

# Copolymerization of *N*-(4-Carboxyphenyl) Itaconimide or *N*-(4-Carboxyphenyl) Itaconamic Acid with Methyl Methacrylate

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Received 10 September 2004; accepted 30 January 2005

DOI 10.1002/app.22338

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** This paper describes the synthesis and characterization of *N*-(4-carboxyphenyl) itaconamic acid (CPA) and *N*-(4-carboxyphenyl) itaconimide (CPI) obtained by reacting itaconic anhydride with *p*-aminobenzoic acid. Structural and thermal characterization of CPA and CPI was done using <sup>1</sup>H-NMR, FTIR, and differential scanning calorimetry (DSC). Copolymerization of CPA or CPI with methyl methacrylate (MMA) in solution was carried out at 60 °C using azobisisobutyronitrile as an initiator and dimethyl acetamide or THF as solvent. Feed compositions having varying mole fractions of CPA or CPI ranging from 0.05–0.20 or 0.1–0.5 were taken to prepare copolymers. Copolymerizations were terminated at low percentage conversion. Structural characterization of copolymers was done by <sup>1</sup>H-NMR and elemental analysis. Copolymer composition was determined using percentage nitrogen content. The reactivity ratios were  $r_1$  (MMA) =  $0.68 \pm 0.06$  and  $r_2$  (CPI) =  $0.46$

$\pm 0.06$ . The intrinsic viscosity  $[\eta]$  was determined using an Ubbelohde suspension level viscometer.  $[\eta]$  decreased with increasing mole fraction of *N*-(*p*-carboxyphenyl) itaconimide or *N*-(*p*-carboxyphenyl) itaconamic acid in copolymers. Glass transition temperature and thermal stability of the copolymers were determined using DSC and thermogravimetric analysis, respectively. The glass transition temperature ( $T_g$ ) as determined from DSC scans increased with increasing amounts of CPA or CPI in copolymers. A significant improvement in the char yield was observed upon copolymerization. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1909–1915, 2005

**Key words:** copolymerization; radical polymerization; glass transition; methyl methacrylate copolymers; *N*-(4-carboxyphenyl) itaconimides

## INTRODUCTION

The copolymerization of methyl methacrylate (MMA) with *N*-aryl substituted maleimides is well documented in the literature.<sup>1–8</sup> The structure of the maleimide monomers had a large effect on the glass transition temperature; however, it was very difficult to incorporate high amounts of maleimides as it has a 1, 2-disubstituted double bond, which have a low tendency to homopolymerize due to kinetic considerations.<sup>9</sup> Itaconimides, which contain 1,1-disubstituted double bond outside the ring, are expected to be more reactive than maleimides; therefore, the copolymerization of methyl methacrylate with *N*-aryl substituted itaconimides having electron withdrawing (-Cl group) or electron releasing group (-CH<sub>3</sub>) was carried out in our laboratories.<sup>10</sup> Since the increase in  $T_g$  of PMMA was found to be much higher when *N*-(*p*-carboxyphenyl)

maleimides was used as comonomer compared to the copolymer based on *N*-(4-chlorophenyl)maleimide and MMA, it was therefore of interest to investigate the copolymerization behavior of *N*-(4-carboxyphenyl) itaconimide (CPI) or *N*-(4-carboxyphenyl) itaconamic acid (CPA) with MMA.

The present article deals with the synthesis and characterization of CPA or CPI monomers and their radical copolymerization with MMA using dimethyl acetamide and/or tetrahydrofuran (THF) as solvent. Several copolymer samples were prepared by varying the mole fraction of CPA or CPI from 0.05–0.20 or 0.1–0.5 in the initial feed. Structural characterization of the copolymers was done using elemental analysis and <sup>1</sup>H-NMR. Thermal characterization of the copolymers was done using differential scanning calorimetry (DSC) and thermogravimetric analysis.

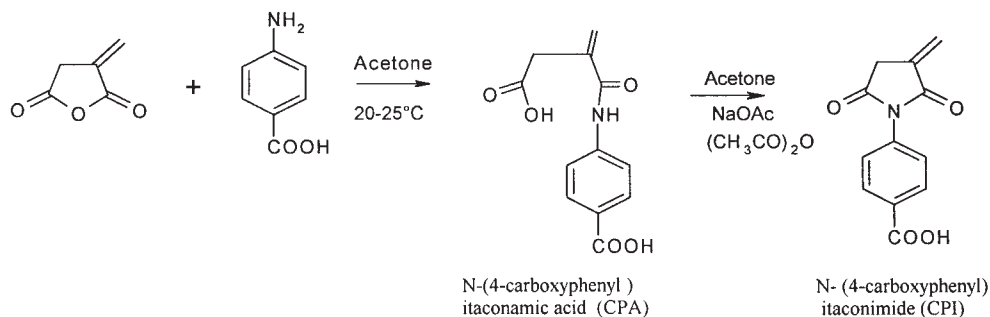
## EXPERIMENTAL

### Materials

Itaconic acid (Merck), *p*-aminobenzoic acid (Loba Chemie), methanol (S.D. Fine Chem.), chloroform (S.D. Fine Chem.), dimethyl acetamide (CDH), phosphorus

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Contract grant sponsor: Council of Scientific and Industrial Research.



**Scheme 1** Reaction scheme for the preparation of CPA/CPI monomers.

pentoxide (Qualigens), and silica gel for column chromatography (CDH) were used as supplied. Acetone (Qualigens) was dried overnight over potassium carbonate, followed by distillation. Acetic anhydride (S.D. Fine Chem.) was used after distillation. Anhydrous sodium acetate (CDH) was obtained by fusion. THF (CDH) was dried by refluxing with metallic sodium and benzophenone, followed by distillation. Azobisisobutyronitrile (AIBN) (High Polymer Labs) was recrystallized using chloroform. MMA (Merck) was washed with dilute sodium hydroxide to remove the inhibitor, followed by repeated washing with distilled water until neutral. It was dried over anhydrous sodium sulfate overnight and distilled under reduced pressure.

#### Preparation of itaconic anhydride

Itaconic anhydride was prepared from itaconic acid using an excess of phosphorus pentoxide as dehydrating agent and chloroform as solvent. The purity of crystals was checked by DSC (m.p. 69 °C) and structural characterization was done by <sup>1</sup>H-NMR [methylene protons (2H, S) at  $\delta = 3.6$  ppm, vinylidene protons at  $\delta = 6.5$  ppm (1H, S), and  $\delta = 5.9$  ppm (1H, S)]. This is due to the fact that the two protons are diastereotopic. Yield was found to be ~80%. The detailed procedure was reported in our earlier paper.<sup>10</sup>

#### Preparation of CPA and CPI monomers

Preparation of CPA and CPI was carried out according to the procedure reported by Searle<sup>11</sup> using acetone as solvent according to the following reaction scheme (Scheme 1).

#### Procedure

Itaconic anhydride (0.25 mol) was dissolved in a minimum amount of dry acetone taken in a three-neck round-bottom flask equipped with a magnetic stirrer and a reflux condenser. 4-Aminobenzoic acid (0.25 mol) dissolved in a minimum amount of dry acetone

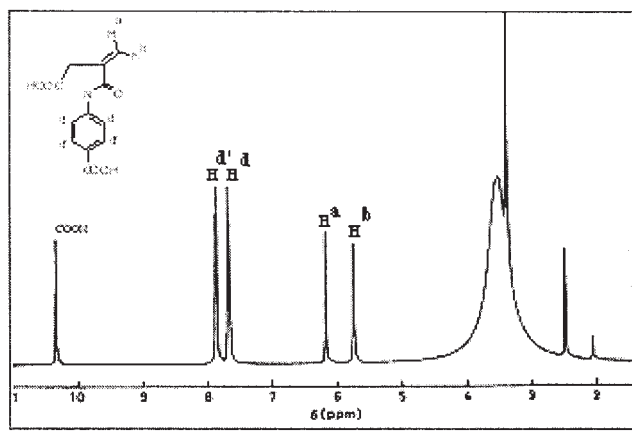
was added slowly with vigorous stirring. The CPA precipitated out from the solution. The precipitate was filtered, washed with acetone, and dried, giving CPA in 95% yield.

To prepare the CPI monomer, cyclization of CPA was carried out by addition of 75 mL of dry acetone, 40 mL of acetic anhydride, and 4 g of sodium acetate to CPA (0.25 mol) obtained in the first step. The mixture was refluxed for 2–3 h until a clear solution was obtained. The solution was cooled to room temperature and poured in ice-cold water. The product was extracted with ethyl acetate. The organic layer was washed with distilled water, dried, and concentrated to give CPI. The purification of the monomer was done by passing the solution of the monomer in THF through a silica gel column and then concentrating the THF solution to give CPI in 80% yield.

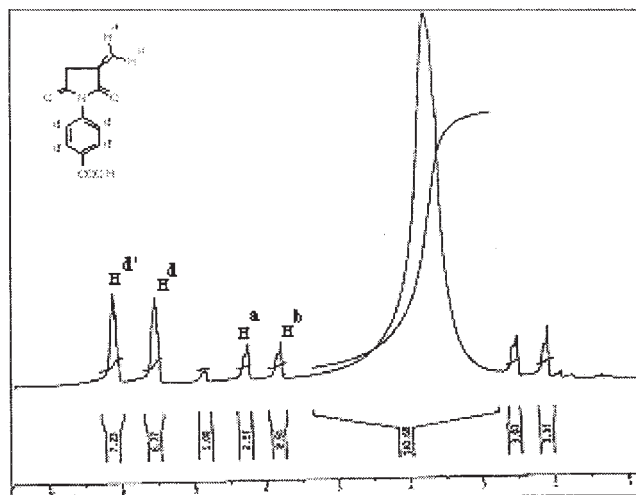
The monomers prepared were characterized by DSC, FTIR, and <sup>1</sup>H-NMR. In the DSC scans of monomers, an endothermic transition due to melting was observed. The melting points noted from the endothermic peak position were 236.3 and 199.8 °C for CPA and CPI, respectively.

In the FTIR spectrum of the CPI monomer, the characteristic absorption bands due to the imide group were observed at  $1709 \pm 3$  and  $1770 \pm 3$  cm<sup>-1</sup>. The absorption band due to  $-C=C$  stretching was observed at  $1662$  cm<sup>-1</sup>. The broad peaks at  $3450$  and  $1700$  cm<sup>-1</sup> show the presence of a  $-COOH$  group.

In the <sup>1</sup>H-NMR spectrum of CPA in DMSO-*d*<sub>6</sub> [Fig. 1(a)], proton resonance signal due to carboxyl proton was observed at 10.5 ppm whose integration value corresponds to one carboxyl against the two carboxyl groups present in the compound. This could be due to the fact that the  $-COOH$  attached to the aromatic ring is more acidic and undergoes hydrogen exchange too fast to be observed in <sup>1</sup>H-NMR. Proton resonance signals due to aromatic protons were observed at  $\delta = 7.6$ – $7.8$  ppm. The two singlets corresponding to the vinylidene protons were observed at  $\delta = 6.1$  and  $5.7$  ppm. The resonance signals due to methylene protons and that due to  $-NH$  protons got merged in the resonance



(a)



(b)

**Figure 1**  $^1\text{H-NMR}$  spectra of monomers (a) CPA and (b) CPI in  $\text{DMSO-}d_6$ .

signal for the DMSO at 3.2–3.5 ppm. Similarly, in the  $^1\text{H-NMR}$  spectrum of CPI in  $\text{DMSO-}d_6$  [Fig. 1(b)], the proton resonance signals due to aromatic protons were observed at  $\delta = 7.4\text{--}8.0$  ppm. The two singlets corresponding to the vinylidene protons were observed at  $\delta = 6.5$  and 5.7 ppm and those due to methylene protons got merged in the resonance signal for the DMSO in the region 3.0–3.5 ppm. The proton resonance signal observed at  $\delta = 6.8$  and 2.0 ppm may be attributed to the vinyl proton and the methyl group of citraconimide. The isomerization of itaconimide to citraconimide may be responsible for this signal. Such isomerization has been earlier reported by various authors.<sup>14,15</sup> The mole fraction of citraconimide to itaconimide was calculated from the ratio of the intensity of protons at  $\delta = 2.0$  and 5.7 ppm and was 1 : 3.

### Preparation of copolymers of CPA and CPI with MMA

Copolymerization of CPA or CPI with MMA was carried out in dimethyl acetamide or THF using AIBN as an initiator at 60 °C under nitrogen atmosphere. The mole fraction of CPA and CPI in the initial feed was varied from 0.05 to 0.20 and 0.1 to 0.5, respectively. A 30% (w/v) solution of monomers in the solvent was placed in a three-neck round-bottom flask equipped with a reflux condenser,  $\text{CaCl}_2$  guard tube, and nitrogen gas 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 using 1% AIBN (w/w) as an initiator. The reaction was stopped at low conversion (10–15%) by pouring the contents of the flask into a large excess of methanol. The precipitated polymer was washed repeatedly with hot methanol to remove unreacted monomers and was dried in a vacuum oven.

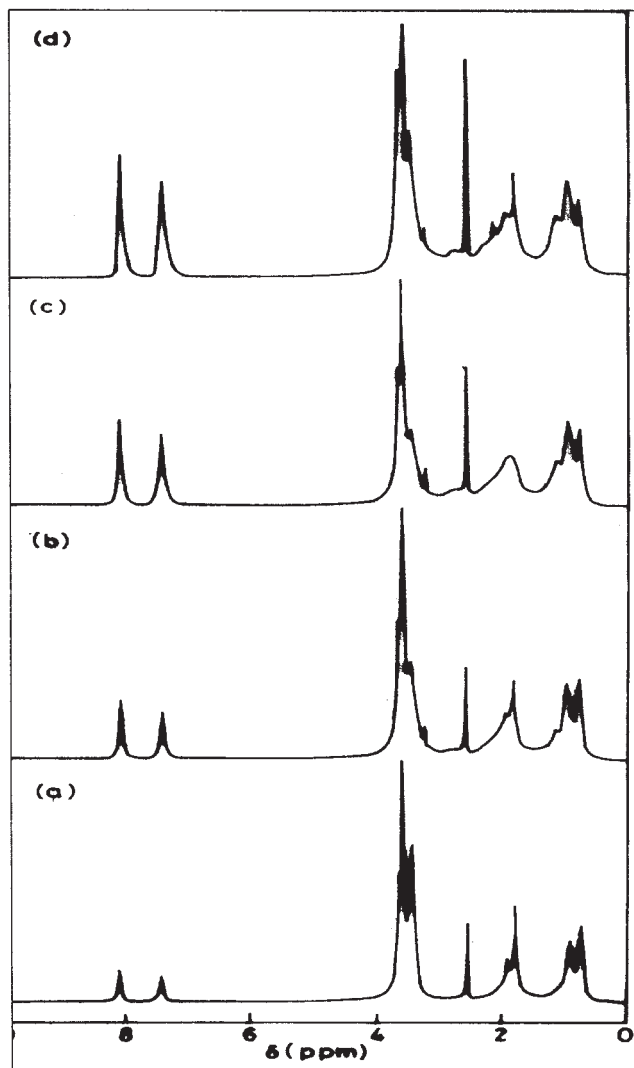
The copolymers of *N*-(4-carboxyphenyl) itaconamic acid and *N*-(4-carboxyphenyl) itaconimide with MMA have been designated CPA-MMA and CPI-MMA followed by a numerical suffix indicating the mole fraction of the CPA or CPI in the feed multiplied by 10. For example, a copolymer prepared by taking 0.2 mol fraction of CPA and CPI has been designated CPA-MMA-2 and CPI-MMA-2, respectively.

### CHARACTERIZATION

$^1\text{H-NMR}$  and FTIR spectroscopic techniques were used for structural characterization of the copolymers.  $^1\text{H-NMR}$  spectra of the monomers and copolymers were recorded on a Bruker spectropin DPX 300 spec-

**TABLE I**  
Polymerization Conditions, Sample Designation, Percentage Conversion and Intrinsic Viscosity (at  $30 \pm 0.1$  °C) in DMF of CPA-MMA and CPI-MMA Copolymers (Temperature of Polymerization  $60 \pm 1$  °C)

Sample designation	Mole fraction of monomers in feed		Conversion (%/min)	$[\eta]$ (mL/g)
	CPI or CPA	MMA		
CPA-MMA-0.5	0.05	0.95	0.09	25.3
CPA-MMA-1.0	0.10	0.90	0.07	22.4
CPA-MMA-1.5	0.15	0.85	0.04	22.2
CPA-MMA-2.0	0.20	0.80	0.009	—
CPI-MMA-1	0.10	0.90	0.07	16.8
CPI-MMA-2	0.20	0.80	0.06	12.6
CPI-MMA-3	0.30	0.70	0.05	—
CPI-MMA-4	0.40	0.60	0.05	12.5
CPI-MMA-5	0.50	0.50	0.01	—



**Figure 2**  $^1\text{H-NMR}$  spectra of CPI-MMA copolymers: (a) CPI-MMA-1, (b) CPI-MMA-2, (c) CPI-MMA-3, and (d) CPI-MMA-4.

trometer using  $\text{DMSO-}d_6$  as solvent and tetramethylsilane as an internal standard. FTIR spectra of the monomers were recorded in KBr pellets using a Nicolet FTIR spectrophotometer. Elemental analysis using Elementar Vario EL was also done to determine the copolymer composition.

The intrinsic viscosity of the polymers at  $30 \pm 0.1$  °C was determined in DMF using an Ubbelohde suspension level viscometer.

A TA 2100 thermal analyzer having a 910 DSC module was used for the thermal characterization of monomers and copolymers. DSC scans were recorded in static air atmosphere at a heating rate of 10 °C/min using  $5 \pm 1$  mg of powdered samples. Thermal stability was determined by recording TG/DTG traces in nitrogen atmosphere (flow rate = 60  $\text{cm}^3/\text{min}$ ) using a TA 2100 thermal analyzer having a 951 TG module. A heating rate of 20 °C/min and a sample size of  $10 \pm 1$  mg was used in each experiment.

## RESULTS AND DISCUSSION

The details of feed composition, percentage conversion per minute, and intrinsic viscosity of the copolymers are given in Table I. Homopolymers of CPA and CPI could not be prepared. Copolymers with mole fraction of CPA higher than 0.2 could not be prepared, whereas a mole fraction of CPI ranging from 0.1–0.5 could be used successfully for the preparation of copolymers. Percentage conversion per minute decreased with increasing mole fraction of the comonomer (CPA or CPI).

Intrinsic viscosity  $[\eta]$  is a measure of hydrodynamic volume and depends on molecular weight as well as on the size of the polymer coil in solution. In CPA-MMA or CPI-MMA copolymers, a decrease in  $[\eta]$  was observed as the comonomer content (CPA or CPI) in the initial feed was increased.

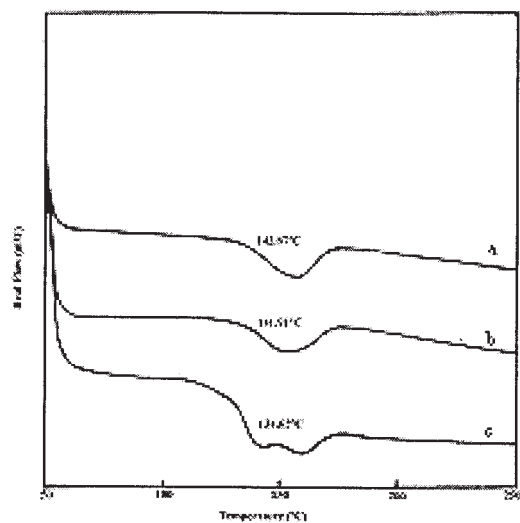
Figure 2 shows the  $^1\text{H-NMR}$  spectra of CPI-MMA copolymers. In the  $^1\text{H-NMR}$  of CPI-MMA copolymers, two singlets at  $\delta = 8.0$  and 7.4 ppm corresponding to aromatic protons of CPI were observed. The intensity of the signals due to aromatic protons increased with increasing concentration of CPI in the initial feed. The signal due to methoxy of MMA at  $\delta = 3.59$  ppm got merged with signal due to DMSO and hence cannot be used for the determination of copolymer composition. The other characteristic signals observed at  $\delta = 2.0$ –1.7 and 1–0.7 ppm were due to  $-\text{CH}_2$  and  $-\text{CH}_3$  protons of MMA, respectively. Similarly, for the CPA-MMA copolymers, the aromatic protons were observed at  $\delta = 7.8$  and 7.6 ppm, whereas the characteristic signals for  $-\text{CH}_2$  and  $-\text{CH}_3$  were observed at  $\delta = 1.9$ –1.4 and 0.9–0.7 ppm, respectively.

Percentage nitrogen content was used to calculate the mole fraction of CPI and/or CPA monomers in CPI-MMA or CPA-MMA copolymers and the results are given in Table II.

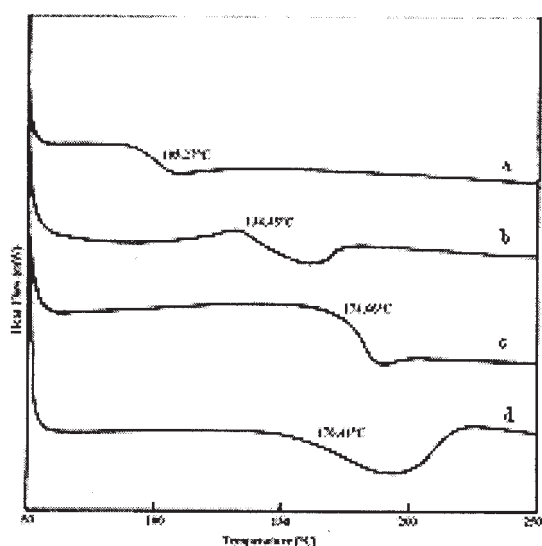
Copolymer composition data were used to calculate the reactivity ratios of the monomers using the Fine-

**TABLE II**  
Details of Feed Composition and Results of Copolymer Composition Determined from Nitrogen Content in CPA-MMA and CPI-MMA Copolymers

Sample designation	Mole fraction of CPI or CPA in feed	% Nitrogen	Mole fraction CPI/CPA in copolymer
CPA-MMA-0.5	0.05	0.93	0.074
CPA-MMA-1.0	0.10	1.00	0.080
CPA-MMA-1.5	0.15	1.04	0.082
CPA-MMA-2.0	0.20	1.16	0.095
CPI-MMA-1	0.10	1.59	0.130
CPI-MMA-2	0.20	2.49	0.230
CPI-MMA-3	0.30	3.20	0.330
CPI-MMA-4	0.40	3.78	0.420
CPI-MMA-5	0.50	4.00	0.460



(a)



(b)

Figure 3 DSC scans of (a) CPA-MMA copolymers and (b) CPI-MMA copolymers.

man-Ross and Kelen-Tüdös methods. In CPI-MMA copolymers, the value of  $r_1$  (methyl methacrylate) was  $0.68 \pm 0.06$  and that of CPI ( $r_2$ ) was  $0.46 \pm 0.06$ . These results show a higher reactivity ratio of methyl methacrylate compared to CPI monomer.

The DSC scans of various copolymers were recorded primarily to study the effect of copolymer structure and composition on the glass transition temperature ( $T_g$ ) of the copolymers. Figure 3 shows the DSC scans of CPA-MMA and CPI-MMA copolymers. A shift in the baseline due to glass transition was observed in all samples. To fully characterize the glass

TABLE III  
Results of DSC Scans of CPA-MMA and CPI-MMA Copolymers (Heating Rate 10 °C/min)

Sample designation	Mole fraction of CPI or CPA in Copolymer	$T_e$ (°C)	$T_g$ (°C)	$T_f$ (°C)
CPA-MMA-0.5	0.074	98.3	103.53	116.1
CPA-MMA-1.0	0.080	134.4	142.87	149.7
CPA-MMA-1.5	0.082	134.2	141.91	148.7
CPA-MMA-2.0	0.095	127.3	134.62	138.6
CPI-MMA-1	0.13	95.8	105.27	114.1
CPI-MMA-2	0.23	130.2	134.45	144.8
CPI-MMA-3	0.33	150.9	174.66	182.7
CPI-MMA-4	0.42	154.8	176.44	198.5

transition region, the following temperatures were noted and the results of the DSC traces are summarized in Table III.

$T_e$  = extrapolated onset temperature

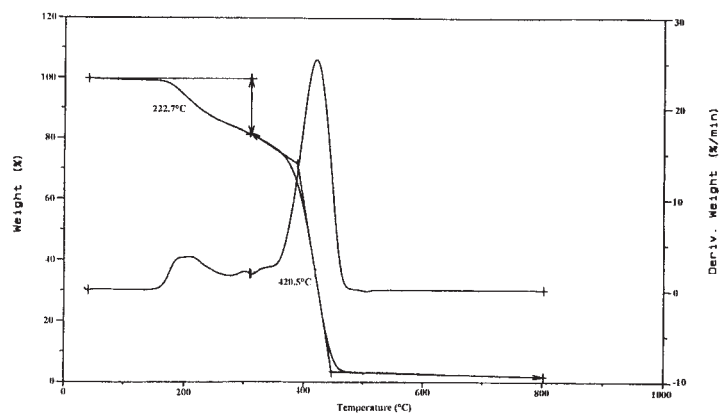
$T_g$  = glass transition temperature

$T_f$  = extrapolated end set temperature

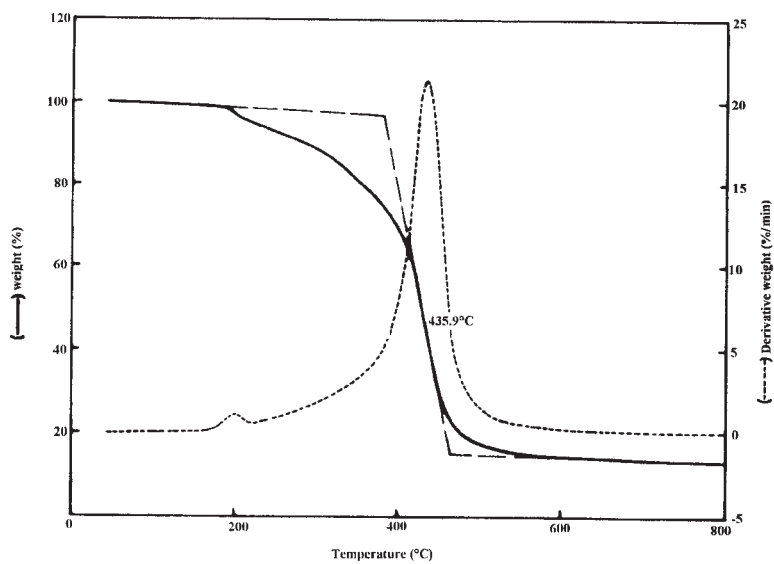
$T_g$  of the CPI-MMA copolymers was higher than that of PMMA and it increased with increasing amount of comonomer (CPI) in the PMMA backbone. This increase in  $T_g$  could be due to the introduction of a rigid and polar imide group, which hinders the mobility of the backbone. About a 76 °C increase in  $T_g$  was observed after incorporating 0.4 mol fraction of CPI. In CPA-MMA copolymers, samples having 0.07–0.095 mol fraction of CPA could be prepared and  $T_g$  did not show much effect as a function of composition. However, upon comparing the  $T_g$  of CPA-MMA copolymers with that of CPI-MMA copolymers prepared using 0.1 mol fraction of CPA/or CPI, i.e., sam-

TABLE IV  
Results of Thermogravimetric Analysis in Nitrogen Atmosphere (Heating Rate 10 °C/min)

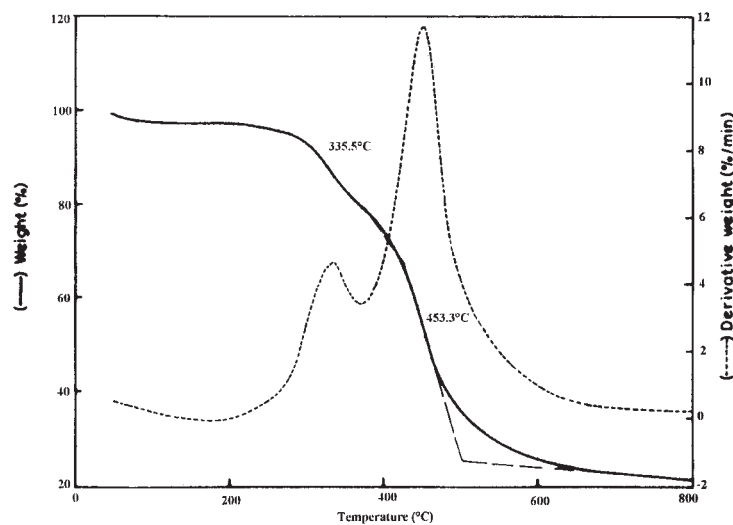
Sample designation	$T_e$ (°C)	$T_{max}$ (°C)	$T_f$ (°C)	% Char yield at 700 °C
CPA-MMA-0.5	159.1	222.7	268.1	1.3
CPA-MMA-1.0	313.6	420.5	472.7	6.6
CPA-MMA-1.5	155.6	242.2	268.9	4.5
CPA-MMA-2.0	313.3	420.0	468.9	3.2
CPI-MMA-1	173.0	224.7	273.0	18.9
CPI-MMA-2	313.5	424.7	473.0	18.5
CPI-MMA-3	182.0	253.9	278.6	14.7
CPI-MMA-4	330.3	424.7	479.8	21.2
CPI-MMA-5	359.5	449.4	504.5	32.2
	268.5	435.9	522.5	
	240.0	331.1	368.8	
	368.8	444.4	582.2	
	271.1	335.5	373.3	
	373.33	453.3	582.2	
	231.11	313.3	360.0	
	360.0	473.3	588.9	



(a)



(b)



(c)

Figure 4 TG/DTG traces of copolymer samples (a) CPA-MMA-0.5, (b) CPI-MMA-2, and (c) CPI-MMA-4.

ples CPA-MMA-1 and CPI-MMA-1, the  $T_g$  of CPA-MMA copolymer was higher than that of CPI-MMA despite having only 0.08 mol fraction of CPA in sample CPA-MMA-1 compared to 0.13 mol fraction of CPI in CPI-MMA-1. The high  $T_g$  observed in CPA-MMA copolymers can be explained on the basis of inter/intramolecular hydrogen bonding. In CPA-MMA copolymers, carboxyl content is higher compared to CPI-MMA; it also has amide groups that may be responsible for inter/intramolecular H-bonding and thus increasing  $T_g$ . Increase in  $T_g$  upon hydrogen bonding has been well reported in the literature.<sup>12</sup> On the other hand, a decrease in  $T_g$  was observed in CPA-MMA-2, which had the highest amount of CPA. This can be explained on the basis of molecular weight, as intrinsic viscosity showed a significant decrease with increasing amount of CPA in the feed.

The relative thermal stability of the copolymers was assessed by comparing initial decomposition temperature ( $T_i$ ), final decomposition temperature ( $T_f$ ), temperature of maximum rate of weight loss ( $T_{max}$ ), and percentage char at 700 °C. The results of the thermal behavior of copolymers are summarized in Table IV.

In the case of PMMA, three-step degradation has been reported.<sup>13,14</sup> The first step of degradation (150–250 °C) is attributed to head-to-head linkages; the second step (250–300 °C) was due to end unsaturation, and the third step (350–500 °C) was due to depropagation. In the CPA-MMA copolymers, a two-step degradation was observed and a weight loss of 18–25% was observed in the temperature range of 150–300 °C. Weight loss in this temperature range (150–300 °C) increased with increasing amount of CPA in the copolymers and can be attributed to the loss of water due to cyclization.

In the case of CPI-MMA copolymers, a single-step degradation was observed in samples with lower mole fraction of CPI in the feed, i.e., CPI-MMA-1 and CPI-MMA-2, whereas two-step degradation was observed for the samples with higher ratio of CPI in the feed, i.e., CPI-MMA-3, CPI-MMA-4, and CPI-MMA-5. All samples were stable up to 230 °C and started losing weight above this. A significant improvement in the char yield was observed upon incorporation of CPI in the PMMA backbone and it showed an increase with increasing amount of itaconimide. About 32% increase

in the char yield at 700 °C was observed upon incorporation of 0.46 mol fraction of CPI in the PMMA backbone. The TG/DTG traces of CPA-MMA-1, CPI-MMA-2, and CPI-MMA-4 samples are shown in Figure 4.

## CONCLUSIONS

From these results the following can be concluded:

1. CPA and CPI can be successfully copolymerized with MMA;
2. a significant improvement in  $T_g$  was observed upon incorporation of very low mole fractions of these monomers;
3. copolymerization of MMA with CPI resulted in a significant increase in the thermal stability.

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