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Thermal Decomposition and Glass Transition Temperature of Poly(ethyl Methacrylate) and Poly(n-butyl Methacrylate)

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ABSTRACT

The thermal decomposition and the glass transition temperature of poly(ethyl methacrylate) (PEMA) and poly(n-butyl methacrylate) (PnBuMA) 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 temperature, T_g. For all values of weight loss, α, the thermal stability of the polymers follows the order poly(methyl methacrylate) (PMMA) > PEMA > PnBuMA > poly(isobutyl methacrylate) (PiBuMA) suggesting that, as the bulk size of the substituent increases, the thermal stability decreases. GPC molecular weight distribution data show that PEMA decomposition is dominated by depolymerization. Isothermal decomposition of PnBuMA is also depolymerization controlled. A major part of the low molecular weight fraction ($\overline{M}_w \times 10^{-3}$ =

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76 to 96, $\overline{M}_n \times 10^{-3}$ = 52 to 74) volatilizes yielding monomer, whereas a minor part of the same fraction undergoes chain recombinations yielding higher molecular weight products with an $\overline{M}_w \times 10^{-5}$ of 8.0 and an $M_n \times 10^{-5}$ of 6.0. Activation energy values of decomposition for PEMA (58 kJ/mol) and PnBuMA (70 kJ/mol) (at infinite molecular weight) are lower than those reported in the literature. T_{g_∞} of 345 ± 5 K for PEMA and 293 ± 5 K for PnBuMA are in good agreement with the literature values.

INTRODUCTION

Data on the thermal degradation [1] and the glass transition temperature (T_g) [2-12] of poly(ethyl methacrylate) (PEMA) has been reported. Limited data are also available on the thermal degradation [1, 13, 14] and the T_g [2, 5, 7-10, 15-17] of poly(n-butyl methacrylate) (PnBuMA). Grassie and McCallum [1] observed that the thermal degradation behaviors of PEMA and PnBuMA are quite similar. Sazanov et al. [13] reported that the thermal degradation of poly(isobutyl methacrylate) (PiBuMA) is very similar to that of PnBuMA. In another study [18] on the thermal decomposition of poly(methyl methacrylate) (PMMA) and PiBuMA, it was shown that although the overall degradation patterns of polyalkyl methacrylates (PAMA) are similar, there are subtle differences observed in the gel permeation chromatographic (GPC) studies of the undecomposed and decomposed products of PAMA. For instance, in the isothermal decomposition of PMMA at low temperatures (235°C) and percent weight loss (α = 10%), the longer polymer chains depolymerize first and are followed by the shorter chains. In the case of the isothermal decomposition of PiBuMA however, the reverse was observed: the shorter chains depolymerize first, then the longer ones. Furthermore, some of the shorter chains are found to undergo chain recombinations, yielding very high molecular weight products.

It was thought that it would be of interest to follow the thermal decomposition of atactic samples of PEMA and PnBuMA by GPC and T_g. The principal results obtained are summarized in the following paragraphs.

EXPERIMENTAL

PEMA and PnBuMA samples obtained from the Aldrich Chemical Co. were used as received. Viscosity-average molecular weight, $\overline{M}_v$, of PEMA was calculated from the intrinsic viscosity data

TABLE 1. Solution Properties of Polymers Used for GPC Calibration

Sample	Solvent	Temperature (°C)	$[\eta]$ (dL/g)	$\overline{M}_v \times 10^{-4}$	k_H[a]	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	Toluene	30	0.136	4.2	0.86	145	4.3	0.7	6.1
PMMA-2	Toluene	30	0.284	12.0	0.46	140	13.1	4.1	3.2
PMMA-0	Toluene	30	0.822	54.0	0.48	134.5	66.3	22.2	3.0
PEMA-0	Ethyl acetate	35	0.690	31.5	0.22	136	34.0	12.6	2.7
	Butanone	23	0.717	37.5	0.05				
PnBuMA-0	Benzene	30	0.584	25.6	0.36	136	32.0	7.3	4.4

[a] k_H is the Huggins coefficient.

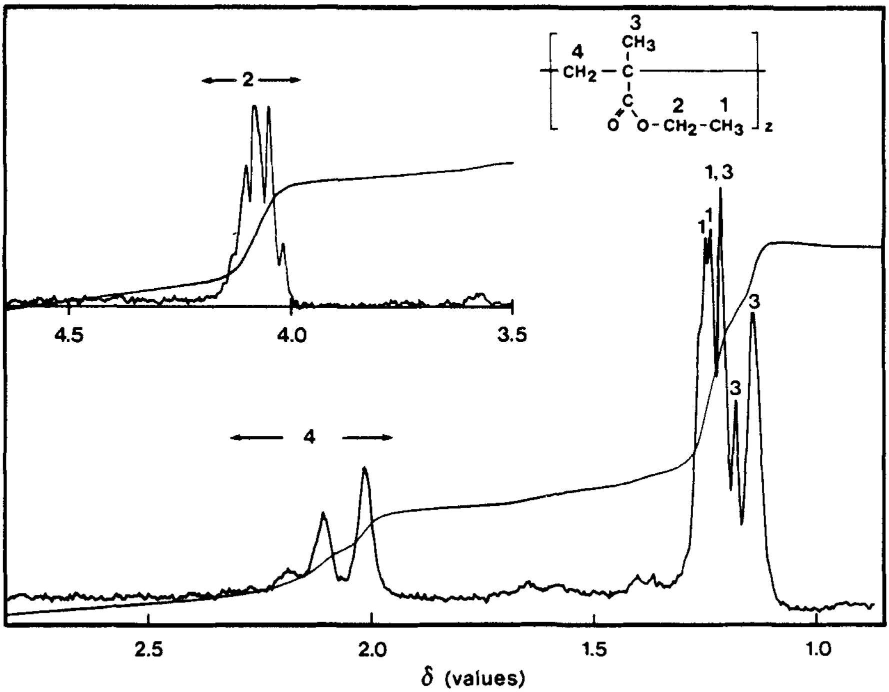

FIG. 1. 220 MHz proton spectrum of PEMA-0.

obtained in ethyl acetate at 35°C [19] and in butanone at 23°C [20]. Molecular weight distributions of PEMA were obtained with a Waters Associates model 200 GPC [21-30]. Making use of the viscosity and the GPC molecular weight distribution data of PEMA and PMMA [18], a calibration curve relating elution volume, V_e, and molecular weight M, yielded: log M = 15.96 - 0.078 V_e.

Similarly, $\overline{M}_v$ values of PnBuMA were calculated from intrinsic viscosity data obtained in benzene at 30°C [31]. Making use of the viscosity and the GPC data, V_e was found to relate to M as follows: log M = 15.61 - 0.078 V_e. Calculated values of the weight-average molecular weight $\overline{M}_w$ and the number-average molecular weight $\overline{M}_n$ for PEMA and PnBuMA are presented in Table 1.

Nuclear magnetic resonance (NMR) analyses of undecomposed samples PEMA-0 and PnBuMA-0, later used for decomposition studies, were carried out with a Varian 220 MHz NMR spectrometer in o-dichlorobenzene at 110°C using tetramethylsilane (TMS) as the internal standard. The highlights of the spectra of PEMA-0 (Fig. 1) and PnBuMA-0 (Fig. 2) are as follows.

For PEMA-0

a) $-OC\underline{H}_2-$ at δ = 4.01, 4.04, 4.07, 4.11 and 4.14 (pentuplet)

b) $-C\underline{H}_2-$ at δ = 2.02, 2.11, and 2.20 (triplet)

$-C\underline{H}_3$ at δ = 1.15, 1.19, and 1.23 (triplet with peak width of 9 Hz)

$-CH_2-C\underline{H}_3$ at δ = 1.23, 1.245, and 1.26 (triplet with peak width of 3.3 Hz)

PEMA-0 is an atactic polymer with a P_m value of 0.31.

For PnBuMA-0

$-OC\underline{H}_2-$ at δ = 3.64, 3.66, 3.69, 3.72, and 3.75 (pentuplet)

$-C\underline{H}_2-$ at δ = 2.04, 2.13, and 2.22 (triplet)

$-OCH_2-C\underline{H}_2-CH_2-$ at δ = 1.55, 1.58, 1.61, 1.64, 1.67, and 1.7 (sextuplet)

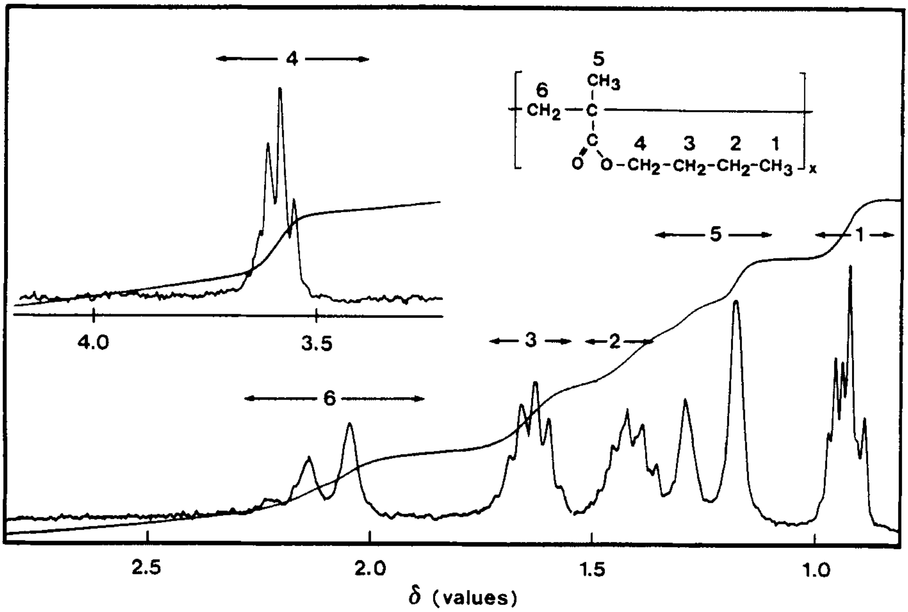

FIG. 2. 220 MHz proton spectrum of PnBuMA-0.

$-OCH_2-CH_2-C\underline{H}_2-$ at $\delta = 1.35$, 1.38, 1.41, 1.44, and 1.47 (pentuplet)

$-C\underline{H}_3$ at $\delta = 1.41$ (mm), 1.29 (mr), 1.17 (rr). $P_m = 0.22$

$$-(CH_2)_3-C\underline{H}_3 \text{ at } \begin{cases} \delta = 0.88,\ 0.91, \text{ and } 0.94 \text{ (triplet)} \\ \delta = 0.90,\ 0.93, \text{ and } 0.96 \text{ (triplet)} \end{cases}$$

PnBuMA-0 is an atactic polymer with a P_m value of 0.22.

A Perkin-Elmer (model 2B) differential scanning calorimeter (DSC) operating with pure dry helium was used for the isothermal decompositions of PEMA and PnBuMA whereas a second Perkin-Elmer instrument, the 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 the decomposed polymer were determined with the DSC apparatus [32-34].

RESULTS AND DISCUSSION

Thermal Decomposition of PEMA and PnBuMA

In Tables 2 and 3 are summarized the values of $\overline{M}_w$, $\overline{M}_n$, and the polydispersity ratio $\overline{M}_w/\overline{M}_n$ obtained with PEMA (Table 2) and PnBuMA (Table 3) both before and after isothermal treatments 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. 3. For comparison purposes, data for the 50 min isothermal treatment of PMMA and PiBuMA [18] are also plotted in this figure. One notes that for low values of α the data obtained with PEMA and PMMA fit a single curve while those obtained with PiBuMA and PnBuMA fit yet another single curve. For identical values of α, the respective decomposition temperatures for PnBuMA are 40 to 50°C lower than those for PEMA. For all values of α, the thermal stability of the four polymers follows the order PMMA > PEMA > PnBuMA > PiBuMA. It is interesting to note that as the bulk size of the substituent increases, the thermal stability of the polymer decreases.

In Fig. 4 are shown normalized GPC distributions of undecomposed and decomposed samples of PEMA. The maxima at elution count 27.25 (135.25 mL) in the GPC distributions of both the undecomposed and the decomposed polymers do not change. The values of $\overline{M}_w$ and $\overline{M}_n$ (Table 2) change but slightly. The decreases in $\overline{M}_w$ and $\overline{M}_n$ arise from depolymerization reactions alone and no chain scissions are involved.

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

		Volatilized fraction				Residue			
Sample	Decomposition temperature (°C)	Weight loss α (%)	$\overline{M}_w \times 10^{-3}$ (GPC)	$\overline{M}_n \times 10^{-3}$ (GPC)	$\overline{M}_w/\overline{M}_n$	Weight % (100-α)	$\overline{M}_w \times 10^{-3}$ (GPC)	$\overline{M}_n \times 10^{-3}$ (GPC)	$\overline{M}_w/\overline{M}_n$
PEMA-0	25	0.0	-	-	-	100.0	340	126	2.7
PEMA-1	220	9.1	273	252	1.1	90.9	352	141	2.5
PEMA-2	235	12.1	344	239	1.4	87.9	323	133	2.4
PEMA-3	250	17.9	368	255	1.4	82.1	309	131	2.4
PEMA-4	260	20.7	332	227	1.5	79.3	324	138	2.3
PEMA-5	270	33.1	419	262	1.6	66.9	280	116	2.4
PEMA-6	280	35.5	384	243	1.6	64.5	295	119	2.5
PEMA-7	290	41.3	333	192	1.7	58.7	326	119	2.9
PEMA-8	300	54.5	392	212	1.9	45.5	255	96	2.7

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

Sample	Decomposition temperature (°C)	Volatilized fraction				Residue			
		Weight loss α (%)	$\overline{M}_w \times 10^{-3}$ (GPC)	$\overline{M}_n \times 10^{-3}$ (GPC)	$\overline{M}_w/\overline{M}_n$	Weight % (100 - α)	$\overline{M}_w \times 10^{-3}$ (GPC)	$\overline{M}_n \times 10^{-3}$ (GPC)	$\overline{M}_w/\overline{M}_n$
PnBuMA-0	25	0.0	-	-	-	100.0	320	73	4.3
PnBuMA-1	200	14.2	87	72	1.2	85.8	346	38	9.2
PnBuMA-2	215	17.8	96	74	1.3	82.2	334	39	8.5
PnBuMA-3	220	18.5	76	54	1.4	81.5	304	33	9.3
PnBuMA-4	225	20.2	76	54	1.4	79.8	426	53	8.0
PnBuMA-5	230	24.6	-	-	-	75.4	-	-	-
PnBuMA-6	235	27.0	-	-	-	73.0	-	-	-
PnBuMA-7	240	30.7	87	52	1.7	69.3	426	62	6.9
PnBuMA-8	245	35.7	87	52	1.7	64.3	315	56	5.6
PnBuMA-9	250	43.7	-	-	-	56.3	-	-	-
PnBuMA-10	255	46.9	-	-	-	53.1	-	-	-

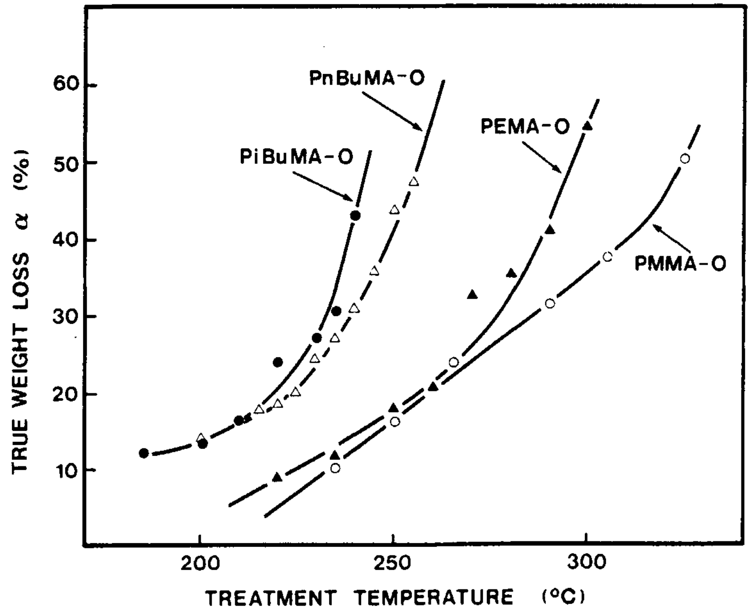

FIG. 3. Variation of % weight loss α with treatment temperature for PMMA-0, PEMA-0, PnBuMA-0, and PiBuMA-0 (see Tables 2 and 3 for other data).

In Fig. 5 the normalized GPC distributions of the decomposed polymers PEMA-2, -4, -6, and -8 are subtracted successively from that of PEMA-0. The volatilized fraction (-) of the polymer is represented by hashed lines. The hashed areas can be converted to distributions as is shown in Fig. 5 for the case PEMA-0/PEMA-8. Values of $\overline{M}_w$ and $\overline{M}_n$ have been calculated from such distributions and are presented in Table 2. These data show that in the depolymerization reactions during the isothermal decompositions of PEMA there is no specific preference for longer (as was the case for PMMA) or shorter (as was the case for PiBuMA) chains. The $\overline{M}_w/\overline{M}_n$ ratio of the volatilized fractions, however, increased with increasing decomposition temperature. The $\overline{M}_w/\overline{M}_n$ ratio of the residue, however, remained constant within ±0.2 of 2.5.

In Fig. 6 are shown normalized GPC distributions of undecomposed and decomposed samples of PnBuMA. The PnBuMA-0 maximum at elution count 27.25 (136.25 mL) moves to 27 (135.0 mL) following 50 min isothermal treatments at temperatures between 200 and 245°C. The $\overline{M}_w$ and $\overline{M}_n$ values (Table 3) of the decomposed residual polymer

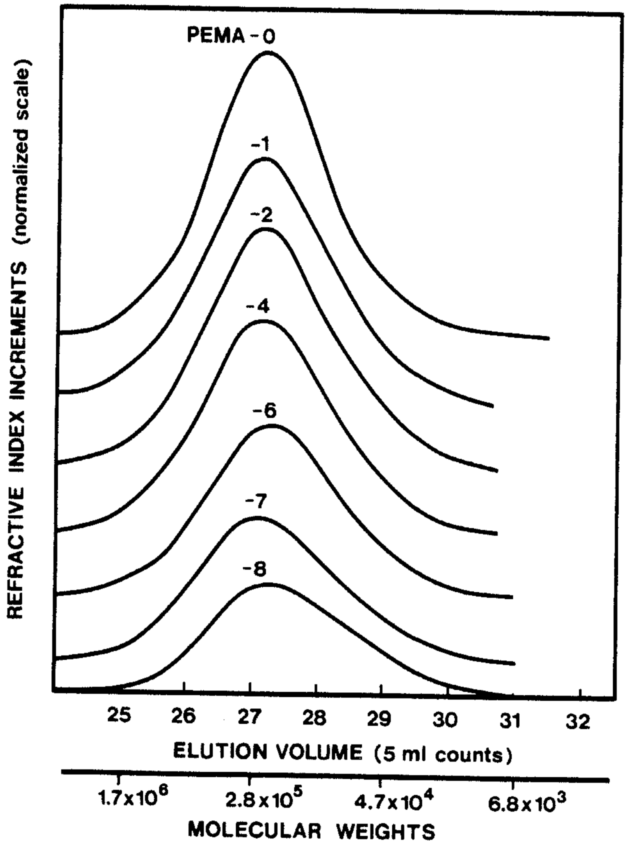

FIG. 4. Normalized GPC molecular weight distributions of undecomposed and decomposed samples of PEMA (see Table 2 for other data).

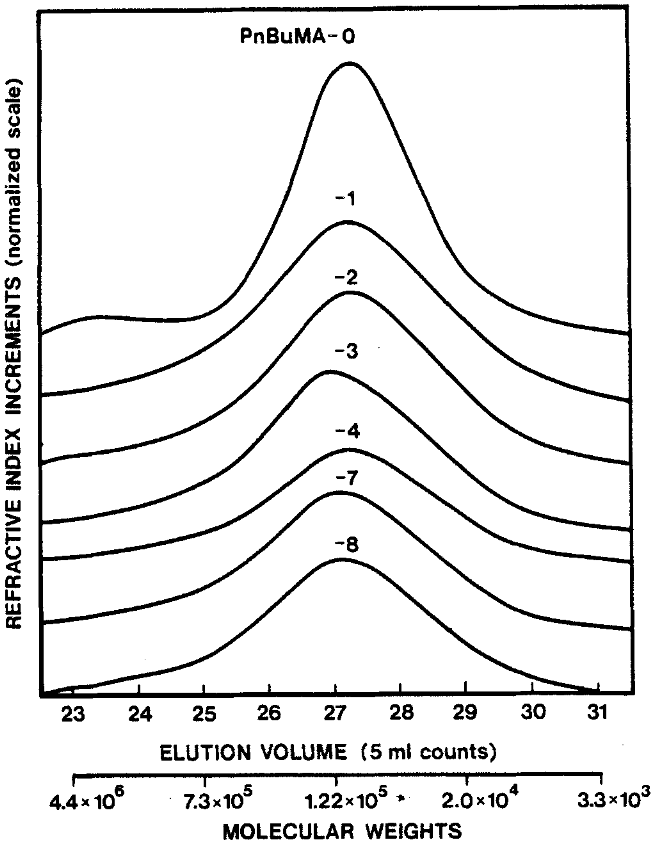

FIG. 5. Graphical method of analysis whereby GPC molecular weight distribution curves are broken down into components. The case of PEMA-0 subjected to 50 min decomposition periods at 235° (PEMA-2), 260° (PEMA-4), 280° (PEMA-6), and 300°C (PEMA-8) (see Table 2 for other data).

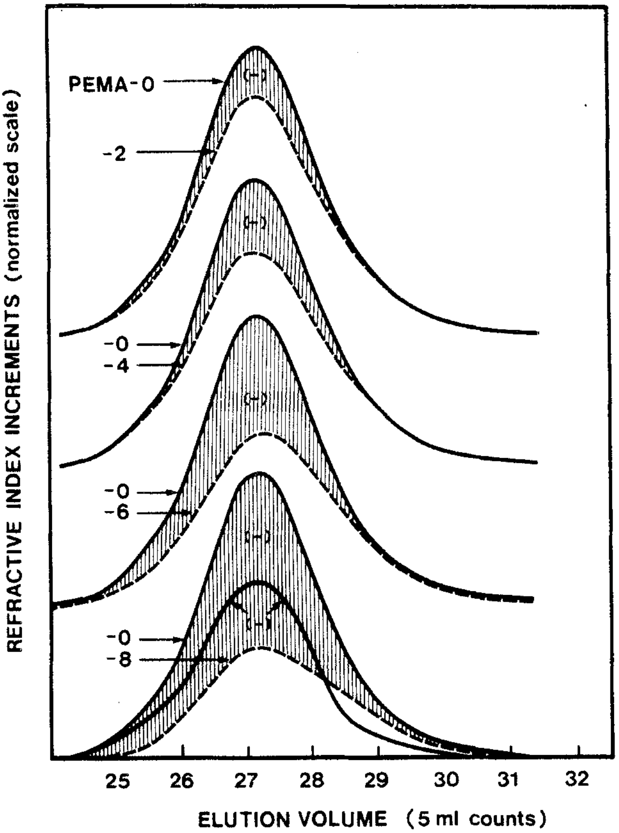

FIG. 6. Normalized GPC molecular weight distributions of undecomposed and decomposed samples of PnBuMA (see Table 3 for other data).

show no definite trends, though $\overline{M}_w/\overline{M}_n$ ratios do decrease with increasing decomposition temperatures.

In Fig. 7 the normalized GPC distributions of the decomposed polymers PnBuMA-1, -3, -4, and -8 are successively subtracted from that of PnBuMA-0. The volatilized fraction (-) of the polymer is represented by vertical hashed lines. The hashed areas are converted into distributions such as is shown in Fig. 7 for the PnBuMA-0/PnBuMA-8 case. Higher molecular weight fractions in the residues $(+)_1$ (horizontal hash lines) can also be converted into molecular weight distributions (not shown here). A horizontal hashed area $(+)_2$ appeared only with PnBuMA-1 and was ignored. Values of $\overline{M}_w$ and $\overline{M}_n$

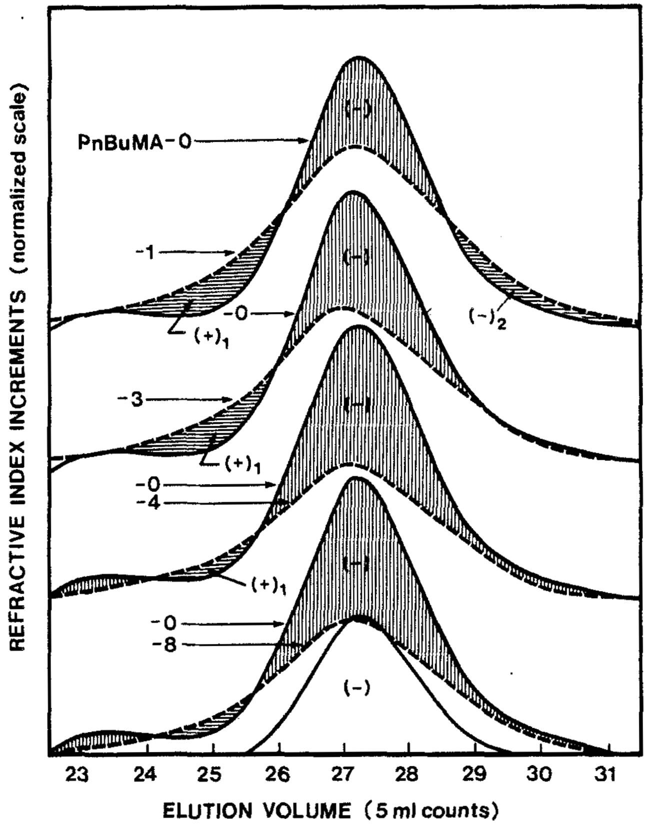

FIG. 7. Graphical method of analysis whereby GPC molecular weight distribution curves are broken down into components. The case of PnBuMA-0 subjected to 50 min decomposition periods at 200° (PnBuMA-1), 220° (PnBuMA-3), 225° (PnBuMA-4), and 245°C (PnBuMA-8) (see Table 4 for other data).

for the volatilized fraction as well as those of the residues are presented in Table 3, while $\overline{M}_w$ and $\overline{M}_n$ values for the higher molecular weight chain-recombination polymers are summarized in Table 4.

Analyses of the data in Tables 3 and 4 reveal that during isothermal degradations a major part of the lower molecular weight fraction ($\overline{M}_w \times 10^{-3} = 76$ to 96, and $\overline{M}_n \times 10^{-3} = 52$ to 74) volatilizes yielding monomer, whereas a minor part of the same fraction recombines to yield higher molecular weight products ($\overline{M}_w \times 10^{-5} = 8$ and $\overline{M}_n \times 10^{-5} = 6$). As is to be expected, the quantity of volatilized material

TABLE 4. GPC Data on PnBuMA Samples Subjected to Isothermal Treatments

	Chain-recombination polymer characteristics			
Sample	Weight %	$\bar{M}_w \times 10^{3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
PnBuMA-1	7.2	792	634	1.3
PnBuMA-2	5.5	737	577	1.3
PnBuMA-3	6.5	829	674	1.3
PnBuMA-4	6.5	829	674	1.3
PnBuMA-7	3.2	690	580	1.2
PnBuMA-8	3.2	690	580	1.2

increases with increasing decomposition temperature while that of the recombination products decreases. The $\bar{M}_w/\bar{M}_n$ ratio of the volatilized fraction increases with increasing decomposition temperature while that of the recombination products remains constant within ±0.5 of 1.25. The thermal behavior of PnBuMA is similar to that of PiBuMA [18] where the volatilized fraction had lower molecular weights compared to those of the overall molecular weight of PiBuMA. Furthermore, as in the case of PnBuMA, PiBuMA also yielded higher molecular weight chain-recombination products. May it be mentioned that PMMA [18] and PEMA do not yield chain-recombination products.

In Fig. 8 are shown curves representing the dynamic thermogravimetric decomposition of PMMA-0, PEMA-0, PnBuMA-0, and PiBuMA-0 at a heating rate of 20 K/min. 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 5. PMMA-0 followed zero-order kinetics. The order of importance of the activation energies is PnBuMA = PiBuMA > PEMA > PMMA. For comparison purposes, activation energies for the decomposition of two polyisobutylene samples PIB-CO and PIB-DO are also tabulated [38]. These are higher than those of the methacrylate series. The activation energy values of 58 kJ/mol for PEMA-0 and 70 kJ/mol for PnBuMA-0 are lower than those reported in the literature [1].

Glass Transition of PEMA and PnBuMA

The T_g of a polymer is heating-rate dependent [21-30] as well as cooling-rate dependent [36, 37]; however, recent work on substituted polystyrenes [21-30] showed that the cooling rate had no significant

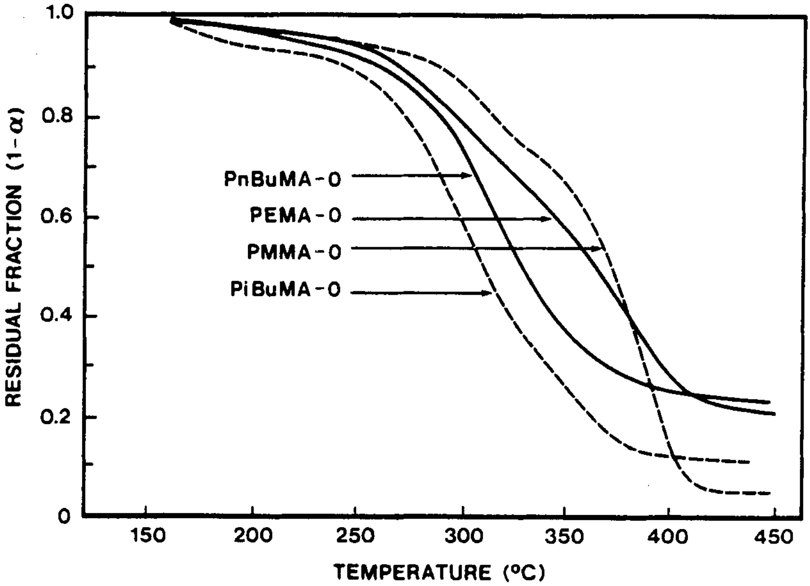

FIG. 8. Dynamic thermogravimetric decompositions of PMMA-0, PEMA-0, PnBuMA-0, and PiBuMA-0 at a heating rate of 20 K/min (see Table 5 for other data).

TABLE 5. Activation Energy Values for the Thermal Decomposition of PEMA and PnBuMA

Sample	$\overline{M}_n \times 10^{-4}$ (GPC)	Activation energy (kJ/mol)[a]	
		n = 0	n = 1
PMMA-0	22.2	42	-
PEMA-0	12.6	-	58
PnBuMA-0	7.3	-	70
PiBuMA-0	22.2	-	67
PIB-CO	26.4	183	-
PIB-DO	13.7	-	278

[a] n is the order of reaction.

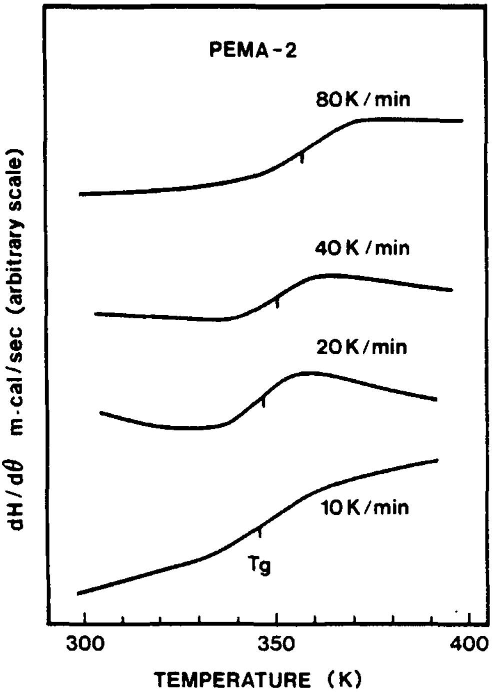

FIG. 9. Typical DSC thermograms of a decomposed PEMA-2 sample recorded in the glass transition region at various heating rates. Cooling rate: constant at 320 K/min (see Table 6 for other data).

effect on T_g. In the present study, a cooling rate of 320 K/min was therefore used. In Figs. 9 (PEMA-2) and 10 (PnBuMA-4) are shown typical DSC thermograms recorded at various heating rates. As expected, T_g increases with increasing heating rate. T_g data obtained with a cooling rate of 320 K/min and heating rates of 80, 40, 20, and 10 K/min for undecomposed and decomposed polymer samples are summarized in Tables 6 (PEMA) and 7 (PnBuMA). T_{g_e} values of the PEMA samples remain constant within ±5 K of 345. This is in good agreement with the literature value of 338 K for atactic PEMA [2-12]. T_{g_e} values of the PnBuMA samples also remained unchanged on isothermal decompositions, yielding an average value of 293 ± 5 K which likewise is in excellent agreement with the literature value of 293 K [2, 5, 7-10, 15-17].

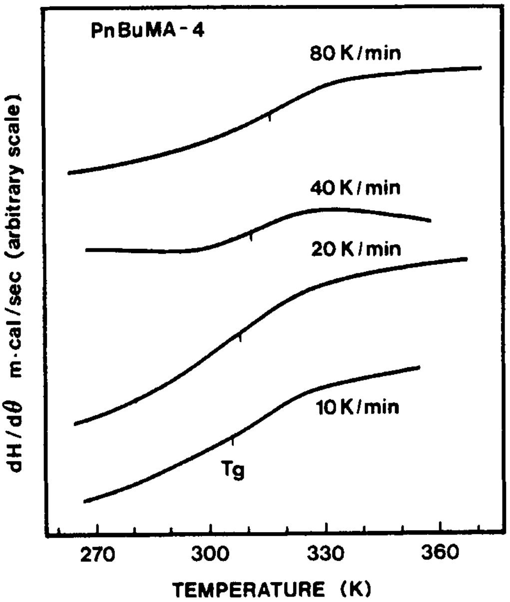

FIG. 10. Typical DSC thermograms of a decomposed PnBuMA-4 sample recorded in the glass transition region at various heating rates. Cooling rate: constant at 320 K/min (see Table 7 for other data).

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

	$\overline{M}_n \times 10^{-3}$	T_g at various heating rates (°K/min)				T_{g_e}[a]
Sample	(GPC)	80	40	20	10	(1 K/min)
PEMA-0	126	354	351	349	347	339
PEMA-1	141	359	356	352	350	345
PEMA-2	133	357	350	347	346	340
PEMA-3	131	358	356	355	355	351
PEMA-4	138	363	361	357	356	347
PEMA-5	116	360	356	354	-	345
PEMA-6	119	363	359	355	-	345
PEMA-7	119	363	361	358	-	348

[a] Extrapolated value at a heating rate (q) of 1 K/min using the equation: $\log q = a - b/T_g$ [32-34].

TABLE 7. Variation of T_g as a Function of Heating Rates for Undecomposed and Decomposed Samples of PnBuMA

Sample	$\overline{M}_n \times 10^{-3}$ (GPC)	T_g at various heating rates (°K/min) 80	40	20	10	T_{ge}[a] (1 K/min)
PnBuMA-0	73	304	301	298	297	288
PnBuMA-1	38	315	309	309	306	295
PnBuMA-2	39	310	308	306	308	298
PnBuMA-3	33	311	308	307	309	298
PnBuMA-4	53	316	311	309	309	298
PnBuMA-5	-	314	310	307	-	292
PnBuMA-6	-	313	310	309	-	295
PnBuMA-7	62	312	310	305	302	290
PnBuMA-8	56	314	309	306	302	290
PnBuMA-9	-	317	311	309	-	298
PnBuMA-10	-	310	306	304	-	297

[a] See footnote in Table 6.

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

1. For all values of α, the thermal stability of the polymers studied follows the order PMMA > PEMA > PnBuMA > PiBuMA. As the bulk size of the substituent increases, the thermal stability decreases.
2. Thermal behavior of PEMA is similar to that of PMMA [18] whereas that of PnBuMA is closer to that of PiBuMA [18]. During the isothermal decomposition of PEMA, the depolymerization reactions do not show any preference for long or short chains; however, in the isothermal decomposition of PnBuMA (as was also the case for PiBuMA), a major part of the lower molecular weight fraction ($\overline{M}_w \times 10^{-3} = 76$ to 96 and $\overline{M}_n \times 10^{-3} = 52$ to 74) volatilizes yielding monomer whereas a minor part of the same fraction recombines to yield higher molecular weight products with an $\overline{M}_w \times 10^{-5}$ of 8 and an $\overline{M}_n \times 10^{-5}$ of 6.

3. Activation energies for the decomposition of polymers follow the order PnBuMA > PiBuMA > PEMA > PMMA. These values are lower than those reported in the literature.
4. T_{g_e} values for PEMA (345 ± 5 K) and PnBuMA (293 ± 5 K) are in good agreement with the reported values of 343 K (PEMA) and 293 K (PnBuMA) in the literature.

Studies on the thermal decomposition as well as the glass transition temperatures of poly(cyclohexyl methacrylate) and poly(phenyl methacrylate) are in progress and will be reported shortly.

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