer chains. In the case of PiBuMA, the shorter chains depolymerize first. Short-chain polymer is also shown to undergo chain recombination, yielding very high molecular weight products.
3. The activation energies of decomposition for PMMA-0 and PiBuMA-0 were found to be lower than those reported in the literature.
4. Although the T_{g_∞} value of 331 K for PiBuMA agrees reasonably well with the value (326 K) reported in the literature, a T_{g_∞}

TABLE 5. Variation of T_g as a Function of Heating Rate for Undecomposed and Decomposed Samples of PMMA

	$\overline{M}_n$ × 10^{-3}	T_g (K) at various heating rates (K/min)				T_{g_e}[a] (K),
Sample	GPC	80	40	20	10	1 K/min
PMMA-0	222	399	397	396	395.5	393
PMMA-1	182	405	401	400	-	394
PMMA-2	166	404	402	400	400	394
PMMA-3	162	404	402	400	400	394
PMMA-4	157	405	403	401	400	394
PMMA-5	133	404	402	400	400	394
PMMA-6	120	402	401	400	-	395

[a] Extrapolated value at a heating rate (q) of 1 K/min using the equation $\log q = a - b/T_g$ [75-77].

TABLE 6. Variation of T_g as a Function of Heating Rate for Undecomposed and Decomposed Samples of PiBuMA

	$\overline{M}_n$ × 10^{-3}	T_g (K) at various heating rates (K/min)				T_{g_e}[a] (K),
Sample	GPC	80	40	20	10	1 K/min
PiBuMA-0	222	345	342	339	337	328
PiBuMA-1	250	349	346	342	343	332
PiBuMA-2	203	349	346	343	343	332
PiBuMA-3	197	347	345	339	-	326
PiBuMA-4	212	349	345	343	340	331
PiBuMA-5	188	351	347	346	345	336
PiBuMA-6	179	347	343	339	-	326
PiBuMA-7	162	347	345	339	-	326

[a] See footnote in Table 5.

value of 394 K for atactic PMMA is quite a bit higher than the literature value of 378 K.

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