

# Structure–Property Relationship in Copolymers of Methacrylic Acid Esters. I. Thermal Behavior

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## SYNOPSIS

This article describes the synthesis and thermal characterization of copolymers of methyl methacrylate (MMA) and alkyl methacrylates. The copolymerization was carried out using different mol fractions (0.05–0.25) of alkyl methacrylates, i.e., octyl methacrylate (OMA)/decyl methacrylate (DMA)/lauryl methacrylate (LMA)/stearyl methacrylate (SMA), in the initial feed at 80°C. The copolymer composition was determined from <sup>1</sup>H-NMR. The thermal stability of the copolymers was investigated by thermogravimetric analysis and pyrolysis gas chromatography. A two/three-step degradation was observed in the copolymer samples. The monomers were the major product of degradation in most of the copolymers except in SMA/MMA copolymers where the product of side-group elimination was also observed. An attempt was also made to determine the yield of the monomers during degradation and then to evaluate the copolymer composition. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Copolymerization of methyl methacrylate (MMA) with several alkyl methacrylates such as 2-hydroxyethyl methacrylate,<sup>1</sup> ethyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate,<sup>2</sup> iso-octyl methacrylate, isodecyl methacrylate,<sup>3</sup> lauryl methacrylate, and cetyl methacrylate<sup>4</sup> has been investigated in the past with an aim to study the effect of structure on the property of copolymers. Our recent studies using equimolar quantities of MMA and octyl/decyl/lauryl methacrylate (OMA/DMA/LMA) and stearyl methacrylate (SMA) comonomers revealed that the rate of copolymerization increases with an increase in the size of the alkyl side group.<sup>5</sup> Thermal stability of these copolymers was also evaluated. However, the scope of this study was limited because only a fixed feed composition was used.

To modify the impact behavior of PMMA while keeping its useful properties (i.e., optical clarity, environmental stability), it is necessary to incorporate

only low mol fractions of comonomers in the PMMA backbone. A comprehensive study is, therefore, needed to evaluate the effect of low mol fractions of comonomers in the PMMA backbone on the thermal behavior. The present studies were undertaken keeping this objective in mind.

## EXPERIMENTAL

Methyl methacrylate (MMA, Fluka) was purified by washing with 10% NaOH followed by water, dried overnight over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and distilled under reduced pressure. The initiator, benzoyl peroxide (BPO, Loba Chemie), was recrystallized from chloroform before use. Methacrylic acid (Fluka), octanol (Aldrich), decanol (Aldrich), dodecanol (Aldrich), and octadecanol were used as such.

### Preparation of Alkyl Methacrylate Monomers

Methacrylic acid esters were prepared by the acid-catalyzed esterification of methacrylic acid with the corresponding alcohol in the presence of catalytic amounts of *p*-toluene sulfonic acid (0.75% by weight of reactants) and hydroquinone as the inhibitor. The

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reaction was carried out in a round-bottom flask fitted with a reflux condenser and a Dean Stark water separator. One mole of alcohol (i.e., octanol/dodecanol, or octadecanol) was dissolved in benzene (500 mL) containing hydroquinone, and 1.44 mol of methacrylic acid was added. The solution was refluxed until the theoretical amount of water was collected. Then, it was cooled and washed successively with water and sodium bicarbonate. The organic layer was dried over  $\text{Na}_2\text{SO}_4$  and benzene removed under reduced pressure. The alkyl methacrylates thus obtained were purified by distillation under reduced pressure (yield  $\sim 90\%$ ).

### Copolymerization Studies

Copolymerization of MMA with OMA, DMA, LMA, and SMA was carried out in bulk at  $80^\circ\text{C}$  using 1% (w/w) BPO as an initiator. The mol fraction of alkyl methacrylates in the feed was taken as 0.05, 0.1, 0.15, 0.20, and 0.25. These copolymer samples have been designated as OM, DM, LM, and SM, respectively. The various copolymers are described by appending a hyphen after the designated names fol-

lowed by a numeral indicating the mol % of comonomer in the initial feed. For example, a copolymer sample of MMA prepared by taking 5 mol % of OMA in the initial feed has been designated as OM-5.

A known quantity of the monomers was placed in the three-necked flask fitted with water condenser and an inlet tube for passing nitrogen. The whole assembly was placed in an oil bath maintained at  $80^\circ\text{C}$ . Dry nitrogen was passed through the flask for 10 min and then 1% (w/w) BPO was added. The time of polymerization was varied so as to keep the conversion low ( $< 12\%$ ). After the desired interval of time, the solution was poured slowly in methanol with continuous stirring. The precipitated polymer was filtered and dried in a vacuum oven at  $60^\circ\text{C}$  for 24 h. The copolymers were purified by dissolving in chloroform and reprecipitating in methanol.

### Characterization

Molecular characterization of copolymers was done by intrinsic viscosity measurements at  $30 \pm 1^\circ\text{C}$  using chloroform as the solvent and an Ubbelohde

**Table I** Copolymerization of MMA with Alkyl Methacrylate

Sample Designation	Conversion (%)	$[\eta]$ (dL/g)	Mol Fraction of MMA in Feed	Mol Fraction of MMA in Copolymer	
				Grassie Method	Ratio Method
OM-5	10.3	0.40	0.962	0.950	0.917
OM-10	11.0	0.45	0.892	0.923	0.855
OM-15	12.1	0.41	0.865	0.872	0.807
OM-20	9.6	0.42	0.802	0.810	0.762
OM-25	11.6	0.45	0.750	0.665	0.634
DM-5	10.0	0.53	0.950	0.946	0.939
DM-10	9.2	0.74	0.887	0.894	0.869
DM-15	10.3	0.68	0.856	0.875	0.808
DM-20	12.0	0.62	0.792	0.756	0.783
DM-25	11.5	0.61	0.754	0.719	0.734
LM-5	9.6	0.24	0.954	0.960	0.930
LM-10	10.3	0.39	0.909	0.909	0.855
LM-15	10.9	0.45	0.843	0.818	0.820
LM-20	11.0	0.51	0.799	0.788	0.789
LM-25	11.2	0.50	0.755	0.778	0.743
SM-5	12.0	0.53	0.951	0.944	0.946
SM-10	11.8	0.57	0.905	0.875	0.903
SM-15	11.6	0.56	0.867	0.837	0.848
SM-20	10.5	0.55	0.806	0.740	0.761
SM-25	10.8	0.59	0.755	0.710	0.719

suspension level viscometer.  $^1\text{H-NMR}$  spectra of the copolymers were recorded in  $\text{CDCl}_3$  using a Jeol FT-NMR (JNM-FX100) spectrophotometer and tetramethylsilane as an internal standard.

Thermal behavior of the copolymers was evaluated in nitrogen atmosphere using a DuPont 1090 thermal analyzer having a 951 TG module at a heating rate of  $10^\circ\text{C}/\text{min}$ . Of the polymer sample,  $10 \pm 2$  mg was used in each experiment. The relative thermal stability was evaluated by comparing the initial decomposition temperature ( $T_i$ ), temperature of maximum rate of weight loss ( $T_{\text{max}}$ ), and final decomposition temperature ( $T_f$ ).

A Shimadzu GC-9A gas chromatograph attached to pyrolyzer Pyr-2 was used for pyrolysis gas chromatographic (GC) studies. Pyrolysis was done at  $400^\circ\text{C}$ . Pyrolyzed products were directly fed to a nonpolar 20 m-long column packed with 5% silica gel (SE-30). The temperature of both injector and detector was kept at  $280^\circ\text{C}$ . Nitrogen was used as a carrier gas with a flow rate of  $30$  mL/min. A hydrogen air flame ionization detector was used. The col-

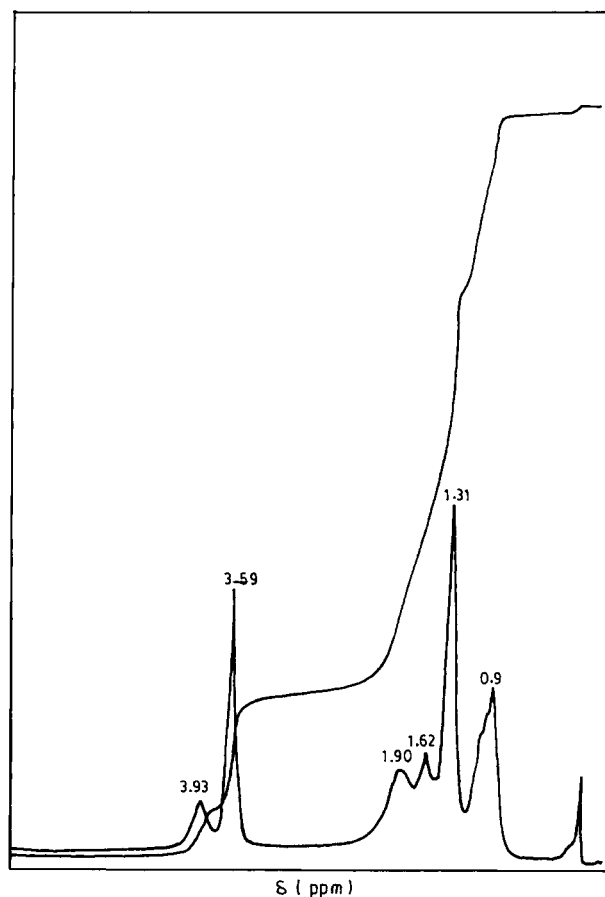


Figure 1  $^1\text{H-NMR}$  spectrum of the OM-25 copolymer.

Table II Reactivity Ratios of MMA ( $r_1$ ) and Alkyl Methacrylates ( $r_2$ ) by Kelen-Tüdös Method

Sample Designation	$r_1$	$r_2$
MMA : OMA	0.50	0.71
MMA : DMA	0.60	0.89
MMA : LMA	0.45	0.88
MMA : SMA	0.65	0.72

umn was held initially at  $80^\circ\text{C}$  for 2 min and then heated up to  $230^\circ\text{C}$  at a heating rate of  $8^\circ\text{C}/\text{min}$ . The final temperature was held constant for 15 min. Pyrolysis was done at  $400^\circ\text{C}$ .

## RESULTS AND DISCUSSION

The details of the feed composition of the comonomers together with their designations are given in Table I. Typical  $^1\text{H-NMR}$  spectra of the OM copolymers are given in Figure 1. The two hydrogens of the  $-\text{OCH}_2$  group present in alkyl methacrylate moieties of copolymers produce a singlet around  $\delta = 3.94$  ppm, whereas the peak at  $\delta = 3.59$  ppm has been assigned to the ester methoxy group ( $-\text{OCH}_3$ ) of MMA. The methyl protons of the alkyl side chain appear at  $\delta = 0.9$  ppm, the methylene [ $(-\text{CH}_2)_n$ ] at  $\delta = 1.31$  ppm,  $-\text{OCH}_2\text{CH}_2$  proton at  $1.62$  ppm, and the  $\alpha$ -methyl group at  $\delta = 1.90$  ppm.

The copolymer composition was determined by taking the ratio of  $-\text{OCH}_2$  protons of alkyl methacrylate and  $-\text{OCH}_3$  protons of MMA. The Grassie method<sup>6</sup> was also used to evaluate the copolymer composition by taking the ratio of downfield protons ( $-\text{OCH}_2 + -\text{OCH}_3$ ) to total protons. The copolymer composition as determined by the ratio method and the Grassie method are also tabulated in Table I. The copolymer composition as determined by the ratio method and the Grassie method were not identical in copolymers containing low mol fractions of alkyl methacrylates. This is because in

Table III  $Q$  and  $e$  Values of Methacrylic Acid Esters

Monomer	$Q$	$e$
OMA	2.34	1.42
DMA	1.78	1.19
LMA	2.54	1.36
SMA	1.69	1.27

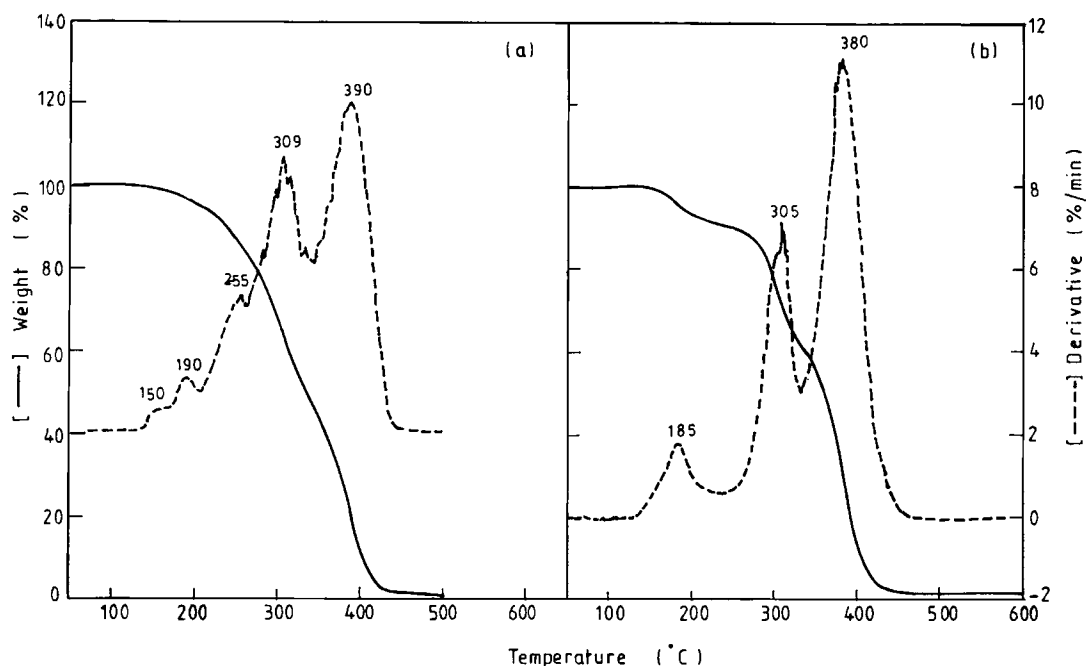


Figure 2 TGA traces of (a) SM-5 and (b) SM-25 copolymer samples.

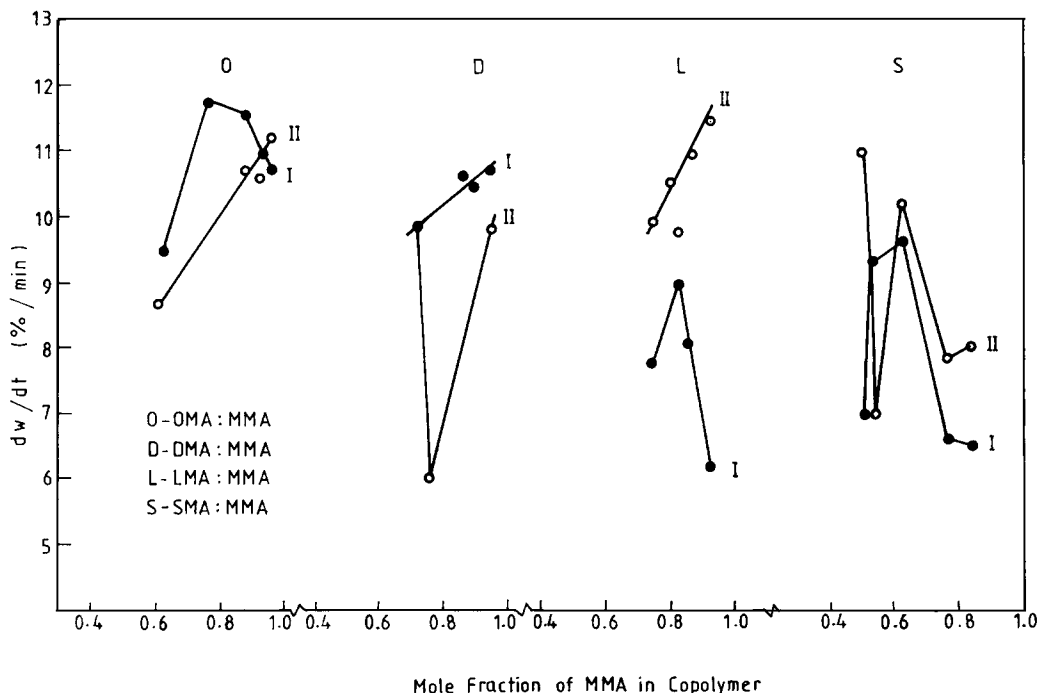
the ratio method the determination of the area under  $-\text{OCH}_2$  and  $-\text{OCH}_3$  protons was a bit difficult due to overlapping of the resonance signals. Hence,

an element of an error may be introduced in the determination of the copolymer composition.

The monomer reactivity ratios for copolymeri-

Table IV Thermogravimetric Analysis of Alkyl Methacrylate Copolymers

Sample Designation	$T_{\text{max}3}$ (°C)	$T_{\text{max}4}$ (°C)	$T_f$ (°C)	Wt. Loss (%) 150–250°C	Wt. Loss (%) 250–450°C
PMMA	311.4	396.8	421	—	99
OM-5	305.0	387.0	411.7	4	95
OM-10	305.5	385.0	409.6	5	94
OM-15	306.4	383.5	—	3	96
OM-20	308.5	—	367.1	14	85
OM-25	306.0	380.2	406.4	9	90
DM-5	305.7	391.2	419.5	2	97
DM-10	306.2	—	370.2	9	90
DM-15	311.9	—	—	14	85
DM-20	305.1	379.0	414.5	13	84
DM-25	300.5	380.6	407.7	5	94
LM-5	310.0	389.0	417.6	5	94
LM-10	302.3	387.5	412.8	2	87
LM-15	304.3	381.6	407.5	9	90
LM-20	307.1	—	358.6	11	88
LM-25	300.5	383.8	409.5	9	90
SM-5	309.0	388.0	415.0	15	84
SM-10	300.0	386.0	416.0	17	82
SM-15	309.5	383.0	408.4	8	91
SM-20	307.6	374.3	406.0	8	91
SM-25	307.0	382.0	409.0	10	89



**Figure 3** Plot of rate of weight loss vs. copolymer composition. Temperature range: (I) 280–320°C; (II) 320–450°C.

zation of MMA ( $r_1$ ) with OMA, DMA, LMA, and SMA ( $r_2$ ) were determined using the Kelen-Tüdös method and the copolymer composition as determined by the Grassie method was used for such calculations (Table II).

$Q$  and  $e$  values of the Alfrey and Price equation were also determined for the various alkyl methacrylates. For MMA, the  $Q$  value was taken as 0.78, and the  $e$  value, as 0.40. The results are given in Table III.

The intrinsic viscosity for most of the copolymers was higher than 0.4 dL/g. A slight increase in  $[\eta]$  was observed on increasing the alkyl methacrylate content (Table I).

### Thermal Behavior

Thermogravimetric studies were carried out in a nitrogen atmosphere to investigate the effect of the alkyl group of methacrylic acid esters on the thermal stability of the copolymers. PMMA was stable up to 250°C and started losing weight above this temperature. It showed a two-step degradation with  $T_{\max}$  at 311 and 397°C. The degradation at lower temperature may be attributed to the scission initiated by chain-end unsaturation and that at higher temperature due to the unzipping of the backbone ini-

tiated by random scission. All the copolymers showed two- or three-step degradation. The  $T_{\max}$  and  $T_f$  values in the copolymers were lower than in PMMA.

In SM-5 and SM-10 copolymers, four-step degradation was observed. The  $T_{\max}$  values for each step for SM-5 were at 190, 260, 308, and 388°C, and for SM-10, at 160, 230, 303, and 386°C. In SM copolymers having a higher mol fraction of SMA (0.15–0.25), a three-step degradation was observed (Fig. 2).

On increasing the mol fraction of the comonomers,  $T_{\max}$  and  $T_f$  values decreased slightly (Table IV), thereby showing the decreased thermal stability of copolymers having a higher concentration of the long side-chain alkyl group.

In all the copolymers, major weight loss occurred above 250°C. Weight loss was less than 20% below 250°C in MMA-alkyl methacrylates; the rate of weight loss (% wt loss/min) at  $T_{\max}$  was determined for the last two steps (i.e., in the temperature range of 280–450°C from DTG curves). The plots for the rate of weight loss vs. copolymer composition are given in Figure 3. The rate of weight loss increased linearly for the last step ( $T_{\max}$ ,  $382 \pm 8^\circ\text{C}$ ) for the OMA-MMA and LMA-MMA copolymers and it followed a linear relationship for the weight loss in

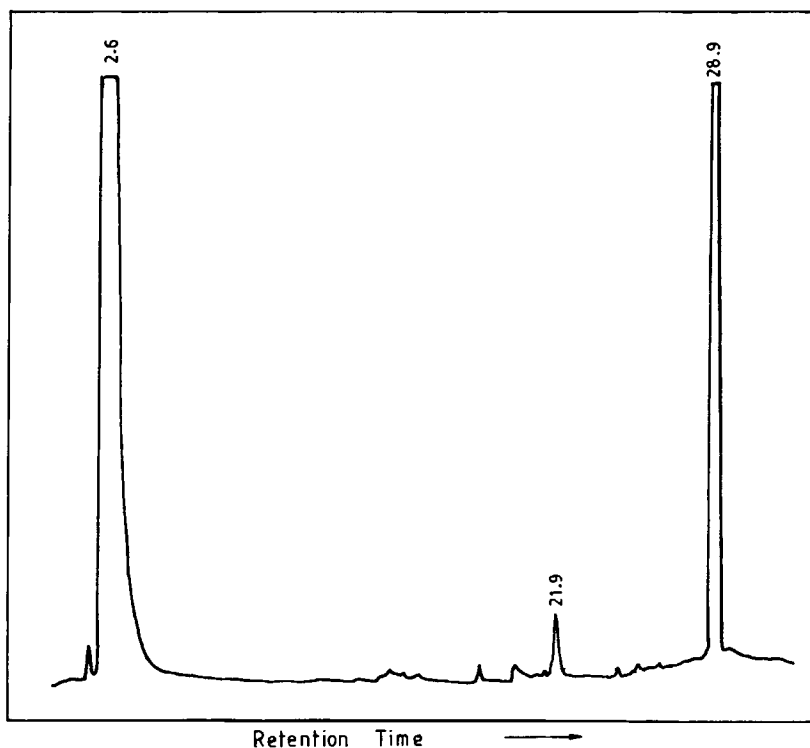


Figure 4 Pyrogram of SM-15 copolymer sample.

Table V Copolymer Composition by Pyrolysis-GC Method

Sample Designation	Mol Fraction of MMA in Copolymer
OM-5	0.926
OM-10	0.897
OM-15	—
OM-20	0.716
OM-25	0.674
DM-5	0.965
DM-10	0.888
DM-15	—
DM-20	0.695
DM-25	0.670
LM-5	0.944
LM-10	0.897
LM-15	0.875
LM-20	0.768
LM-25	0.693
SM-5	0.937
SM-10	0.907
SM-15	0.872
SM-20	—
SM-25	0.709

the temperature range of 290–310°C for the DMA–MMA system. In other cases, no systematic correlation was found between the rate of weight loss and the copolymer composition.

Pyrolysis GC studies were also carried out to investigate the degradation products of PMMA and copolymers. Such studies have earlier been used by Ohtami et al.<sup>7</sup> for the determination of the structure of complex MMA copolymers. Ferlanto et al.<sup>8</sup> used this technique for poly(methyl methacrylate-co-ethyl acrylate).

Analysis of thermally degraded products in pyrolyzed fractions of different copolymer samples was performed on a nonpolar column heated at a programmed rate. Pyrolysis of PMMA leads to depolymerization with a quantitative monomer yield (98.3%), giving a single peak at the retention time of  $2.6 \pm 0.1$  min. Pyrolysis of OM, DM, and LM copolymers under similar conditions gave two major peaks, one of which appeared at a retention time of  $2.6 \pm 0.1$  min and the other at  $15.6 \pm 0.2$ ,  $19 \pm 0.5$ , and  $22 \pm 0.1$  min (Fig. 4). Using the standard monomer samples, the retention times were identified to be of MMA and corresponding alkyl methacrylates (OMA, DMA, and LMA), suggesting, thereby, depolymerization as the major route of

degradation in copolymers. Pyrolyzed products of SM copolymers showed another additional peak that was analyzed to be octadecene by comparison of the peak retention time with that of an authentic sample. It is evident from the pyrolysis GC studies that degradation of SM copolymers at 400°C occurs with the random scission of the polymer backbone, giving the monomer and decomposition of the ester group.

Copolymer composition was also determined by pyrolysis GC studies by taking the ratio of the peak areas corresponding to monomers obtained on pyrolysis of the copolymer samples. The copolymer composition thus determined are given in Table V. These results clearly indicate a discrepancy in the copolymer composition by pyrolysis GC studies and <sup>1</sup>H-NMR. Some loss of monomer during pyrolysis and formation of side products may be responsible for this discrepancy.

The Department of Non-Conventional Energy Sources, Government of India, is gratefully acknowledged for sponsoring this project and providing a fellowship to one of the authors (S.A.). Thanks are due to Dr. R. V. Swamy,

Director, D.R.D.E., Gwalior, for his keen interest in the work and providing the pyrolysis GC facilities.

## REFERENCES

1. M. S. Choudhary and I. K. Varma, *Eur. Polym. J.*, **15**, 975 (1979).
2. I. K. Varma, M. Patnaik, and V. Choudhary, *J. Therm. Anal.*, **36**, 617 (1990).
3. I. K. Varma, M. V. Nair, and V. K. Karan, *J. Therm. Anal.*, **35**, 989 (1989).
4. I. K. Varma, M. V. Nair, V. K. Karan, and D. S. Varma, *Thermochim. Acta*, **142**, 189 (1989).
5. S. Agarwal, V. Choudhary, and I. K. Varma, *J. Appl. Polym. Sci.*, to appear.
6. M. Grassie, B. J. D. Torrence, J. D. Fortune, and J. D. Gemmel, *Polymer*, **6**, 653 (1965).
7. H. Ohtami, T. Asai, and S. Tsuge, *Macromolecules*, **18**, 1148 (1985).
8. E. C. Ferlanto, H. K. Lindeman, and C. A. Lucchesi, *J. Appl. Polym. Sci.*, **15**, 445 (1971).

Received February 26, 1994

Accepted March 14, 1994