

Synthesis, Characterizations and Thermal Behavior of Methyl Methacrylate and *N*-(*p*-carboxyphenyl) Methacrylamide/Acrylamide Copolymers

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ABSTRACT: The synthesis, characterization, and thermal properties of copolymers of methyl methacrylate (MMA) and *N*-(*p*-carboxyphenyl) methacrylamide/acrylamide (CPMA/CPA) are described. The copolymerization was carried out in solution by taking different mole fractions (0.1–0.5) of CPMA/CPA in the initial feed using azobisisobutyronitrile as an initiator and dimethylformamide as a solvent at 60°C. The copolymer composition was determined from ¹H-NMR spectra by taking the ratio of the proton resonance signal due to the —OCH₃ of MMA ($\delta = 3.59$ ppm) and the aromatic protons ($\delta = 7.6$ – 7.8 ppm) of CPMA/CPA. The monomer reactivity ratios of MMA:CPMA and MMA:CPA were determined using the Fineman Ross and Kelen Tudos methods and were found to be 1.32 ± 0.01 [MMA], 1.11 ± 0.02 [CPMA], 2.60 ± 0.01 [MMA], and 0.20 ± 0.01 [CPA]. Incorporation of these comonomers in the MMA backbone resulted in an improvement in the glass-transition temperature and thermal stability. The percent char also increased with the increase of CPMA/CPA content in the copolymers. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 259–267, 2000

Key words: methyl methacrylate; *N*-(*p*-carboxyphenyl); methacrylamide; acrylamide; copolymerization

INTRODUCTION

In our earlier article^{1–14} we reported the copolymerization of methyl methacrylate (MMA) with a variety of vinyl monomers, such as alkyl (meth)acrylates and *N*-aryl maleimides, that have electron donating or electron withdrawing groups on the phenyl ring. The nature and the position of the substituent in *N*-aryl maleimides and the length and nature of the alkyl group (linear or branched) in the side chain of alkyl (meth)acrylates was investigated to study the effect of the structure of the comonomers on the copolymerization, thermal, and

physicomechanical behavior. A significant increase in the glass-transition temperature (T_g) and the thermal stability was observed in the MMA:*N*-aryl maleimide copolymers that had electron withdrawing groups. The effect was further pronounced if the substituent was capable of participating in the formation of inter- or intramolecular hydrogen bonds. From these observations it was considered of interest to systematically investigate the copolymerization behavior of MMA with monomers having polar amide linkages and electron withdrawing groups capable of participating in H bonding.

For this purpose, *N*-(*p*-carboxyphenyl) acrylamide (CPA) and *N*-(*p*-carboxyphenyl) methacrylamide (CPMA) monomers were synthesized and their copolymerization behavior with MMA was investigated.

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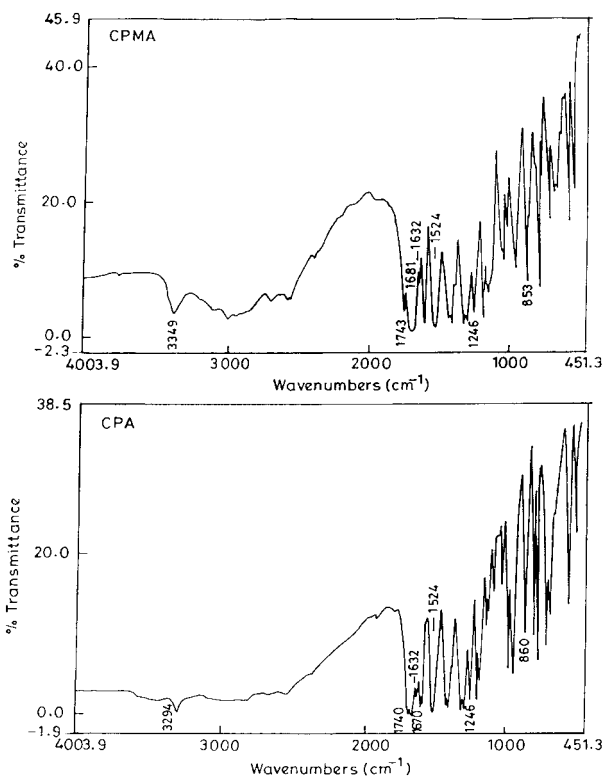


Figure 1 FTIR spectra of CPMA and CPA monomers.

EXPERIMENTAL

Materials

Acrylic acid (CDH), methacrylic acid (CDH), *p*-aminobenzoic acid (Loba Chemie), hydroquinone (Loba Chemie), and dimethylformamide (DMF, Qualigens) were used as received. Thionyl chloride (S.D. Fine Chemicals) was distilled before use. Azobisisobutyronitrile (AIBN, High Polymer Labs.) was recrystallized from chloroform.

The MMA (CDH) was purified by washing with 10% NaOH solution until the sodium hydroxide layer became colorless. Then it was washed repeatedly with distilled water until neutral. The washed monomer was dried overnight over anhydrous sodium sulfate and then distilled under reduced pressure.

Synthesis of CPA and CPMA Monomers

Preparation of Acryloyl or Methacryloyl Chloride

Acryloyl or methacryloyl chloride monomer was prepared by taking 100 mL of acrylic acid (1.38

mol) or methacrylic acid (1.16 mol) and 0.1 g hydroquinone in a round-bottom flask equipped with a dropping funnel and a condenser; 1.2 mol of thionyl chloride (excess) was added dropwise to this solution with constant stirring. The temperature was kept constant at between 25 and 30°C. After the complete addition of thionyl chloride the temperature was raised to 80°C for 4 h. The methacryloyl chloride formed was distilled at 97°C.

Preparation of CPA and CPMA Monomers

One hundred grams of *p*-aminobenzoic acid (0.73 mol) was dissolved in 10% sodium hydroxide solution (150 mL); 1 g of hydroquinone was added to inhibit the polymerization and it was followed by the slow addition of 100 mL (1 mol) of methacryloyl chloride at room temperature with vigorous stirring for 2 h. The precipitated CPMA thus obtained was washed with water until neutral. The monomer was purified by passing a methanol solution of the monomer

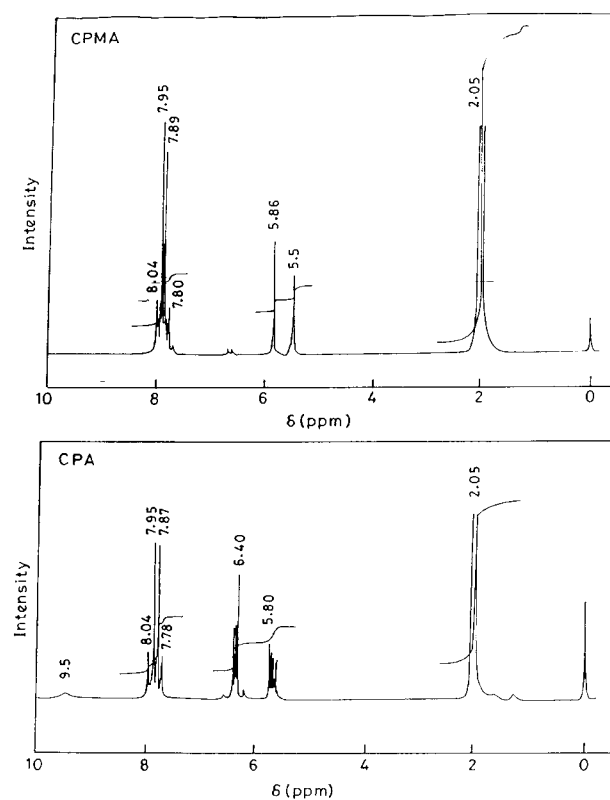


Figure 2 $^1\text{H-NMR}$ spectra of CPMA and CPA in d_6 -acetone.

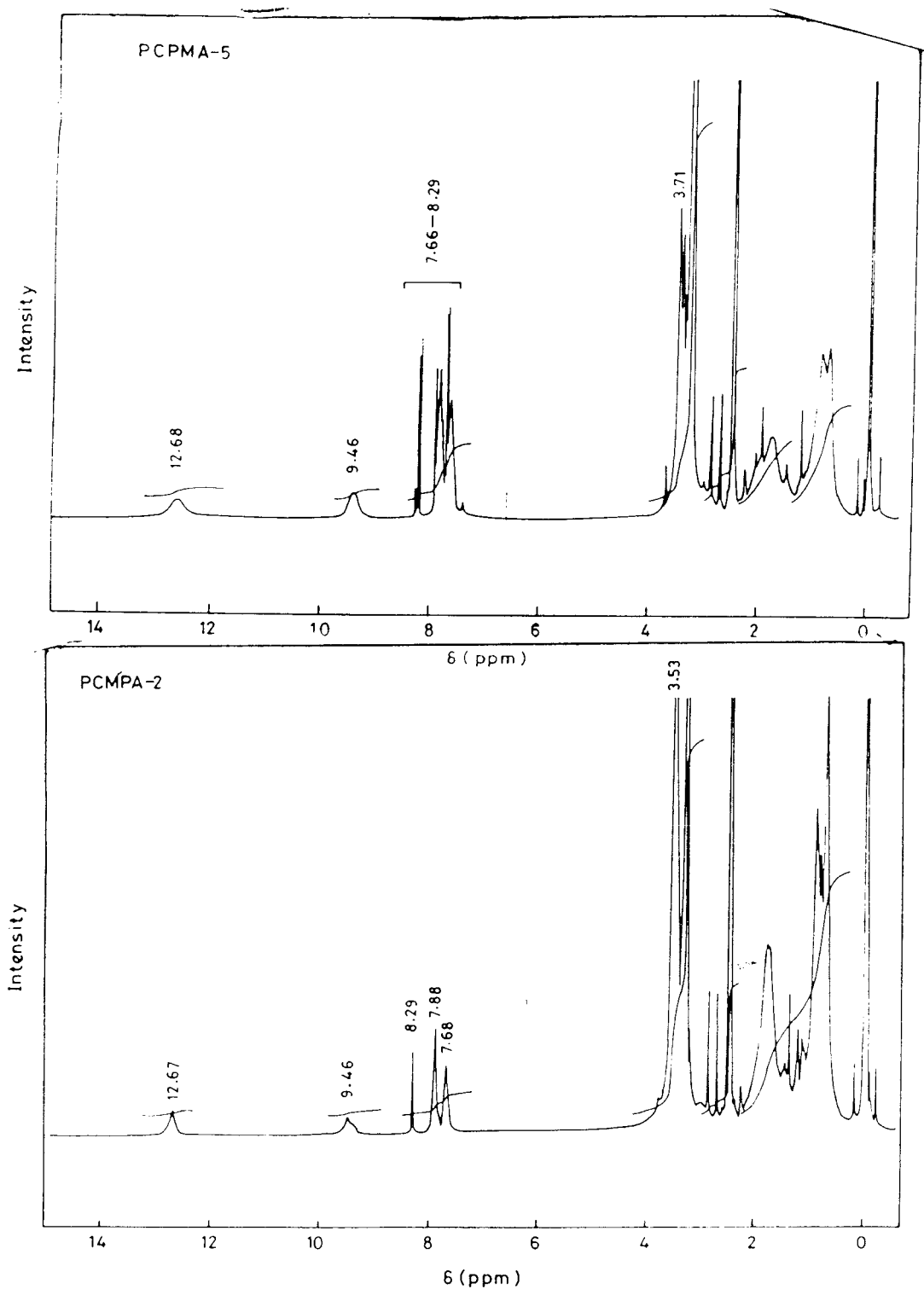


Figure 3 $^1\text{H-NMR}$ spectra of MMA-CPMA copolymers.

through an alumina column. Similarly CPA was prepared by reacting acryloyl chloride with *p*-aminobenzoic acid using the procedure de-

scribed above. CPA and CPMA were obtained as white powder with a yield in the range of 70–75%.

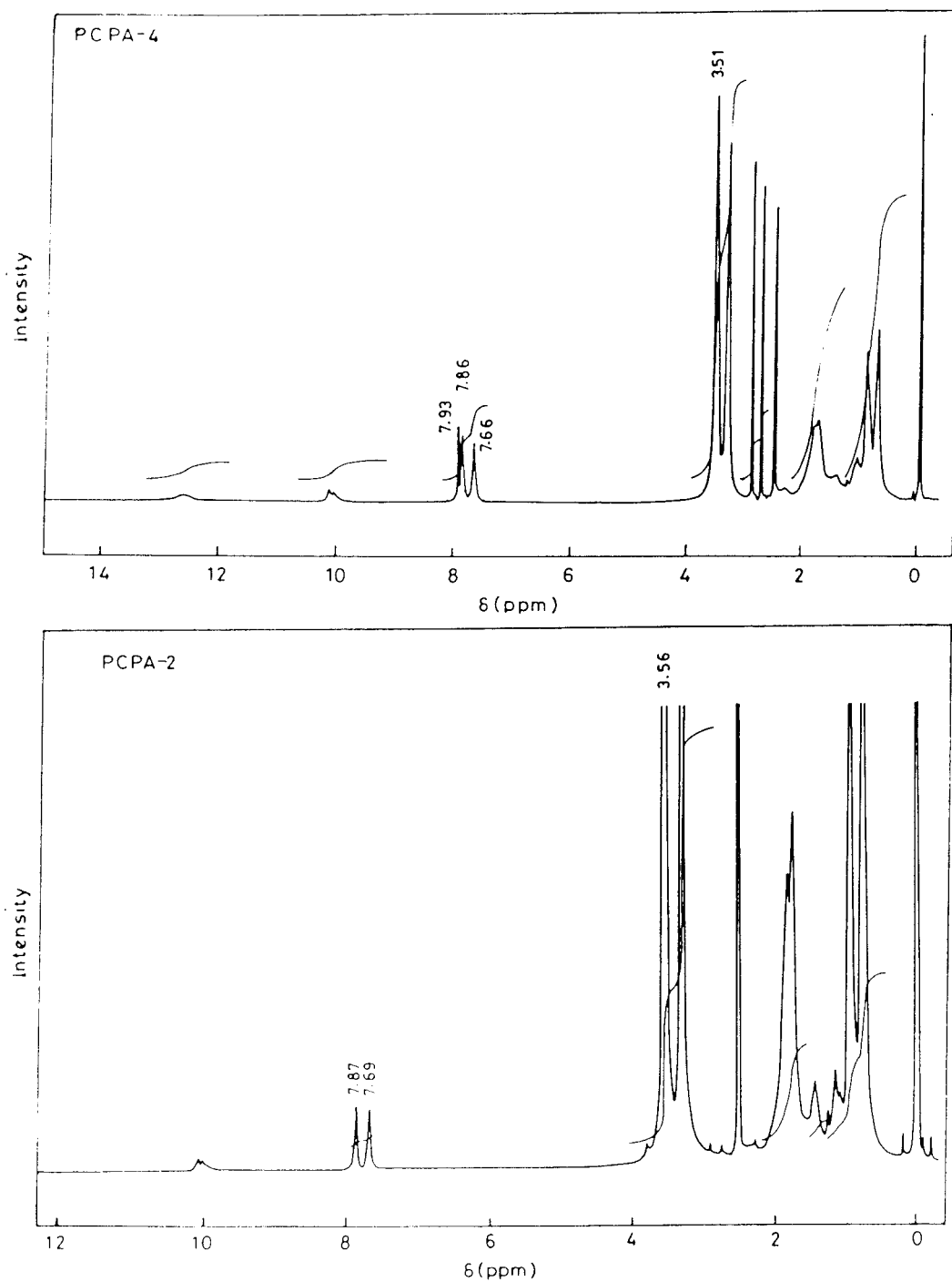


Figure 4 ¹H-NMR spectra of MMA-CPA copolymers.

Copolymerization of MMA with CPA or CPMA

Copolymerization of MMA with CPA or CPMA was carried out in DMF using AIBN as an initiator under a nitrogen atmosphere at 60°C. The

mole fraction of CPA/CPMA in the initial feed was varied from 0.1 to 0.5. A 20% (w/w) solution of the monomers in DMF was placed in a three-necked round-bottom flask equipped with a reflux condenser, a CaCl₂ drying tube, and a nitrogen gas

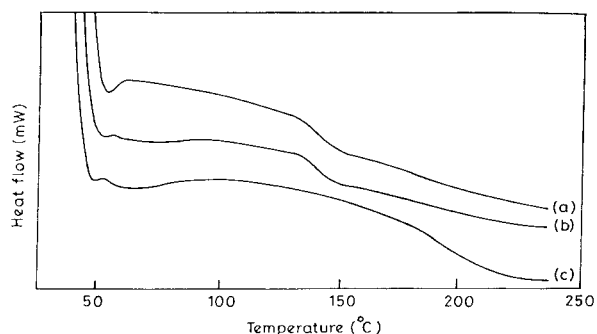
Table I Copolymerization of MMA with CPMA/CPA

Sample	Mole Fraction of Comonomers		Conv (%) / min
	Feed	Copolymer	
PCPMA-1	0.10	0.09	0.07
PCPMA-2	0.20	0.15	0.07
PCPMA-3	0.30	0.17	0.08
PCPMA-4	0.40	0.41	0.08
PCPMA-5	0.50	0.47	—
PCPA-1	0.10	0.09	0.10
PCPA-2	0.20	0.08	0.11
PCPA-3	0.29	0.13	0.11
PCPA-4	0.39	0.18	0.06

inlet tube. The whole assembly was placed in a thermostatted oil bath and stirred using a magnetic stirrer. Nitrogen was passed through the reaction mixture and the temperature was raised to 60°C. The polymerization was initiated by adding 1% AIBN (w/w). The reaction was stopped at low conversion ($\leq 15\%$) by pouring the contents of the flask into a mixture of water and methanol. The precipitated polymer was separated, washed with the methanol and water, and then dried in a vacuum oven at 50–60°C. The copolymer samples are designated by adding a prefix P to the letter designation of the comonomer and a numerical suffix indicating the mole fraction of the comonomer in the initial feed multiplied by 10. For example, a copolymer prepared by taking a 0.1 mol fraction of CPMA is designated as PCPMA-1.

Characterization of Monomers and Copolymers

The $^1\text{H-NMR}$ spectra of the monomers and polymers were recorded on a Jeol JNM-FX100 FT-NMR spectrometer using deuterated acetone as a

**Figure 5** DSC scans of PCPMA-1 (curve a), PCPMA-3 (curve b), and PCPMA-5 (curve c) copolymers.

solvent and tetramethylsilane as an internal standard. The FTIR spectra of the monomers were recorded in KBr pellets using a Biorad Digilab FTS-40 FTIR spectrophotometer.

A DuPont 9900 thermal analyzer with a 910 DSC module and a 951 TG module was used for the thermal characterization of monomers and copolymers. DSC scans were recorded in a static air atmosphere at a heating rate of 10°C/min by using 7 ± 1 mg of powdered samples. In order to have the same thermal history, the samples were first heated from 50 to 150°C followed by cooling in the DSC cell to room temperature. The same sample was reheated from 50 to 250°C to record the DSC scans. The TG and DTG traces were recorded in a nitrogen atmosphere at a flow rate of 60 mL/min. A heating rate of 10°C/min and a sample size of 10 ± 1 mg was used in each experiment.

RESULTS AND DISCUSSION

Characterization of Monomers

Figure 1 shows the IR spectra of CPMA and CPA monomers. In the IR spectra of CPMA/CPA, the

Table II Reactivity Ratios and Q and e Values of MMA (r_2) and Comonomers (r_1)

Sample	Monomer Reactivity Ratio					
	Fineman Ross		Kelen Tudos		Q_1	e_1
	r_1	r_2	r_1	r_2		
MMA-CPMA	1.13	1.33	1.10	1.32	1.66	1.03
MMA-CPA	0.20	2.60	0.21	2.61	0.41	1.18

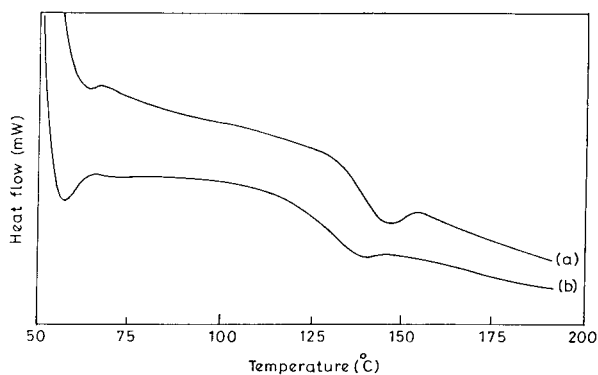
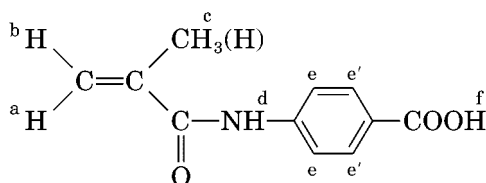


Figure 6 DSC scans of PCPA-1 (curve a) and PCPA-2 (curve b) copolymers.

characteristic peaks due to the carbonyl of the —COOH group at 1743 cm^{-1} , the vinyl group at 1632 cm^{-1} , and the $>C=O$ of amide at 1682 cm^{-1} for CPMA and 1670 cm^{-1} for CPA were observed. The absorption peak at 853 cm^{-1} was observed due to a parasubstituted benzene ring. The —NH of the amide group for CPA and CPMA was observed at 3294 and 3349 cm^{-1} , respectively. The characteristic absorption due to N—H bending and C—N stretching was observed at 1524 and 1246 cm^{-1} , respectively.

The $^1\text{H-NMR}$ spectra of CPA/CPMA recorded in d_6 -acetone are shown in Figure 2. Six and seven sets of protons are present in the CPA/CPMA monomers. The aromatic protons (e, e') appeared as a multiplet at $7.8\text{--}8.04\text{ ppm}$.



The two olefinic protons (a and b) in the CPMA are magnetically nonequivalent and appeared as a singlet at 5.5 and 5.86 ppm , respectively. However, in the CPA the olefinic protons a at $5.68\text{--}5.8\text{ ppm}$ and b and c at $6.26\text{--}6.64\text{ ppm}$ were observed as multiplets.

A singlet due to the $\alpha\text{-CH}_3$ protons of CPMA (c) was observed at 2.05 ppm . In the CPA a singlet observed at $\delta = 2.05\text{ ppm}$ could be due to the presence of some impurities in the deuterated acetone. The proton signals due to —CONH (d) and —COOH (f) were not observed in CPMA whereas a signal due to the —CONH proton was

observed at 9.5 ppm in the CPA. The integration was used to calculate the number of protons. Integration of the $\alpha\text{-CH}_3$ signal in the CPMA did not match because of the overlapping with the —CH_3 protons of acetone.

In the DSC scan an endothermic transition due to melting was observed. The CPA and CPMA showed a sharp melting peak at 245 and 227°C , respectively.

Characterization of Copolymers

The $^1\text{H-NMR}$ spectra of MMA:CPMA (PCPMA) and MMA:CPA (PCPA) copolymers are shown in Figures 3 and 4, respectively. The aromatic protons of the side chain of CPA/CPMA appeared at $\delta = 7.6\text{--}7.9\text{ ppm}$ and the characteristic —OCH_3 signal of MMA of the copolymers was observed at $\delta = 3.59 \pm 0.01\text{ ppm}$. The proton resonance signal due to —CONH and —COOH was observed at $\delta = 9.5 \pm 0.2$ and 12.6 ppm , respectively. The ratio of the intensity of the aromatic protons and the methoxy protons was used to calculate the mole fraction of monomers in the copolymers. In the $^1\text{H-NMR}$ spectra of PCPMA/PCPA copolymers the intensity of the signals due to aromatic protons increased with increasing CPMA/CPA content. The copolymer composition was therefore determined by taking the ratio of the intensity of signals due to the —OCH_3 protons of MMA and the aromatic protons of CPMA/CPA. The results of copolymer composition thus determined are summarized in Table I. An increase in the mole fraction of the comonomer in the feed resulted in an increase in the comonomer content in the copolymer.

From the knowledge of the copolymer composition, monomer reactivity ratios (i.e., r_1 and r_2) were calculated using Fineman Ross and Kelen Tudos methods. The results are given in Table II.

Table III DSC Scans of MMA-CPA/CPMA Copolymers

Sample	T_e ($^\circ\text{C}$)	T_g ($^\circ\text{C}$)	T_f ($^\circ\text{C}$)
PMMA	115	118	123
PCPMA-1	134	139	143
PCPMA-3	131	142	147
PCPMA-5	184	194	206
PCPA-2	120	129	137
PCPA-1	127	135	145

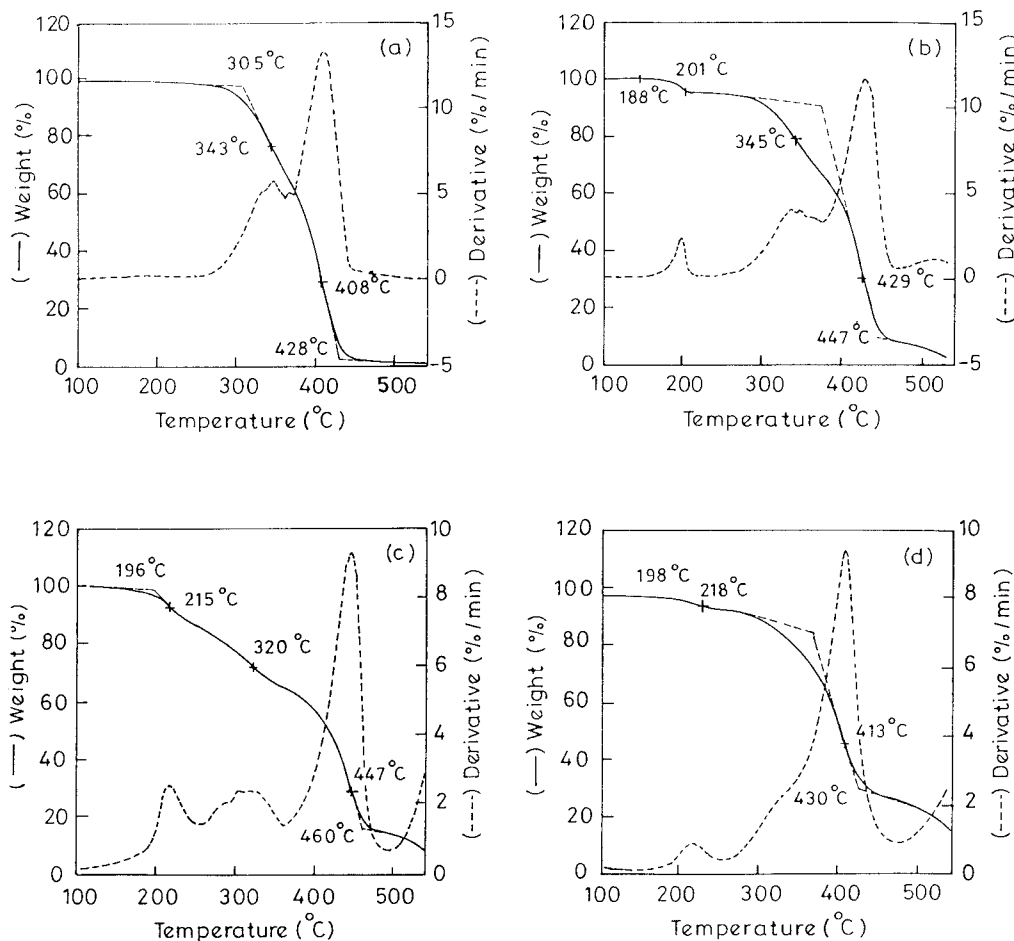


Figure 7 TG/DTG traces of copolymers in a nitrogen atmosphere for (a) PCPMA-1, (b) PCPMA-3, (c) PCPMA-4, and (d) PCPMA-5 (heating rate = 10°C/min).

In the MMA-CPA copolymer the reactivity ratio of MMA was higher as compared to the comonomers, thereby indicating that the copolymers were richer in MMA and the growing polymer radical has a preference for MMA as compared to CPA. In the MMA-CPMA copolymer the reactivity ratio was similar and the r_1r_2 product was slightly greater than unity. Hence, both monomers showed the same preference for adding one or the other of the two monomers. The values of Q and e for the comonomers were calculated from the Alfrey Price equation¹⁵ using the value of Q and e for MMA as 0.78 and 0.4, respectively (Table II). The Q value for CPA is lower than that for the CPMA monomer. The e values, which depend on the electronic requirements of the substituent, were similar in CPA and CPMA.

The DSC traces of the copolymers are shown in Figures 5 and 6 and the glass-transition region

was characterized by noting T_e (extrapolated onset temperature), T_g (midpoint temperature), and T_f (extrapolated end-set temperature). The results are summarized in Table III. The T_g increased with the increase in CPA/CPMA content in the copolymer. This increase in T_g could be due to the increased intermolecular interactions or the presence of a rigid phenyl group. Introduction of CPA/CPMA is also expected to enhance the T_g because of inter- or intramolecular hydrogen bonding. Copolymers of CPA/CPMA with very low mole fractions of comonomer showed an increase in the T_g of 21–27°C. In the DSC traces of PCPA copolymers with higher mole fractions of CPA monomers the glass-transition temperature could not be detected. In the copolymers with a 0.5 mol fraction of CPMA (i.e., PCPMA-5) the T_g increased by ~76°C. The increase in the T_g due to the inter- or intramolecular hydrogen bonding or

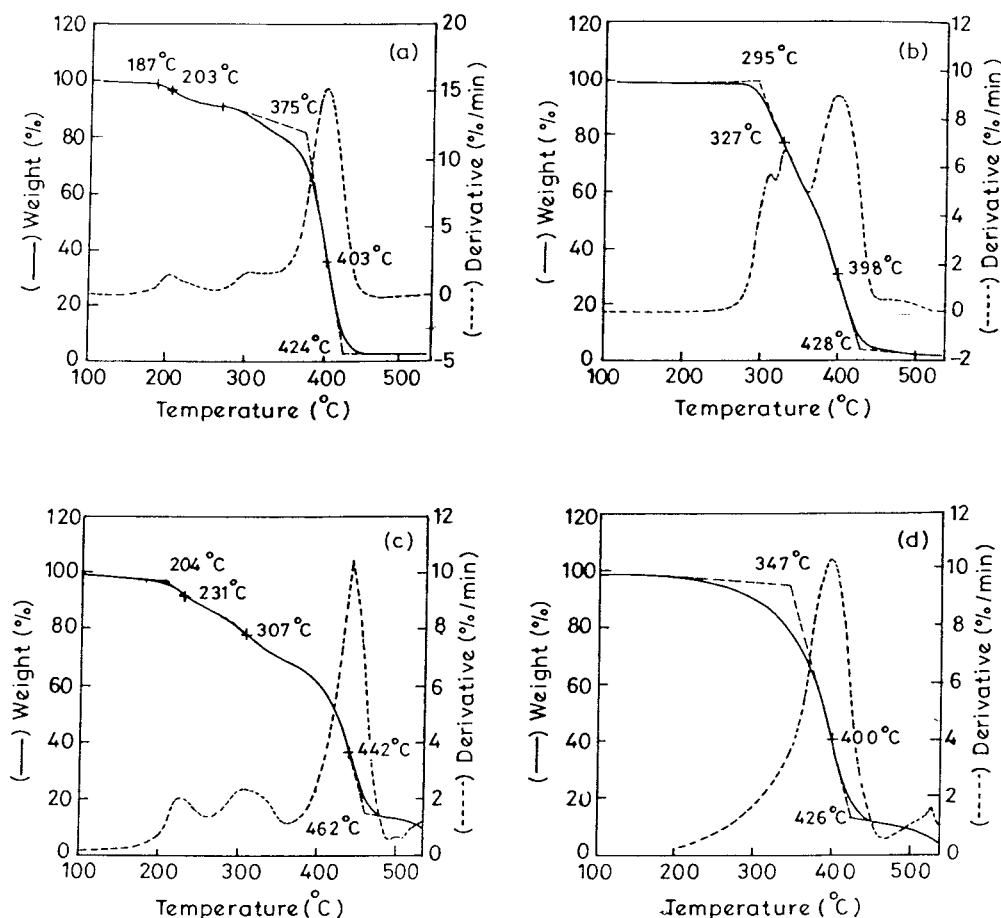


Figure 8 TG/DTG traces of copolymers in a nitrogen atmosphere for (a) PCPA-1, (b) PCPA-2, (c) PCPA-3, and (d) PCPA-4 (heating rate = 10°C/min).

strong interactions was reported by various authors.^{16–19} Poly(acrylic acid) showed stronger interactions with poly(2-vinyl pyridine)/poly(4-vinyl pyridine), resulting in the positive deviation in T_g as compared to poly(methacrylic acid). Similarly, the presence of dye in a polymer, instead of producing a plasticization effect, produced an anti-plasticization effect when strong interactions were present.^{20,21}

Figures 7 and 8 show the TG/DTG traces of PCPMA and PCPA copolymers. PCPMA-1 and PCPMA-5 showed a two step decomposition whereas PCPMA-3 and PCPMA-4 showed a three step decomposition. PCPA copolymers with low mole fractions of CPA monomer (0.08–0.13) showed a multistep decomposition whereas the PCPA-4 sample showed a single step decomposition. The stability of the copolymers was compared by comparing the weight loss in the temperature ranges (°C) of 150–250 (stage I), 250–

375 (stage II), and 375–500 (stage III). The percent char left at 500°C was also noted (Table IV). Weight loss in the first stage increased with an increasing mole fraction of the comonomer (up

Table IV Thermal Behavior of MMA-CPMA Copolymers

Sample	Percent Weight Loss at			Char at 500°C (%)
	150–250°C	250–375°C	375–500°C	
PCPMA-1	0.8	39.7	59.0	0.8
PCPMA-3	4.8	27.7	60.4	7.1
PCPMA-4	12.7	23.8	49.3	14.2
PCPMA-5	4.8	22.2	46.0	27.0
PCPA-1	7.0	9.4	80.0	2.3
PCPA-2	0.5	52.5	44.7	2.3
PCPA-3	9.9	22.9	50.6	12.9
PCPA-4	2.9	31.7	54.0	9.4

to ~41 mol % CPMA) in the copolymer followed by a decrease. In stages II and III there was a decrease in the weight loss with increasing CPMA content in the copolymers. The percent char increased with the increasing mole fraction of CPMA. In PCPA copolymers the percent weight loss showed no definite trend as a function of copolymer composition. The percent char increased with increasing CPA content in the copolymers up to 13 mol % (PCPA-3), followed by a decrease.

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