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Thermal Decomposition and Glass Transition Temperature of Poly(phenyl Methacrylate) and Poly(cyclohexyl Methacrylate)

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ABSTRACT

The thermal decomposition and the glass transition temperature T_g of poly(phenyl methacrylate) (PPhMA) and poly(cyclohexyl methacrylate) (PcHMA) 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, e.g., T_g. For all values of weight-loss α, the thermal stability of the polymers follows the order: Poly(methyl methacrylate) (PMMA) = PcHMA > poly(ethyl methacrylate) (PEMA) > PPhMA > poly(n-butyl methacrylate) (PnBuMA) > poly(isobutyl methacrylate) (PiBuMA). In the depolymerization reactions that occur during the isothermal decomposition of PPhMA, there is no specific preference for longer or shorter chains although a minor fraction of the volatilized fraction with an $\overline{M}_w \times 10^{-5}$ of 2.5 and an $\overline{M}_n \times 10^{-5}$ of 1.5 does undergo chain

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recombination yielding high molecular weight products with an $\overline{M}_w \times 10^{-6}$ of 1.35 and an $\overline{M}_n \times 10^{-6}$ of 1.0 to 1.23. In the case of PcHMA, depolymerizations did show a preference for longer chains. No chain recombination, however, was found to take place. Activation energy of decomposition for substituted polymethacrylates follows the order: PnBuMA = PiBuMA > PEMA > PcHMA > PMMA > PPhMA. T_{g_e} values of PPhMA samples varied from 362 K for undecomposed polymers to 396 K for a polymer treated at 300°C. The literature value of 383 K does fall within this range. In the case of PcHMA, an average T_{g_e} of 356 ± 6.0 K is not far removed from the reported value of 359 K.

INTRODUCTION

Studies on the glass transition temperature T_g of poly(phenyl methacrylate) (PPhMA) [1-3] and poly(cyclohexyl methacrylate) (PcHMA) [3-6] have been reported; however, no data are available on the thermal degradation of these polymers. In earlier studies reported from this laboratory on the thermal decomposition of poly(methyl methacrylate) (PMMA) [7], poly(isobutyl methacrylate) (PiBuMA) [7], poly(ethyl methacrylate) (PEMA) [8], and poly(n-butyl methacrylate) (PnBuMA) [8], it was shown that: 1) depolymerization reactions exclusively account for the total weight-loss α, and 2) the overall weight-average and number-average molecular weight values $\overline{M}_w$ and $\overline{M}_n$ of the decomposed residues do not change drastically with those of the undecomposed polymers. In isothermal decompositions at low temperatures ($\alpha \simeq 10\%$), however, longer PMMA chains depolymerize first and are then followed by shorter chains whereas in the isothermal decomposition of PiBuMA shorter PiBuMA chains depolymerize preferentially over the longer ones. In the case of PEMA and PnBuMA, the phenomena of chain-length preference in depolymerizations are not observed. Furthermore, PnBuMA and PiBuMA decompositions are accompanied by chain-chain recombinations yielding high molecular weight products ($\overline{M}_w \times 10^{-6} > 2.0$) in the initial stages of the reaction.

With a view to extending these studies to bulkier substituents, it was thought of interest to investigate the effect of chain length on depolymerization reactions occurring during the thermal decompositions of PPhMA and PcHMA. The principal results obtained are summarized in the following paragraphs.

EXPERIMENTAL

PPhMA and PcHMA were used as received from the Aldrich Chemical Co. Viscosity-average molecular weights, $\overline{M}_v$, of PPhMA were calculated from viscosity data obtained in THF at 25°C [9]. Molecular weight distributions of PPhMA were obtained with a Waters Associates model 200 GPC [10-19]. Making use of the molecular weight distributions of PPhMA and PMMA [7] as well as the viscosity data of PPhMA, the calibration curve relating elution volume V_e and molecular weight M was of the form: $\log M = 16.45 - 0.078\ V_e$.

Similarly, $\overline{M}_v$ values of PcHMA were calculated from viscosity data obtained in benzene at 30°C [20]. Making use of the viscosity and GPC molecular weight distribution data, V_e related to M as follows: $\log M = 15.96 - 0.078\ V_e$.

Calculated values of $\overline{M}_w$ and $\overline{M}_n$ for PPhMA and PcHMA are presented in Table 1.

Nuclear magnetic resonance (NMR) spectra of PPhMA-0 (Fig. 1) and PcHMA-0 (Fig. 2) used for the decomposition studies were obtained with a Varian 220 MHz NMR spectrometer in CCl_4 at 75°C. Tetramethylsilane was the internal standard. The highlights of these spectra are as follows.

For PPhMA-0 (Fig. 1)

Aromatic ring protons at $\delta = 7.02$ (3 protons), $\delta = 7.13$ (2 protons):

$-C\underline{H}_2-$	between $\delta = 1.65$ and 3.0 with peaks at $\delta = 2.00$, 2.02, 2.30, and 2.39
$-C\underline{H}_3$	at $\delta = 1.39$ (rr), 1.48 (mr), and 1.57 (mm)

PPhMA-0 is an atactic polymer with a P_m of 0.30.

For PcHMA-0 (Fig. 2)

$-OC\underline{H}_2-$	types 1A and 2A	Broad peak between $\delta = 4.45$ and 4.77 (maximum at 4.59 δ)
$-CH_2-$	type 4	between $\delta = 1.65$ and 2.0
$-C\overline{H}_2-$	type 1B	between $\delta = 1.65$ and 2.0
$-C\underline{\overline{H}}_2-$	type 2	between $\delta = 1.25$ and 1.65 with a maximum at 1.45
$-C\underline{H}_3$	type 3	$\delta = 0.91$ (rr), $\delta = 1.02$ (mr), $\delta = 1.14$ (mm)

PcHMA-0 is an atactic polymer with a P_m of 0.30.

A Perkin-Elmer differential scanning calorimeter (their model DSC-2) operating with pure dry helium was used for the isothermal

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	Ethylacetate	35	0.690	31.5	0.22	136	34.0	12.6	2.7
PcHMA-0	Benzene	30	0.422	23.1	0.35	138	24.4	7.0	3.5
PPhMA-0	Benzene	30	0.242	21.4	0.31	141	23.1	5.7	4.1

[a] k_H is Huggins coefficient.

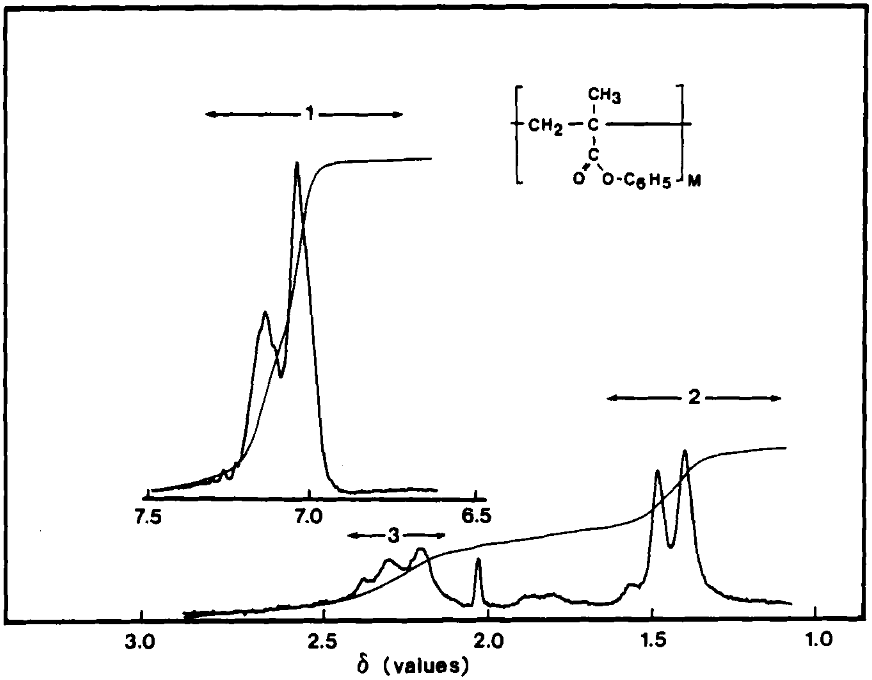

FIG. 1. 220 MHz proton spectrum of PPhMA-0.

decomposition of PPhMA and PcHMA while their thermogravimetric scanning balance (model TGS-1) operating in pure dry nitrogen was used for the dynamic decomposition studies of the polymers. The T_g values of the undecomposed and decomposed polymer samples were determined with the DSC-2 apparatus [21-23].

RESULTS AND DISCUSSION

Thermal Decomposition of PPhMA and PcHMA

In Tables 2, 3, and 4 are summarized values of α (in %), $\overline{M}_w$, $\overline{M}_n$, and the polydispersity ratios ($\overline{M}_w/\overline{M}_n$) obtained with PPhMA (Tables 2 and 3) and PcHMA (Table 4) both before and after their 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 50 min isothermal treatments of PMMA [7], PEMA [8], PnBuMA [8], and

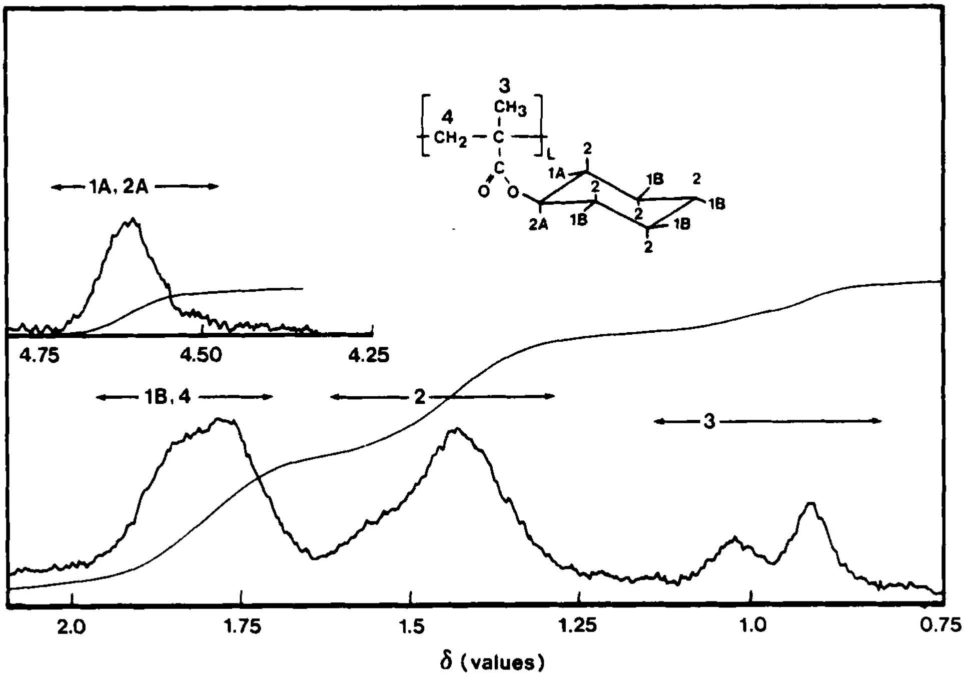

FIG. 2. 220 MHz proton spectrum of PcHMA-0.

PiBuMA [7] are also plotted in this figure. One notes that, for low values of α, PMMA, PEMA, and PcHMA fit one curve while PnBuMA and PiBuMA fit another. The PPhMA curve acts as a bridge between the two, the lower half falling on the PnBuMA and PiBuMA curve, the upper half on the PMMA, PEMA, and PcHMA curve. For identical values of α, the respective decomposition temperatures for PPhMA are lower than those for PcHMA. For all values of α, the thermal stability of the six polymers follows the order: PMMA = PcHMA > PEMA > PPhMA > PnBuMA > PiBuMA.

In Fig. 4 are shown normalized GPC molecular weight distributions of undecomposed and decomposed samples of PPhMA. The maximum at elution count 28.2 (141 mL) in the GPC molecular weight distribution of the undecomposed sample PPhMA-0 shifts to a higher elution count (or lower molecular weights) of 28.5 (142.5 mL) following isothermal treatments. The values of $\overline{M}_w$ and $\overline{M}_n$ for the residual polymer, given in Table 3, however, remain constant with increasing treatment temperature. It would appear that, besides depolymerization, high molecular weight polymer due to chain recombination is also being formed as was the case with PiBuMA [7] and PnBuMA [8].

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

			GPC molecular weights of volatilized fraction							
Sample	Decomposition temperature (°C)	α (%)	Weight[a] %	$\overline{M}_w \times 10^{-3}$	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$	Weight[a] %	$\overline{M}_w \times 10^{-3}$	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$
PPhMA-0	25	0.0	-	-	-	-	-	-	-	-
PPhMA-1	190	9.9	7.9	224	193	1.2	4.3	8.8	5.2	1.7
PPhMA-2	215	17.6	10.7	227	186	1.2	5.0	11.6	5.9	2.0
PPhMA-3	230	22.0	17.0	253	193	1.3	5.4	11.2	6.0	1.9
PPhMA-4	240	23.4	18.0	250	190	1.3	5.4	11.2	6.0	1.9
PPhMA-5	260	29.0	21.0	225	137	1.6	7.8	14.2	7.2	2.0
PPhMA-6	270	31.7	23.0	225	137	1.6	7.8	14.2	7.2	2.0
PPhMA-7	275	34.5	25.5	225	137	1.6	7.8	14.2	7.2	2.0
PPhMA-8	285	39.1	30.0	248	144	1.7	8.3	14.2	7.2	2.0
PPhMA-9	300	39.7	-	-	-	-	-	-	-	-

[a] As calculated from GPC distribution curves.

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

	Chain-recombination polymer characteristics				Overall molecular weights of residues			
Sample	Weight %	$\overline{M}_w \times 10^{-3}$ (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)	$\overline{M}_w/\overline{M}_n$
PPhMA-0	-	-	-	-	100	231	57	4.0
PPhMA-1	2.3	1150	986	1.2	90.1	214	58	3.7
PPhMA-2	1.5	1220	1040	1.2	82.4	211	58	3.7
PPhMA-3	0.9	1350	1230	1.1	78.0	208	54	3.9
PPhMA-4	0.5	1350	1230	1.1	76.6	205	54	3.9
PPhMA-5	-	-	-	-	71.0	198	52	3.8
PPhMA-6	-	-	-	-	68.3	202	56	3.6
PPhMA-7	-	-	-	-	65.5	206	57	3.6
PPhMA-8	-	-	-	-	60.9	196	56	3.5

TABLE 4. Data on PcHMA Samples Subjected to Isothermal Treatments at Various Temperatures for 50 min Periods

Sample	Decomposition temperature (°C)	Volatilized fraction				Residue		
		α (%)	$\overline{M}_w \times 10^{-3}$ (GPC)	$\overline{M}_n \times 10^{-3}$ (GPC)	$\overline{M}_w/\overline{M}_n$	$\overline{M}_w \times 10^{-3}$ (GPC)	$\overline{M}_n \times 10^{-3}$ (GPC)	$\overline{M}_w/\overline{M}_n$
PcHMA-0	25	0.0	-	-	-	244	70	3.5
PcHMA-1	250	14.5	231	157	1.5	245	67	3.7
PcHMA-2	265	18.3	217	121	1.8	306	61	5.0
PcHMA-3	270	17.1	-	-	-	263	64	4.1
PcHMA-4	275	22.1	237	150	1.6	251	68	3.7
PcHMA-5	280	25.4	263	153	1.7	233	59	3.9
PcHMA-6	285	25.5	-	-	-	-	-	-
PcHMA-7	290	30.8	261	151	1.7	232	53	4.4
PcHMA-8	300	49.7	285	152	1.9	197	43	4.6

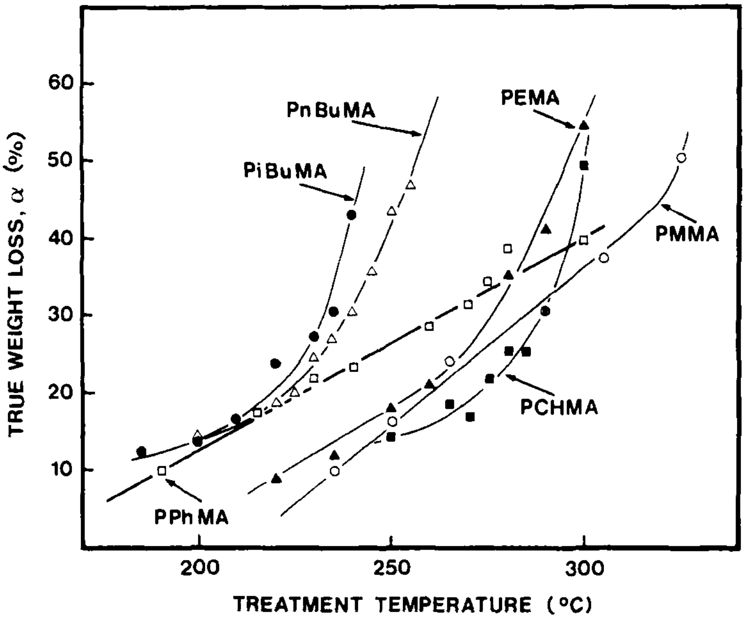

FIG. 3. Variation of α (%) with treatment temperature for PMMA-0, PEMA-0, PnBuMA-0, PiBuMA-0, PPhMA-0, and PcHMA-0. (See Tables 2 and 4 for other data.)

In Fig. 5 the normalized GPC molecular weight distributions of the decomposed polymers PPhMA-1, PPhMA-5, and PPhMA-8 are successively subtracted from that of the undecomposed polymer, PPhMA-0. The volatilized fraction (-) of the polymer is represented by vertical hash lines; chain-recombination polymer $(+)_1$ with horizontal lines; and chain-scission polymer $(+)_2$ also with horizontal lines. As the polymer due to chain scission occurred only with Sample PPhMA-1, the hashed area $(+)_2$ was not converted into a molecular weight distribution. The volatilized fraction (-) (Fig. 5, PPhMA-0/PPhMA-8) and the chain-recombination polymer (distributions not shown here) were, however, converted into molecular weight distributions and values of $\overline{M}_w$ and $\overline{M}_n$ calculated. Those for the volatilized fraction (-) are listed in Table 2 while those for the chain-recombination and residue polymers are presented in Table 3. These data show that the depolymerization reactions involve two different molecular weight distributions: one (major) between elution counts 26 and 30 ($\overline{M}_w \times 10^{-5} = 2.5$ and $\overline{M}_n \times 10^{-5} = 1.5$) and the other (minor) between elution counts 29.5 and 33 ($\overline{M}_w \times 10^{-3} = 8.8$ to 14.2 and $\overline{M}_n \times 10^{-3} = 5.2$ to 7.2).

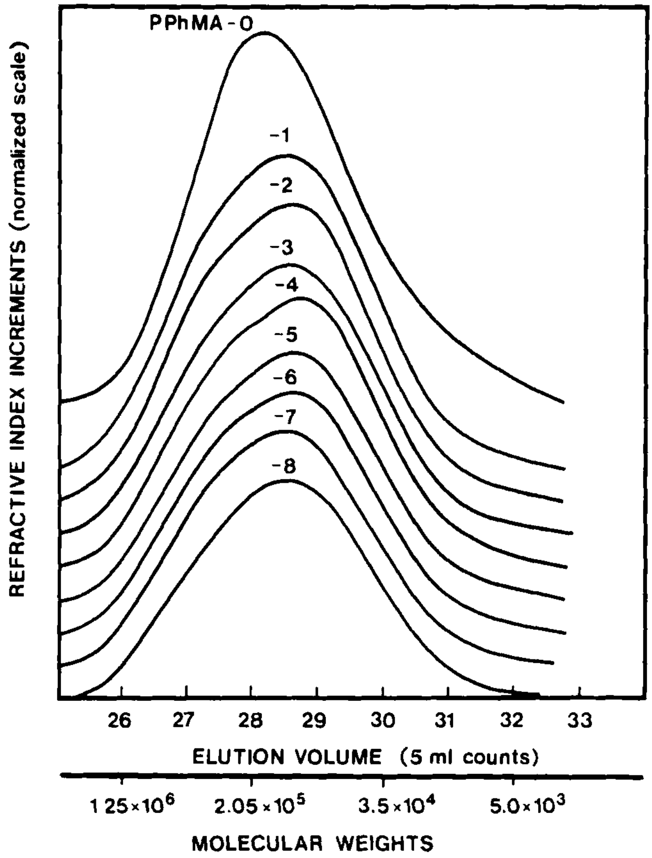

FIG. 4. Normalized GPC molecular weight distributions of undecomposed and decomposed samples of PPhMA. (See Table 2 for other data.)

The proportion of chain-recombination polymer varied from 0.5% (at 275°C) to 2.3% (at 250°C); however, their molecular weights ($\overline{M}_w \times 10^{-6} = 1.35$ and $\overline{M}_n \times 10^{-6} = 1.0$ to 1.23) were quite high (see Table 3). These data show that, in the depolymerization reactions that occur during the isothermal decompositions of PPhMA, there is no specific preference for longer or shorter chains. The chain-recombination polymer, in all probability, results from the volatilized fraction with an $\overline{M}_w \times 10^{-5}$ of 2.5 and an $\overline{M}_n \times 10^{-5}$ of 1.5.

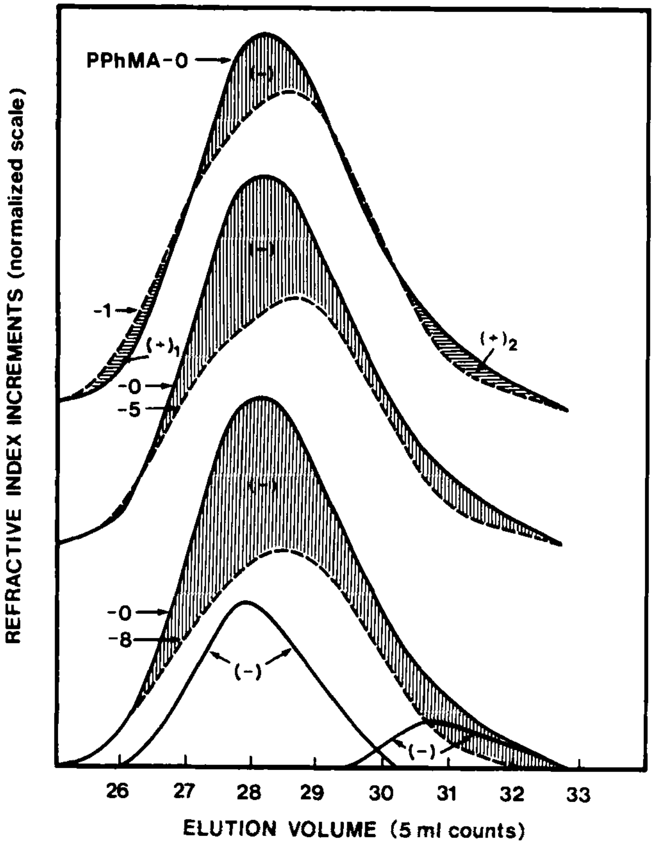

FIG. 5. Graphical method of analysis whereby GPC molecular weight distribution curves are broken down into components. The case of PPhMA-0 subjected to 50 min decompositions at 190 (PPhMA-1), 260 (PPhMA-5), and 285°C (PPhMA-8). (See Tables 2 and 3 for other data.)

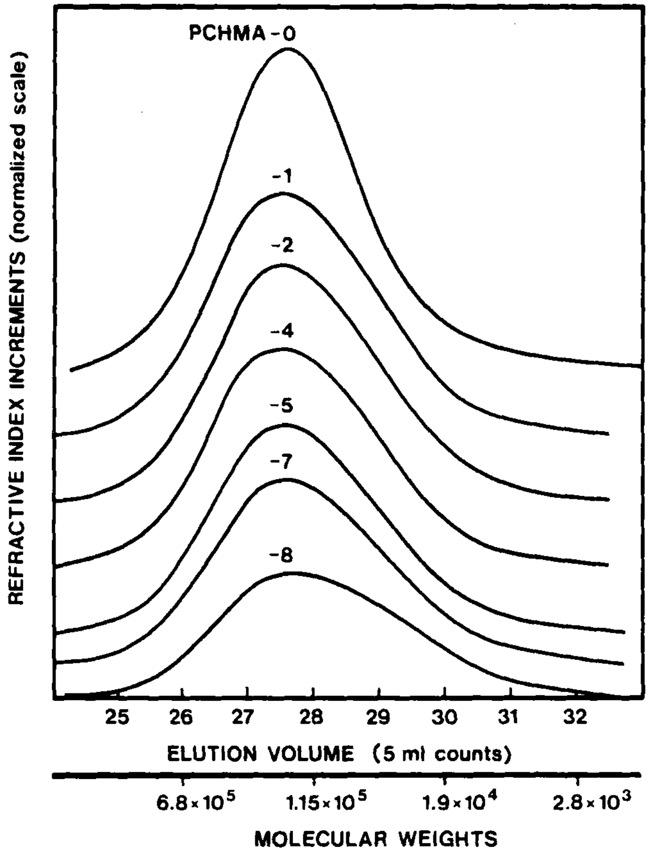

FIG. 6. Normalized GPC molecular weight distributions of undecomposed and decomposed samples of PcHMA. (See Table 4 for other data.)

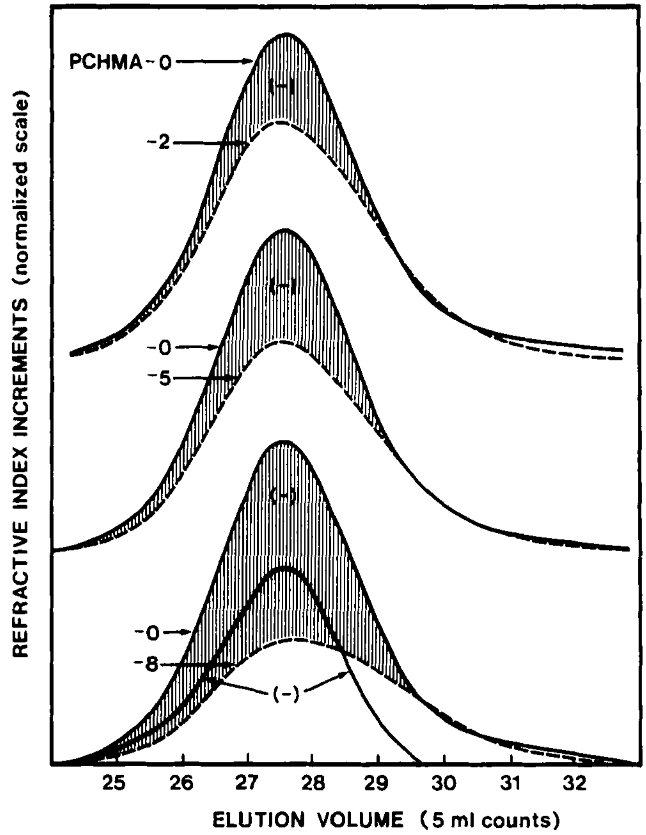

FIG. 7. Graphical method of analysis whereby GPC molecular weight distribution curves are broken down into components. The case of PcHMA-0 subjected to 50 min decompositions at 265 (PcHMA-2), 280 (PcHMA-5), and 300°C (PcHMA-8). (See Table 4 for other data.)

In Fig. 6 are shown the normalized GPC molecular weight distributions of undecomposed and decomposed samples of PcHMA. Their maxima remain unchanged at an elution count of 27.5 (137.5 mL). The values of $\overline{M}_w$ (see Table 4) remain constant while those of $\overline{M}_n$ decrease with increasing treatment temperature.

In Fig. 7 the normalized GPC molecular weight distributions of PcHMA-2, PcHMA-5, and PcHMA-8 are successively subtracted from that of the undecomposed PcHMA-0 sample. The volatilized fraction (-) of the polymer is represented by vertical hash lines.

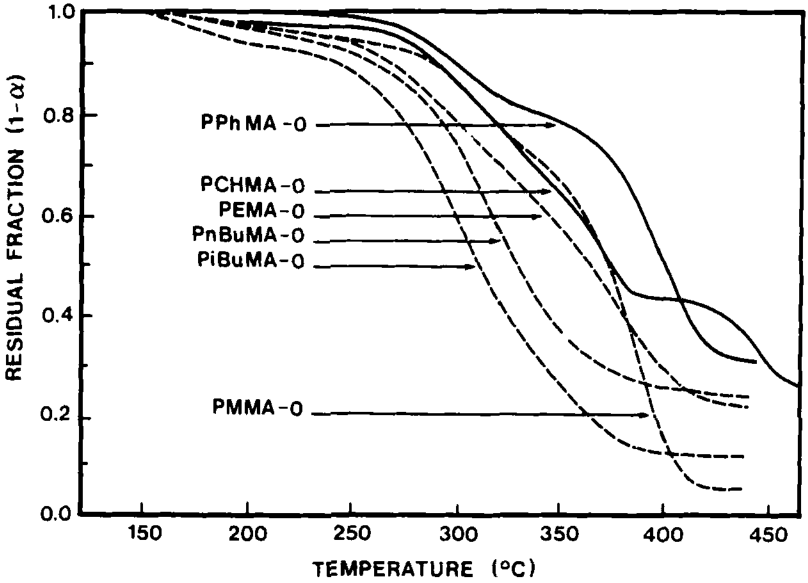

FIG. 8. Dynamic thermogravimetric decompositons of PMMA-0, PEMA-0, PnBuMA-0, PiBuMA-0, PPhMA-0, and PcHMA-0 at a heating rate of 20 K/min. (See Table 5 for other data.)

These hashed areas are converted into molecular weight distributions as shown in Fig. 7 (PcHMA-0/PcHMA-8). $\overline{M}_w$ and $\overline{M}_n$ values for the volatilized fraction are presented in Table 4 as are overall values for the residual polymer. These data show that in the isothermal decomposition of PcHMA, a certain preference is noted for the decomposition of longer chains as was the case with PMMA, but not for shorter ones as was the case with PiBuMA.

In Fig. 8 are shown curves representing the dynamic thermogravimetric decomposition of several polymer samples at a heating rate of 20 K/min. These include PMMA-0, PEMA-0, PnBuMA-0, PiBuMA-0, PPhMA-0, and PcHMA-0. Using the method of Coats and Redfern [24], activation energy values were calculated assuming succesive orders of reaction zero and one. The values obtained with the better fit are presented in Table 5. With the exception of PMMA-0 and PPhMA-0, which obey zero-order kinetics, the polymers follow first-order kinetics. The polymers in descending importance of activation energy fall into the following order: PnBuMA = PiBuMA > PEMA > PcHMA > PMMA > PPhMA.

TABLE 5. Activation Energy Values for the Thermal Decomposition of Various Substituted Polymethacrylates

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
PiBuMA-0	22.2	-	67
PnBuMA-0	7.3	-	70
PcHMA-0	7.0	-	49
PPhMA-0	5.7	31	-

[a] n is the order of reaction.

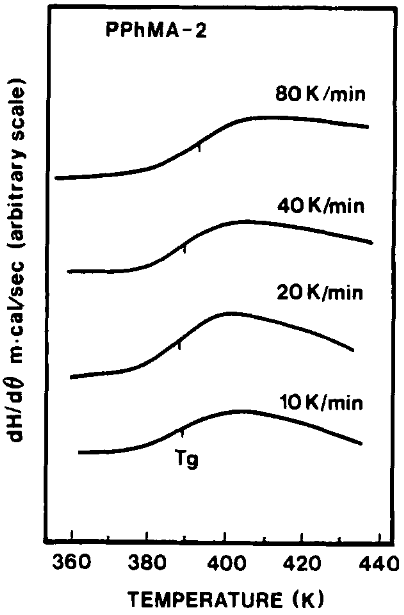

FIG. 9. Typical DSC thermograms of decomposed PPhMA-2 recorded in the glass transition region at various heating rates. Cooling rate constant at 320 K/min. (See Table 6 for other data.)

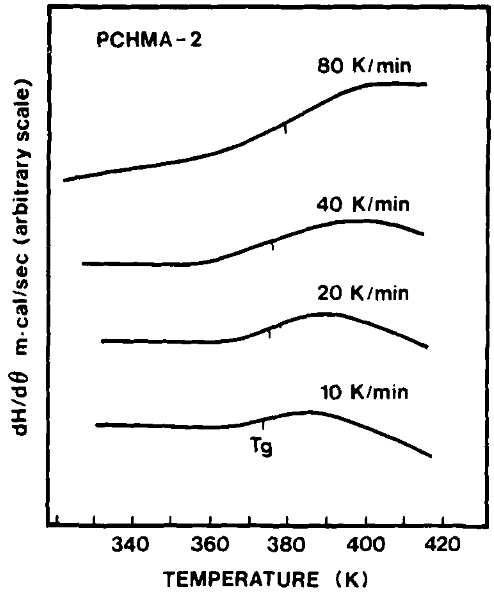

FIG. 10. Typical DSC thermograms of decomposed PcHMA-2 recorded in the glass transition region at various heating rates. Cooling rate constant at 320 K/min. (See Table 7 for other data.)

Glass Transition Temperatures of PPhMA and PcHMA

The T_g of a polymer is heating rate dependent [10-19] and even cooling rate dependent in certain cases [25, 26]. Recent work on substituted polystyrenes [10-19], however, has shown that cooling rate has no significant effect on T_g. Thus, in the present study, a cooling rate of 320 K/min was used throughout the entire T_g measurement procedure. In Figs. 9 (PPhMA-2) and 10 (PcHMA-2) 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 (PPhMA) and 7 (PcHMA). T_{g_e} values (extrapolated to a heating rate of 1 K/min) of PPhMA vary between 362 and 396 K, in spite of the fact that all PPhMA samples have the same $\overline{M}_n$. It is believed that structural changes in the polymer on isothermal

TABLE 6. Variation of T_g as a Function of Heating Rates for Undecomposed and Decomposed Samples of PPhMA

Sample	$\overline{M}_n \times 10^{-3}$ (GPC)	T_g at various heating rates (°K/min)				T_{g_e},[a]
		80	40	20	10	1 K/min
PPhMA-0	57	377	374	371	371	362
PPhMA-1	58	378	376	374	372	366
PPhMA-2	58	393	390	388	389	381
PPhMA-3	54	399	396	394	-	383
PPhMA-4	54	401	398	392	392	386
PPhMA-5	52	405	402	401	-	392
PPhMA-6	56	403	399	397	-	388
PPhMA-7	57	406	402	402	401	394
PPhMA-8	56	403	400	400	400	396
PPhMA-9	-	406	402	400	400	393

[a] Extrapolated value at a heating rate (q) of 1 K/min using the equation: $\log q = a - b/T_g$ [21-23].

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

Sample	$\overline{M}_n \times 10^{-3}$ (GPC)	T_g at various heating rates (°K/min)				T_{g_e},[a]
		80	40	20	10	1 K/min
PcHMA-0	70	372	369	366	363	356
PcHMA-1	67	386	381	378	-	362
PcHMA-2	61	379	376	375	374	368
PcHMA-3	64	385	381	378	-	362
PcHMA-4	68	380	377	374	-	366
PcHMA-5	59	381	381	373	-	365
PcHMA-7	53	387	382	378	-	360

[a] Extrapolated value at a heating rate (q) of 1 K/min using the equation: $\log q = a - b/T_g$ [21-23].

decomposition at various temperatures are responsible for these variations. The literature value of 383 K [1-3] lies well within the range of the present data. Tg_e values of PcHMA samples remain within ± 6 K of 356, which agrees with the literature value of 359 K [3-6].

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 follows the order PMMA = PcHMA > PEMA > PPhMA > PnBuMA > PiBuMA.
2. In the depolymerization reactions that occur during the isothermal decomposition of PPhMA, there is no specific preference for longer or shorter chains. The chain-recombination polymer with $\overline{M}_w \times 10^{-6} = 1.35$ and $\overline{M}_n \times 10^{-6} = 1.0$ to 1.23, in all probability, results from a minor fraction of the volatilized fraction with $\overline{M}_w \times 10^{-5} = 2.5$, and $\overline{M}_n \times 10^{-5} = 1.5$. The depolymerization of PcHMA, however, does show preference for longer chains but no chain-recombination polymer is observed in the decomposition products of this polymer.
3. Activation energies of decomposition for substituted polymethacrylates follow the order PnBuMA = PiBuMA > PEMA > PcHMA > PMMA > PPhMA.
4. Tg_e values for PPhMA range from 362 K (undecomposed PPhMA) to 396 K (PPhMA-8). It is thought that structural changes on isothermal treatment of the polymer are responsible for that. In the case of PcHMA samples, the average Tg_e of 356 ± 6 K is not far removed from the literature value of 359 K.

Studies on the ultrasonic solution decomposition of polymethyl methacrylate and its homologs are underway and will be reported on in due course.

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