

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Copolymers of 2-Hydroxyethyl Methacrylate and Alkyl Methacrylates. Part III. Thermal Behavior

Manjeet S. Choudhary<sup>a</sup>; Indra K. Varma<sup>a</sup>

<sup>a</sup> Centre for Materials Science and Technology Polymer Science Laboratories Indian Institute of Technology, New Delhi, India

**To cite this Article** Choudhary, Manjeet S. and Varma, Indra K.(1983) 'Copolymers of 2-Hydroxyethyl Methacrylate and Alkyl Methacrylates. Part III. Thermal Behavior', *Journal of Macromolecular Science, Part A*, 20: 9, 941 – 956

**To link to this Article:** DOI: 10.1080/00222338308060803

**URL:** <http://dx.doi.org/10.1080/00222338308060803>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## **Copolymers of 2-Hydroxyethyl Methacrylate and Alkyl Methacrylates. Part III. Thermal Behavior**

MANJEET S. CHOUDHARY and INDRA K. VARMA

Centre for Materials Science and Technology  
Polymer Science Laboratories  
Indian Institute of Technology, Delhi  
Hauz Khas, New Delhi 110016, India

### **ABSTRACT**

The relative thermal stability of copolymers of 2-hydroxyethyl methacrylate-ethyl methacrylate (HEMA-EMA) and HEMA-n-butyl methacrylate (HEMA-BMA) was investigated by thermogravimetry in an air/nitrogen atmosphere. The effect of molecular weight on thermal degradation was evaluated by taking five fractions of HEMA-EMA and four of HEMA-BMA copolymers. The enthalpic changes associated with the endothermic transition were evaluated by differential scanning calorimetry. The structural changes taking place in these copolymers during thermal degradation in air at 200°C were investigated by IR.

### **INTRODUCTION**

We earlier reported the synthesis and characterization of 2-hydroxyethyl methacrylate (HEMA)-alkyl methacrylate copolymers [1, 2]. In this paper the thermal behavior of these copolymers is described.

Thermal degradation of HEMA-alkyl acrylate [3] and HEMA-alkyl methacrylate [4] copolymers has been reported in the literature.

Thermal stability of polymers is dependent on their structural characteristics, such as backbone structure, nature of substituents, and structural imperfections. The rate of degradation may also depend upon the molecular weight.

In the present work the effect of molecular weight and HEMA content of the copolymers on the thermal behavior of HEMA-ethyl methacrylate (EMA) and HEMA-butyl methacrylate (BMA) copolymers was investigated. Copolymer samples of different molecular weights were obtained by the fractional precipitation method. The relative stability of the various copolymer fractions was evaluated by thermogravimetric analysis. The structural changes taking place during thermal degradation of these copolymers were investigated by IR spectroscopy.

## EXPERIMENTAL

### Solvents and Materials

DMF (E. Merck) was dried over phosphorous pentaoxide, and the fraction boiling at 154°C was collected. The details of the copolymerization of HEMA-EMA and HEMA-BMA have been reported elsewhere [1]. In Table 1 the composition of various copolymer samples used in the present work is described.

### Fractionation of Polymers

The fractionation of copolymer samples of HEMA-EMA and HEMA-BMA was done by using DMF as a solvent and water as the precipitant [4].

### Thermogravimetric Analysis

Thermogravimetric analysis was carried out using a DuPont 990 thermal analyzer in a nitrogen or air atmosphere. The samples were heated at the uniform heating rate of 10°C/min from room temperature to 600°C. The relative thermal stability of the polymers was evaluated by comparison of the initial decomposition temperature (IDT), the integral procedural decomposition temperature (IPDT) [5], and the activation energy of thermal decomposition (E).

### Differential Scanning Calorimetry (DSC)

A DuPont thermal analyzer was used to determine physical and chemical changes in the copolymers. The samples were heated from room temperature to 450°C at a heating rate of 10°C/min.

TABLE 1. Composition of the Copolymer Samples of HEMA-EMA (EH) and HEMA-BMA (BH), Prepared at 70°C

No.	Sample	Mole fraction of HEMA	Intrinsic viscosity <sup>a</sup> (dL/g)
1	EH <sub>1</sub>	0.2521	0.99
2	EH <sub>3</sub>	0.5766	1.14
3	BH <sub>4</sub>	0.6640	1.42
4	BH <sub>5</sub>	0.6865	1.50

<sup>a</sup>Intrinsic viscosity was determined in DMF at 35°C.

Enthalpic changes associated during endothermic transitions were calculated by using

$$\Delta H = \frac{A}{m} (60BE\Delta qs)$$

where  $\Delta H$  = heat of reaction, mcal/mg

A = area of DSC peak, in.<sup>2</sup>

B = time base, min/in.

E = cell calibration coefficient

$\Delta qs$  = Y-axis sensitivity, mcal/s/in.

m = mass of sample, mg

### IR Studies

The structural changes taking place in HEMA-EMA and HEMA-BMA copolymers during the initial stages of thermal degradation were evaluated by IR spectroscopy. For this purpose a thin film of copolymer was cast on a NaCl disk. The disk was then heated at 200°C in air for various intervals of time (30, 60, 90, and 120 min) and the IR spectra were recorded.

## RESULTS AND DISCUSSION

In the copolymers of HEMA-EMA and HEMA-BMA the factors that can influence thermal behavior are (a) nature of alkyl group of alkyl methacrylate (i.e., ethyl or n-butyl), (b) HEMA content of the copolymers, and (c) molecular weight and molecular weight distribution. The effect of these parameters on the relative thermal stability of co-

polymers was evaluated by thermogravimetric analysis. Two samples each of HEMA-EMA and HEMA-BMA were prepared by copolymerizing these monomers at 70°C using benzoyl peroxide as initiator. The extent of reaction was kept below 10% to eliminate the possibility of branching in the polymers.

### Effect of HEMA Content of the Copolymers on Thermal Behavior

It has been reported [2] that an increase in HEMA content in the initial monomer feed results in an increase in HEMA content in the copolymers. To evaluate the effect of HEMA content on the thermal stability of copolymers, samples containing 25 and 57% HEMA in HEMA-EMA copolymers were chosen. An improvement in thermal stability was observed on increasing the HEMA content (Fig. 1) (Table 2). IPDT values of copolymers containing a higher HEMA content were more than those with a lower HEMA content. Thus the stability at lower temperatures ( $\leq 320^\circ\text{C}$ ) is increased by an increase in HEMA content. Alkyl methacrylates (MMA, EMA, and BMA) as well as HEMA have a quarternary carbon atom in the repeat unit, and therefore the tendency to form a tertiary radical by random chain scission is expected to be similar. However, due to the presence of -OH groups in the side chain in HEMA, cross-linking may take place, thus stabilizing the polymer at lower temperatures. The relative thermal stability of copolymers BH<sub>4</sub> and BH<sub>5</sub> was higher than that of EH<sub>1</sub> and EH<sub>3</sub> copolymers (Table 2).

### Effect of Molecular Weight and Molecular Weight Distribution of Copolymers on Thermal Stability

Fractionation of HEMA-EMA and HEMA-BMA copolymers was done to obtain fractions of different molecular weights. Five fractions having intrinsic viscosities from 0.68 to 1.14 dL/g were obtained in HEMA-

TABLE 2. Effect of the Alkyl Group on the Thermal Behavior of HEMA:EMA and HEMA:BMA Copolymers in Nitrogen Atmosphere

No.	IDT (°C)	IPDT (°C)	T <sub>max</sub> (°C)	°C
1, EH <sub>1</sub>	210	333	265	390
2, EH <sub>3</sub>	255	348	315	370
3, BH <sub>4</sub>	245	370	280	395
4, BH <sub>5</sub>	270	368	410	430

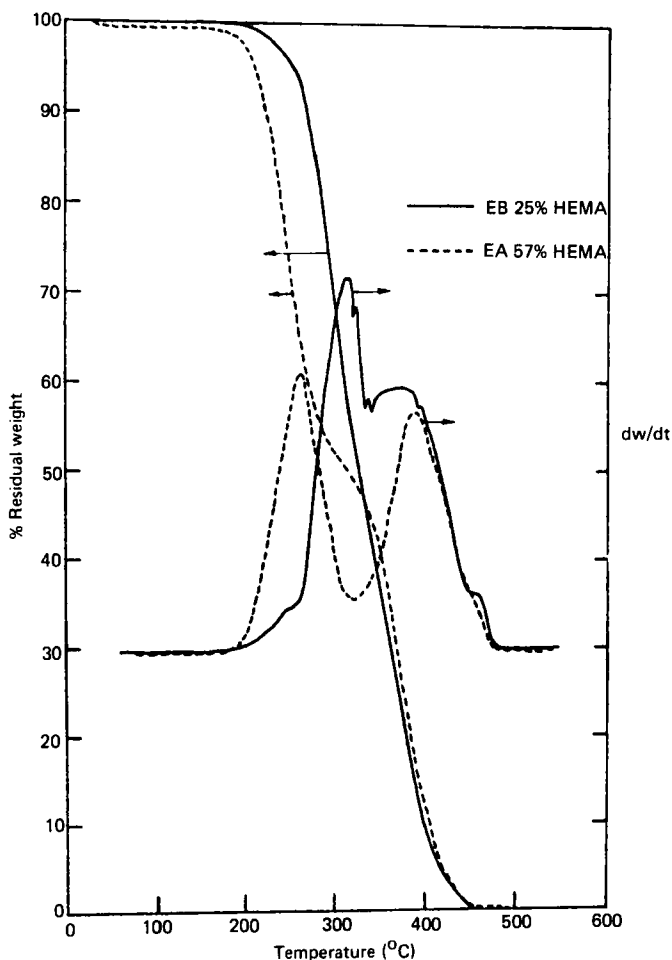


FIG. 1. Thermogravimetric traces of HEMA-EMA copolymers in nitrogen atmosphere.

EMA and four in HEMA-BMA copolymers ( $[\eta]$  1.533 to 3.24 dL/g) (Table 3). The intrinsic viscosity of HEMA-BMA copolymers was higher than that of HEMA-EMA copolymers. The integral weight distribution curves for BH<sub>4</sub> and BH<sub>5</sub> samples are given in Figs. 2(a) and 2(b). Although the  $[\eta]$  values of these copolymers were similar, there was a difference in molecular weight distribution. Sample BH<sub>4</sub> exhibited more heterogeneity with respect to molecular weight than Sample BH<sub>5</sub>. The initial decomposition temperature of BH<sub>5</sub> was almost

TABLE 3. Fractionation of HEMA-Alkyl Methacrylate Copolymers at  $35 \pm 0.1^\circ\text{C}$ 

No.	Polymer	Fraction number	Intrinsic viscosity (dL/g)	Viscosity average molecular weight ( $\times 10^5$ )
1	EH <sub>1</sub>	EB <sub>1</sub>	1.00	1.99
		EB <sub>2</sub>	0.975	1.94
		EB <sub>3</sub>	0.93	1.84
		EB <sub>4</sub>	0.895	1.76
		EB <sub>5</sub>	0.675	1.28
2	EH <sub>3</sub>	EA <sub>1</sub>	1.05	2.24
		EA <sub>2</sub>	1.03	2.06
		EA <sub>3</sub>	1.01	2.02
		EA <sub>4</sub>	1.025	2.06
		EA <sub>5</sub>	0.920	1.81
3	BH <sub>4</sub>	BA <sub>1</sub>	3.24	
		BA <sub>2</sub>	3.15	
		BA <sub>3</sub>	2.65	
		BA <sub>4</sub>	1.53	
4	BH <sub>5</sub>	BB <sub>1</sub>	3.20	
		BB <sub>2</sub>	2.97	
		BB <sub>3</sub>	2.80	
		BB <sub>4</sub>	2.25	

$25^\circ$  higher than that of BH<sub>4</sub> (Table 2), thereby indicating a higher stability of the copolymer sample having a narrow molecular weight distribution.

The molecular weights of the various copolymer fractions were determined from the intrinsic viscosity by using the relationship [1]

$$[\eta] = 2.3 \times 10^{-5} M^{0.875}$$

The molecular weights of various HEMA-EMA copolymers are given in Table 3.

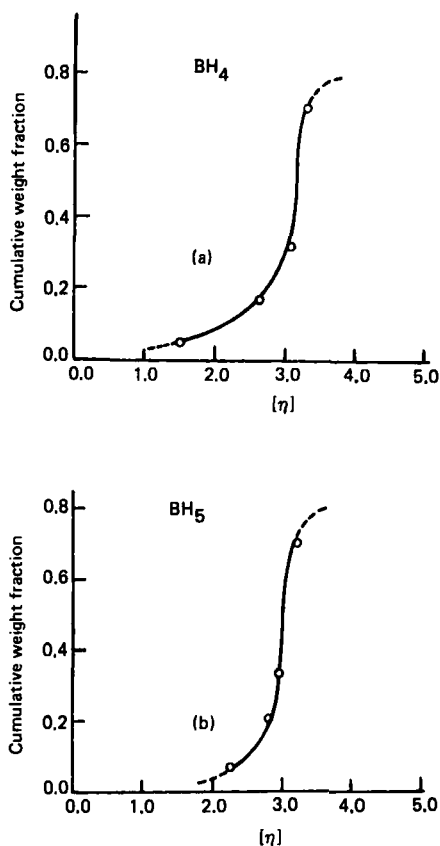


FIG. 2. Integral weight distribution curves for HEMA-BMA copolymers.

The relative thermal stabilities of various fractions of HEMA-alkyl methacrylates having different  $[\eta]$  values were evaluated in nitrogen atmosphere. No systematic trend was observed in the IPDT values of various fractions having different intrinsic viscosities (Tables 4 and 5). For example, Samples  $EA_4$  with  $[\eta] = 1.01$  dL/g and  $EA_7$  with  $[\eta] = 0.92$  dL/g had IPDT values of 333 and 385, respectively, thereby showing that the fraction with a lower  $[\eta]$  is thermally more stable. On the other hand, in  $EA_2$  ( $[\eta] = 1.03$  dL/g) the IPDT value was  $381^\circ\text{C}$ . Similarly, the  $[\eta]$  and IPDT values for Samples  $BA_1$  ( $[\eta] = 3.24$ ) and  $BA_2$  ( $[\eta] = 3.15$  dL/g) were 370 and 343, respectively. These results indicate that fractions having different intrinsic viscosities also had different backbone compositions. A fraction of lower  $[\eta]$  may have a higher HEMA content and consequently its IPDT may be higher.



TABLE 4. Various Percentage Decomposition Temperature (DT), Initial Decomposition Temperature (IDT), and IPDT for HEMA-EMA Copolymers in Nitrogen Atmosphere

Sample	$[\eta]$	IDT	Decomposition temperature (°C) at various % weight loss				IPDT
			10	20	50	90	
EA <sub>1</sub>	1.105	239	250	275	342	430	356
EA <sub>2</sub>	1.03	235	265	298	385	435	381
EA <sub>4</sub>	1.01	250	265	280	310	375	333
EA <sub>5</sub>	1.03	250	295	350	400	450	399
EA <sub>7</sub>	0.92	230	270	300	400	448	385
EB <sub>1</sub>	1.00	250	275	293	347	435	366
EB <sub>2</sub>	0.975	235	250	263	298	380	325
EB <sub>3</sub>	0.93	260	285	305	380	442	383
EB <sub>4</sub>	0.895	260	275	290	320	420	352
EB <sub>5</sub>	0.675	230	250	270	313	415	343

TABLE 5. Various Percentage Decomposition Temperature (DT), Initial Decomposition Temperature (IDT), and IPDT for HEMA-BMA Copolymers in Nitrogen Atmosphere

Sample	$[\eta]$	IDT	Decomposition temperature (°C) at various % weight loss				IPDT
			10	20	50	90	
BA <sub>1</sub>	3.24	245	290	340	380	420	370
BA <sub>2</sub>	3.15	210	280	295	320	420	343
BA <sub>3</sub>	2.65	255	305	355	400	438	386
BA <sub>4</sub>	1.53	260	305	355	400	440	387
BB <sub>1</sub>	3.2	270	290	310	380	435	368
BB <sub>2</sub>	2.97	275	290	320	410	500	402
BB <sub>3</sub>	2.8	240	315	360	400	440	389
BB <sub>4</sub>	2.25	270	305	360	425	500	422

Effect of Atmosphere

A significant decrease in thermal stability was observed when the thermal degradation of HEMA-alkyl methacrylate copolymers was carried out in air. This is clearly reflected in the thermogravimetric traces of fractionated copolymer Samples EA<sub>2</sub> and EA<sub>5</sub> (Fig. 3). A sharp decrease in IPDT values was observed on carrying out the thermal degradation in air, in contrast to the degradation of the same copolymer samples carried out in nitrogen atmosphere (Fig. 4) where higher IPDT values were obtained. Poor thermal stability in O<sub>2</sub>/air atmosphere may be due to oxidative degradation of polymers.

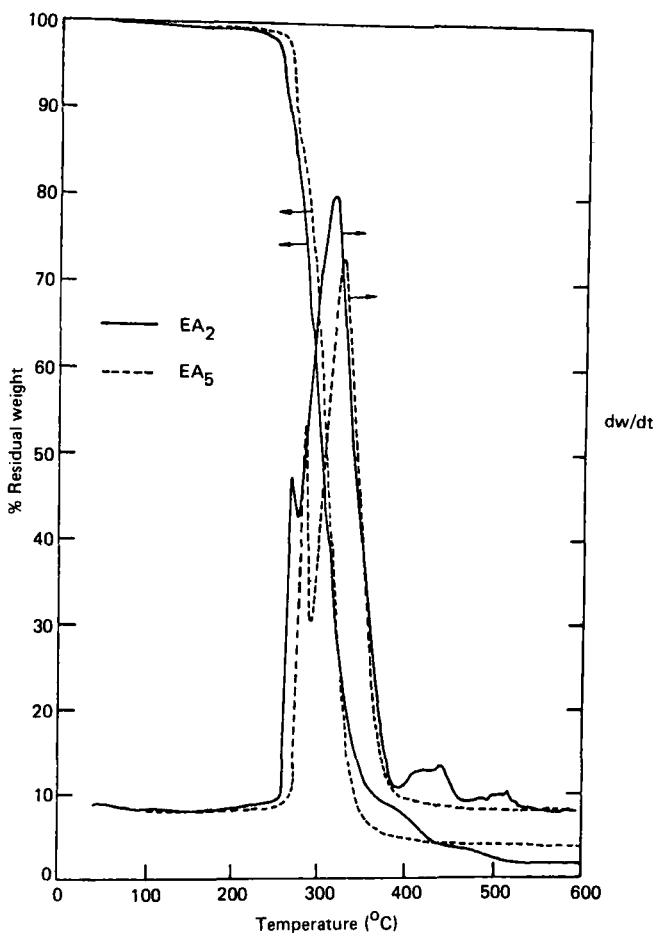


FIG. 3. Thermogravimetric traces of HEMA-EMA copolymer (Sample A) fractions in air atmosphere.

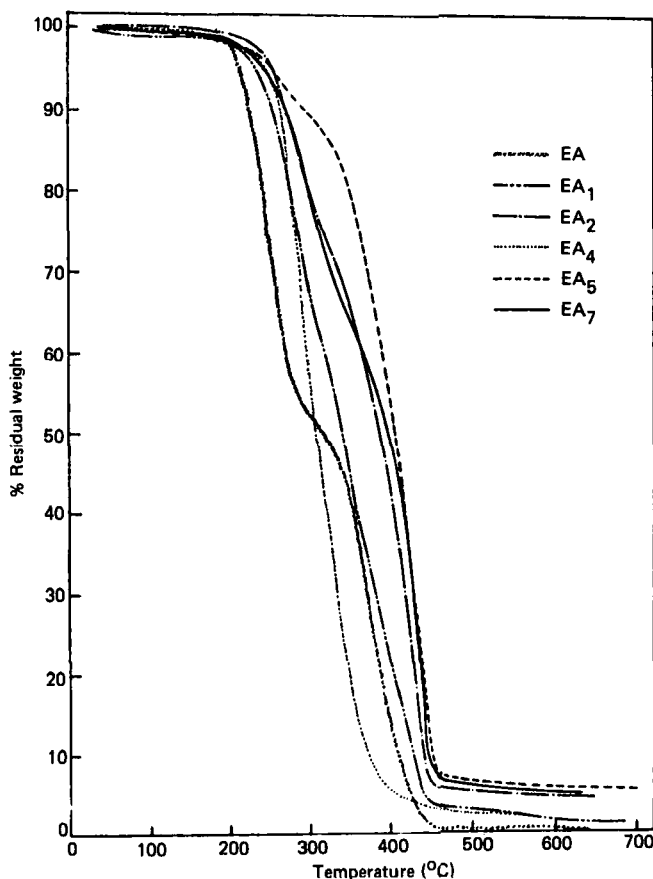


FIG. 4. Thermogravimetric traces of HEMA-EMA copolymer (Sample A) fractions in nitrogen atmosphere.

### Activation Energy of Degradation

$T_{\max}$  values and the values of the activation energy of decomposition ( $E$ ) calculated by the Dharwadkar and Karkhanwala method [6] for HEMA-alkyl methacrylate copolymer fractions are given in Table 6. The activation energy of thermal decomposition of poly(MMA) has been reported to be 136 kJ/mol [7]. The activation energies obtained for the copolymers of HEMA and alkyl methacrylates are lower than those of the corresponding homopolymers. The difference in activation energies is most likely the result of structural irregularities.

TABLE 6. Kinetic Parameter Values for the Thermal Decomposition of HEMA-EMA and HEMA-BMA Copolymers

Sample	T <sub>max</sub> (°C)	Temperature range (°C)	E (kJ/mol)
EA	264, 390	200-320	89.54
EA <sub>1</sub>	305, 370, 415	210-340	84.29
EA <sub>2</sub>	310, 445	330-480	67.76
EA <sub>4</sub>	305, 350	210-330	101.54
EA <sub>5</sub>	460	310-450	77.77
EA <sub>7</sub>	320, 450	350-490	57.54
EB	315, 370	220-350	105.38
EB <sub>1</sub>	315, 415	230-360	119.29
EB <sub>2</sub>	310, 400	270-380	49.22
EB <sub>3</sub>	320, 415	250-350	95.11
EB <sub>4</sub>	315, 370	220-350	114.60
EB <sub>5</sub>	305	210-350	113.56
BA <sub>1</sub>	280, 395	320-440	94.30
BA <sub>2</sub>	310, 410	230-320	86.39
BA <sub>3</sub>	310, 410, 430	320-460	110.83
BA <sub>4</sub>	410, 420	330-450	98.23
BB <sub>1</sub>	318, 410, 430	340-440	60.78
BB <sub>2</sub>	318, 435	330-440	55.69
BB <sub>3</sub>	280, 417	300-450	117.44
BB <sub>4</sub>	310, 440	330-470	74.28

### IR Spectra of Thermally Degraded HEMA-alkyl Methacrylates

The structural changes taking place in HEMA-EMA and HEMA-BMA copolymers during thermal degradation at 200°C in air were also evaluated by IR spectroscopy (1200-4000 cm<sup>-1</sup>) (Fig. 5). Absorption bands appearing at 1735, 2980, and 3500 cm<sup>-1</sup> due to >C=O, >CH<sub>2</sub>, and -OH groups, respectively, decreased in intensity as the sample was heated at 200°C in air. A very significant decrease in intensity of the broad

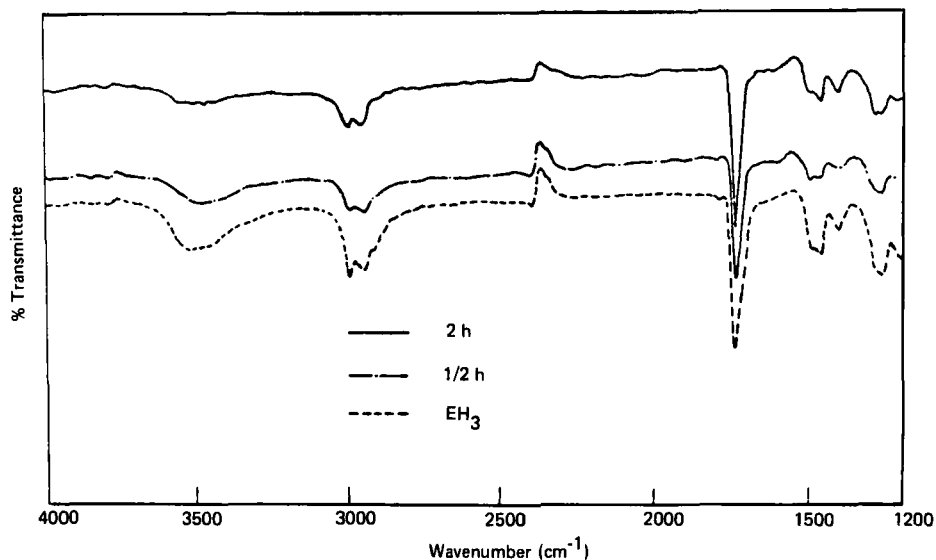
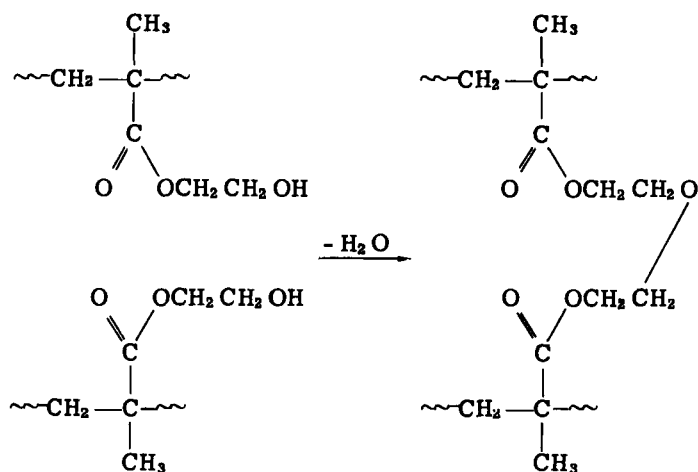
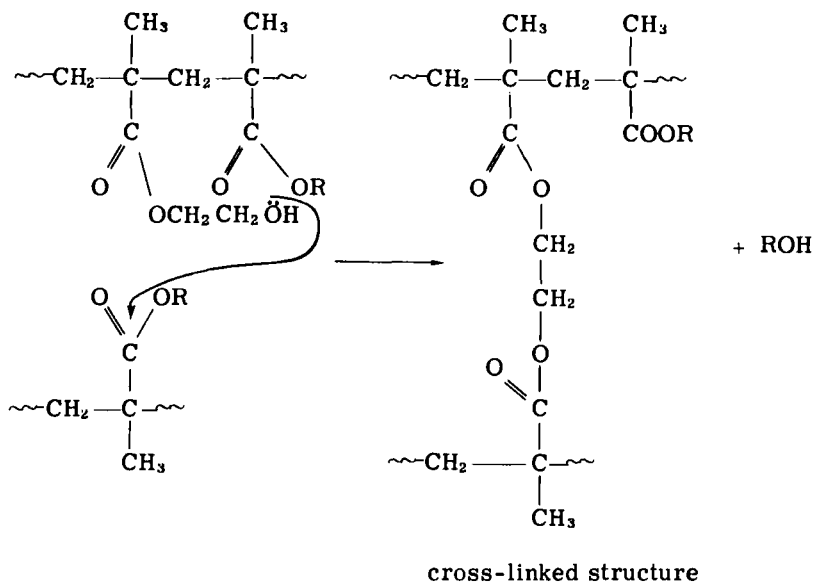


FIG. 5. IR spectra of copolymer of HEMA-EMA ( $\text{EH}_3$ ) degraded in air at  $200^\circ\text{C}$  for various intervals of time.

peak due to the  $-\text{OH}$  group was observed. This could be either (a) due to the loss of water by dehydration reaction or (b) due to the possibility of participation of a hydroxyl group in the transesterification reaction. This would give a cyclic structure or a cross-linked structure.

(a) Dehydration



(b) Intermolecular (cross-linking reaction)

The evidence that PHEMA segments cross-link intermolecularly at elevated temperatures was also obtained from pyrolysis studies of HEMA-alkyl methacrylate copolymers [8]. It was found that the absolute yield of EDMA (which is obtained on the breakdown of such cross-linked structures) increased as the mole fraction of HEMA increased in the copolymers, thereby indicating that cross-linking is the prominent reaction occurring during the thermal degradation of HEMA-alkyl methacrylate copolymers.

### Glass Transition Temperature of HEMA-Alkyl Methacrylate Copolymers

The glass transition temperature and  $\Delta H$  values of copolymers of HEMA-alkyl methacrylates were determined from DSC traces (Fig. 6) which were obtained in an  $\text{N}_2$  atmosphere.

The  $T_g$  of homopolymers [9] PMMA, PEMA, and PBMA are reported to be 100, 50, and  $8^\circ\text{C}$ , respectively. The endothermic transition observed in the temperature range of 50 to  $90^\circ\text{C}$  for HEMA-alkyl methacrylate copolymers is due to glass transition.

In Table 7 a summary of various endothermic transitions observed in the copolymers of HEMA-EMA and HEMA-BMA is given.  $T_g$  values for HEMA-EMA copolymers are found to be higher ( $84\text{--}92^\circ\text{C}$ ) than

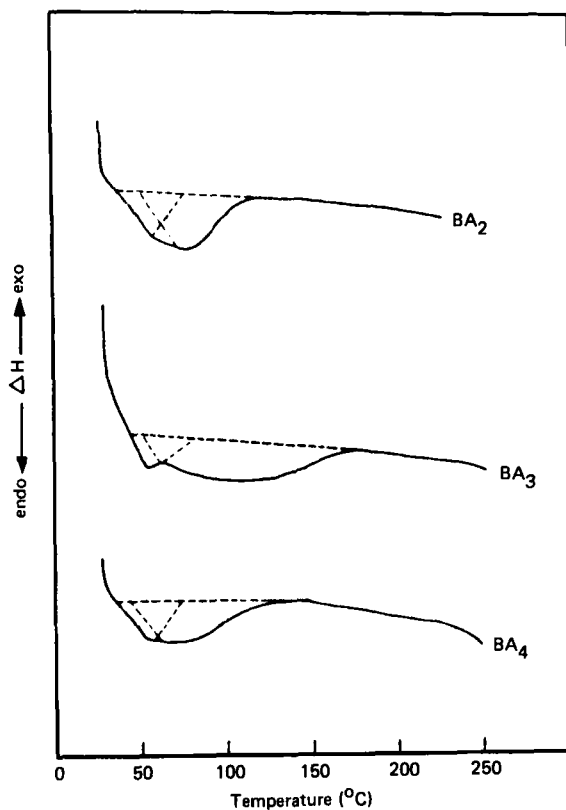


FIG. 6. DSC thermograms of HEMA-BMA copolymers in nitrogen atmosphere.

those of HEMA-BMA copolymers (52–65°C). This effect has also been observed for amorphous poly(alkyl methacrylates) [10] where there is a gradual decrease in the softening points with increasing side chain length.

A multiplicity in the endothermic transition is observed in HEMA-EMA and HEMA-BMA copolymers. This may arise due to the contribution of PHEMA and poly(butyl methacrylate) or poly(ethyl methacrylate) segments of the copolymers. By the extrapolation of these peaks (Fig. 6) an attempt was made to find the area under the curve. From these values the enthalpy of the transition, associated with the endothermic transition below 100°C, was determined (Table 7).

It may be concluded from these studies that incorporation of ethyl methacrylate and butyl methacrylate in hydroxyethyl methacrylate polymers results in a decrease in the  $T_g$ . The thermal stability of

TABLE 7. Enthalpic Changes Associated with Endothermic Transition below 100°C in Copolymers of HEMA-EMA and HEMA-BMA

Sample	Temperature of endothermic transition (°C)	$\Delta H$ (cal/g)
EA	84	2.49
EA <sub>1</sub>	84, 100	1.11, 0.59
EA <sub>3</sub>	92	2.99, 3.58
EA <sub>5</sub>	87	4.66, 2.35
EB	84	-
EB <sub>1</sub>	60, 91	1.97, 1.43
EB <sub>3</sub>	65, 92	2.46, 0.55
EB <sub>5</sub>	69, 91	
BA <sub>1</sub>	59, 74	1.12, 2.20
BA <sub>2</sub>	57, 74	1.12, 2.33
BA <sub>3</sub>	53, 107	0.55, 2.28
BA <sub>4</sub>	64, 81	1.03, 2.30
BB <sub>1</sub>	65, 125	0.55, 0.83
BB <sub>2</sub>	57, 98	1.40, 3.16
BB <sub>3</sub>	65, 85	1.46, 2.76
BB <sub>4</sub>	57, 95	1.25, 2.22

the polymers is increased as the HEMA content is increased. A decrease in hydroxyl groups in the polymers is observed on heating at 200°C. This may be attributed to cross-linking or dehydration reactions.

## REFERENCES

- [1] M. S. Choudhary and I. K. Varma, J. Polym. Sci., Polym. Chem. Ed., Submitted.
- [2] I. K. Varma and S. Patnaik, Eur. Polym. J., 12, 259 (1976).
- [3] I. K. Varma and S. Patnaik, J. Polym. Sci., Polym. Chem. Ed., 17, 3279 (1979).



- [4] M. S. Choudhary and I. K. Varma, Angew. Makromol. Chem., **87**, 75 (1980).
- [5] C. D. Doyle, Anal. Chem., **33**, 77 (1961).
- [6] S. R. Dharwadkar and M. D. Karkhanwala, in Thermal Analysis in Inorganic Material and Physical Chemistry (R. F. Schwenker and P. D. Garn, eds.), Academic, New York, 1969.
- [7] S. L. Madorsky, (a) J. Polym. Sci., **11**, 491 (1953); (b) Thermal Degradation of Organic Polymers, Wiley-Interscience, New York, 1964.
- [8] M. S. Choudhary and K. Lederer, Eur. Polym. J., **18**, 1021 (1982).
- [9] Encyclopedia of Polymer Science and Technology, Vol. 1, 2nd ed. (H. F. Mark, N. G. Gaylord, and N. M. Bikales, eds.), Wiley-Interscience, 1964, p. 299.
- [10] S. S. Rogers and L. Mandelkern, J. Phys. Chem., **61**, 985 (1957).

Accepted by editor April 6, 1983

Received for publication May 14, 1983