

# Copolymerization of *N*-Aryl Substituted Itaconimide with Methyl Methacrylate: Effect of Substituents on Monomer Reactivity Ratio and Thermal Behavior

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**ABSTRACT:** The article describes the synthesis and characterization of *N*-(4-methoxy-3-chlorophenyl) itaconimide (MCPI) and *N*-(2-methoxy-5-chlorophenyl) itaconimide (OMCPI) obtained by reacting itaconic anhydride with 4-methoxy-3-chloroanisidine and 2-methoxy-5-chloroanisidine, respectively. Structural and thermal characterization of MCPI and OMCPI monomers was done by using  $^1\text{H}$  NMR, FTIR, and differential scanning calorimetry (DSC). Copolymerization of MCPI or OMCPI with methyl methacrylate (MMA) in solution was carried out at 60°C using AIBN as an initiator and THF as solvent. Feed compositions having varying mole fractions of MCPI and OMCPI ranging from 0.1 to 0.5 were taken to prepare copolymers. Copolymerizations were terminated at low percentage conversion. Structural characterization of copolymers was done by FTIR,  $^1\text{H}$  NMR, and elemental analysis and percent nitrogen content was used to calculate the copolymer composition. The

monomer reactivity ratios for MMA–MCPI copolymers were found to be  $r_1$  (MMA) =  $0.32 \pm 0.03$  and  $r_2$  (MCPI) =  $1.54 \pm 0.05$  and that for MMA–OMCPI copolymers were  $r_1$  (MMA) =  $0.15 \pm 0.02$  and  $r_2$  (OMCPI) =  $1.23 \pm 0.18$ . The intrinsic viscosity  $[\eta]$  of the copolymers decreased with increasing mole fraction of MCPI/or OMCPI. The glass transition temperature as determined from DSC scans was found to increase with increasing amounts of OMCPI in copolymers. A significant improvement in the char yield as determined by thermogravimetry was observed upon copolymerization. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2391–2398, 2006

**Key words:** *N*-(2-methoxy-5-chlorophenyl) itaconimide; *N*-(4-methoxy-3-chlorophenyl) itaconimide; methyl methacrylate; copolymerization; itaconimide

## INTRODUCTION

Several studies have been done in our laboratories on the synthesis of *N*-monosubstituted itaconimides and maleimides<sup>1–6</sup> and their radical copolymerization with MMA to get a copolymer with higher glass transition temperature ( $T_g$ ) compared to PMMA without affecting its other useful properties. These studies clearly show that the nature as well as position of the substituent had a large effect on  $T_g$ . However, no systematic studies are reported on the copolymerization of disubstituted itaconimides with MMA. It was therefore considered of interest to investigate systematically the effect of simultaneous presence of both  $e^-$ -withdrawing and  $e^-$ -releasing substituents on the aromatic ring in *N*-aryl-substituted itaconimides on the copolymerization behavior with MMA.

This article deals with the synthesis, characterization, and radical copolymerization of *N*-(4-methoxy-3-chlorophenyl) itaconimide (MCPI) and *N*-(2-methoxy-5-chlorophenyl) itaconimide (OMCPI) monomers with MMA using THF as solvent. Several copolymer samples were prepared by varying the mole fractions of MCPI and OMCPI from 0.1 to 0.5 in the initial feed. Structural characterization of the copolymers was done using FTIR,  $^1\text{H}$  NMR, and elemental analysis. Thermal characterization of the copolymers was done using differential scanning calorimetry and thermogravimetric analysis.

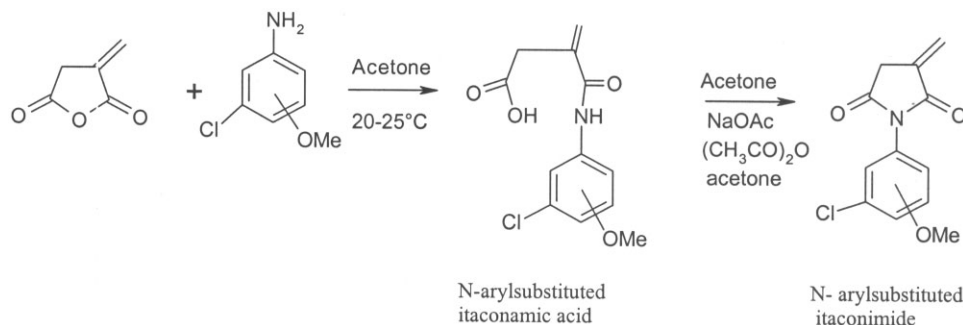
## EXPERIMENTAL

### Materials

Itaconic acid (Merck, Mumbai, India), 2-methoxy-5-chloroanisidine (Sigma–Aldrich, Germany), 4-methoxy-3-chloroanisidine (Sigma–Aldrich, Germany), methanol (s.d. Fine Chem, Mumbai, India), chloroform (s.d. Fine Chem, Mumbai, India), phosphorus pentoxide (Qualigens, Mumbai, India), and silica gel for column chromatography (CDH, Delhi, India) were used as supplied. Acetone (Qualigens, Mumbai, India) was dried overnight over potassium carbonate followed by

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**Scheme 1** Reaction scheme for the preparation of *N*-aryl-substituted itaconimides.

distillation. Acetic anhydride (s.d. Fine Chem, Mumbai, India) was used after distillation. Anhydrous sodium acetate (CDH, Delhi, India) was obtained by fusion. Tetrahydrofuran (THF) (CDH, Delhi, India) was dried by refluxing with metallic sodium and benzophenone followed by distillation. Azobisisobutyronitrile (AIBN) (High Polymer Labs) was recrystallized using chloroform. Methyl methacrylate (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 excess of phosphorus pentoxide as dehydrating agent and chloroform as solvent. The detailed procedure has been reported in our earlier article.<sup>7</sup>

#### Preparation of MPCPI and OMPCPI monomers

MCPI and OMCPI monomers were synthesized according to the procedure reported by Searle<sup>8</sup> using acetone as solvent according to the reaction in Scheme 1.

#### Procedure

Itaconic anhydride (0.25 mol) was dissolved in minimum amount of dry acetone taken in a three-necked round-bottom flask equipped with a magnetic stirrer and a reflux condenser. 4-Methoxy-3-chloroaniline (0.25 mol) dissolved in minimum amount of dry acetone was added slowly with vigorous stirring. 4-Methoxy-3-chlorophenyl itaconamic acid was precipitated out from the solution. The precipitate was filtered, washed with acetone, and dried, giving 4-methoxy-3-chlorophenyl itaconamic acid (80% yield, m.p. 169.3°C), characterized by FTIR (1672, 1695  $\text{cm}^{-1}$ ) and <sup>1</sup>H NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 3.3 (2H, s); 6.1 (1H, s); 5.7 (1H, s); 3.8 (3H, s); 7.7 (1H, s); 7.4 (2H, d); 7.17 (2H, d); 10.0 (1H, s).

To prepare the MCPI monomer, cyclization of 4-methoxy-3-chlorophenyl itaconamic acid was carried out by addition of 75 mL of dry acetone, 40 mL of acetic anhydride, and 4 g of sodium acetate to 3-methoxy-5-chlorophenyl itaconamic acid (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 precipitated monomer (MCPI) was filtered, washed with saturated sodium bicarbonate solution, distilled water, dried, and purified by passing the solution of the monomer in THF through silica bed and then concentrating the THF solution to give MCPI in 70% yield.

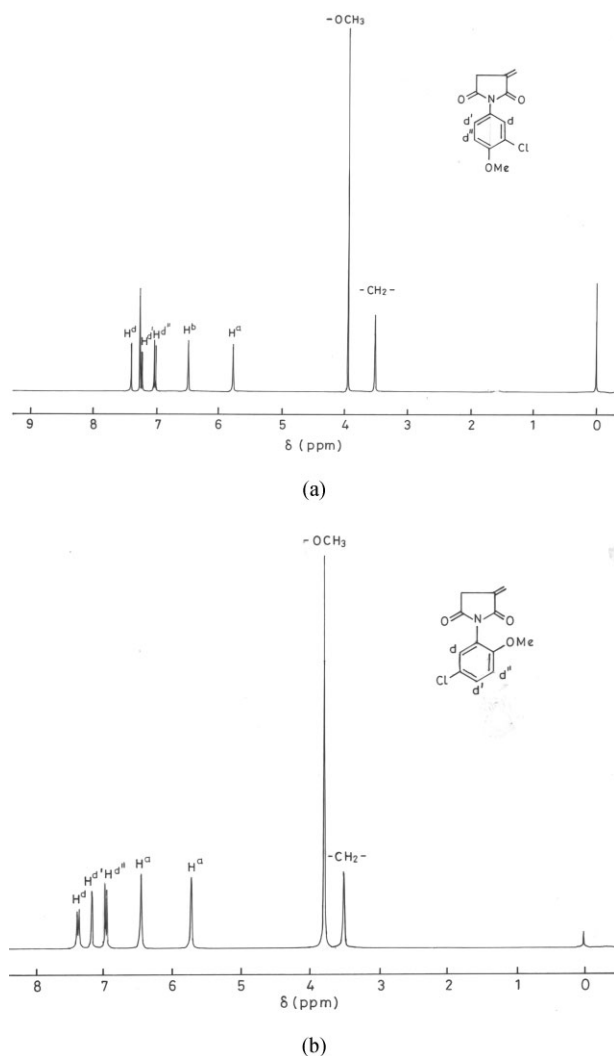
For the preparation of OMCPI, phosphoric acid was used as a catalyst in the first step, i.e., *N*-(2-methoxy-5-chlorophenyl) itaconamic acid was prepared by refluxing 2-methoxy-5-chloroaniline (0.25 moles) and itaconic anhydride (0.25 moles) in acetone using *o*-phosphoric acid (3% v/v) as catalyst. The procedure in the second step was same as used for the preparation of MCPI.

The imide 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 found to be 186.4 and 135.4°C for MCPI and OMCPI, respectively.

In the FTIR spectra of the two monomers, the characteristic absorption bands due to imide group were observed at  $1709 \pm 3$  and  $1770 \pm 3 \text{ cm}^{-1}$ . The absorption band due to  $\text{—C=C—}$  stretching was observed at  $1662 \text{ cm}^{-1}$ .

In the <sup>1</sup>H NMR spectrum of MCPI in  $\text{CDCl}_3$  [Fig. 1(a)], proton resonance signal due to aromatic protons were observed at  $\delta = 7.4\text{--}7.0$  ppm. The two singlets corresponding to the vinylidene protons were observed at  $\delta = 6.4$  and 5.7 ppm. The resonance signals due to methoxy in aromatic ring and that due to methylene protons were observed at 3.9 and 3.5 ppm, respectively.

Similarly in the <sup>1</sup>H NMR spectrum of OMCPI in  $\text{CDCl}_3$  [Fig. 1(b)], the proton resonance signals due to



**Figure 1** <sup>1</sup>H NMR spectra of itaconimide monomers: (a) MCPI and (b) OMCPI.

aromatic protons were observed at  $\delta = 7.4\text{--}6.9$  ppm. The two singlets corresponding to the vinylidene protons were observed at  $\delta = 6.4$  and  $5.7$  ppm and those due to methoxy in aromatic ring and methylene protons were observed at  $3.8$  and  $3.5$  ppm, respectively.

#### Preparation of copolymers of MCPI and OMCPI with MMA

Copolymerization of MCPI/OMCPI with MMA was carried out in nitrogen atmosphere at  $60^\circ\text{C}$  using AIBN as an initiator and THF as solvent. The mole fraction of MCPI and OMCPI in the initial feed was varied from 0.1 to 0.5, respectively. A 30% (w/v) solution of monomers in THF was placed in a three-necked round-bottom flask equipped with a reflux condenser, CaCl<sub>2</sub> guard tube, and a nitrogen gas inlet tube. The whole assembly was placed in a thermostated oil bath and stirred using a magnetic stirrer.

Nitrogen was passed through the reaction mixture and temperature was raised to  $60^\circ\text{C}$ . The polymerization was initiated by using 1% AIBN (w/w) as an initiator. The reaction was stopped at low conversion ( $\sim 10\text{--}15\%$ ) by pouring the contents of the flask into large excess of methanol. The precipitated polymer was washed repeatedly with hot methanol to remove unreacted monomers and was dried in vacuum oven.

Copolymers have been designated as MMA-MCPI and MMA-OMCPI followed by a numerical suffix indicating the mol fraction of the MCPI/OMCPI in the feed multiplied by 10. For example, a copolymer prepared by taking 0.2-mol fraction of MCPI and OMCPI has been designated as MMA-MCPI-2 and MMA-OMCPI-2, respectively.

## CHARACTERIZATION

<sup>1</sup>H NMR and FTIR spectroscopic techniques were used for the structural characterization of the copolymers. <sup>1</sup>H NMR spectra of the monomers and copolymers were recorded on a Bruker spectropin DPX 300 spectrometer using CDCl<sub>3</sub> as solvent and tetramethylsilane as an internal standard. FTIR spectra of the monomers were recorded as thin films using Nicolet FTIR spectrophotometer. Elementar Vario EL was used for C, H, and N analysis.

The intrinsic viscosity of the polymers at  $(30 \pm 0.1)^\circ\text{C}$  was determined in CDCl<sub>3</sub> using an Ubbelohde suspension level viscometer. Waters GPC equipped with high-resolution and high temperature PL gel 5 mm mixed column size of  $300 \times 7.5$  mm<sup>2</sup> along with the refractive index detector was used to determine the molecular weight and molecular weight distribution in copolymers. THF was used as eluent at a flow rate of 1.0 mL/min.

TA 2100 thermal analyser 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  $10^\circ\text{C}/\text{min}$  by using  $5 \pm 1$  mg of powdered samples. Thermal stability was determined by recording TG/DTG traces in nitrogen atmosphere (flow rate =  $60$  cm<sup>3</sup>/min) using a TA 2100 thermal analyzer having a 951 TG module. A heating rate of  $20^\circ\text{C}/\text{min}$  and a sample size of  $10 \pm 1$  mg was used in each experiment.

## RESULTS AND DISCUSSION

### Molecular characterization

The details of feed composition, percent conversion per minute, and intrinsic viscosity of the copolymers are given in Table I. Percent conversion per minute decreased with increasing mole fraction of the comonomer (MCPI or OMCPI).

TABLE I  
 Polymerization Conditions, Sample Designation, Percentage Conversion,  $M_n$ ,  $M_w$ , and Intrinsic Viscosity (at  $30 \pm 0.1^\circ\text{C}$  in  $\text{CHCl}_3$ ) of MCPI and OMCPI Copolymers (Temperature of Polymerization  $60 \pm 1^\circ\text{C}$ )

Sample designation	Mole fraction of monomers in feed		Conversion (%/min)	$[\eta]$ (mL/g)	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	PDI
	MCPI/OMCPI	MMA					
MMA-MCPI-1	0.1	0.9	4.2	16.1	1.18	2.42	2.05
MMA-MCPI -2	0.2	0.8	3.6	14.8	1.52	3.24	2.13
MMA-MCPI -3	0.3	0.7	3.0	11.8	0.84	2.14	2.54
MMA-MCPI -4	0.4	0.6	3.0	8.5	0.58	1.50	2.59
MMA-MCPI-5	0.5	0.5	0.6	—	0.36	0.64	1.78
MCPI-10	1.0	0.0	0.1	—	0.07	0.09	1.28
MMA-OMCPI-1	0.1	0.9	4.2	16.8	6.44	10.1	1.56
MMA-OMCPI-2	0.2	0.8	2.4	12.6	1.26	3.70	2.93
MMA-OMCPI-3	0.3	0.7	2.4	12.5	0.94	2.77	2.95
MMA-OMCPI-4	0.4	0.6	1.2	12.5	1.17	3.25	2.78
MMA-OMCPI-5	0.5	0.5	0.6	—	0.93	2.04	2.19
OMCPI-10	1.0	0.0	0.2	—	0.55	1.78	3.24

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 MMA-MCPI or MMA-OMCPI copolymers, a decrease in  $[\eta]$  was observed as the comonomer content (MCPI or OMCPI) in the initial feed was increased. Number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ), and molecular weight distribution (MWD) of the copolymers were determined by GPC. The MMA-MCPI and MMA-OMCPI copolymers had molecular weight in the range of  $0.36 \times 10^4$ – $1.52 \times 10^4$  ( $M_n$ ) and  $0.64 \times 10^4$ – $3.24 \times 10^4$  ( $M_w$ ) and  $0.93 \times 10^4$ – $6.44 \times 10^4$  ( $M_n$ ) and  $2.04 \times 10^4$ – $10.1 \times 10^4$  ( $M_w$ ), respectively. The polydispersity index (PDI) in MMA-MCPI and MMA-OMCPI copolymers was in the range of 1.28–3.24. MCPI on homopolymerization gave only oligomers, whereas high molecular weight polymer was obtained on homopolymerization of OMCPI. Molecular weight of the copolymers decreased with increasing amount of itaconimide in the copolymers (Table I).

### Structural characterization

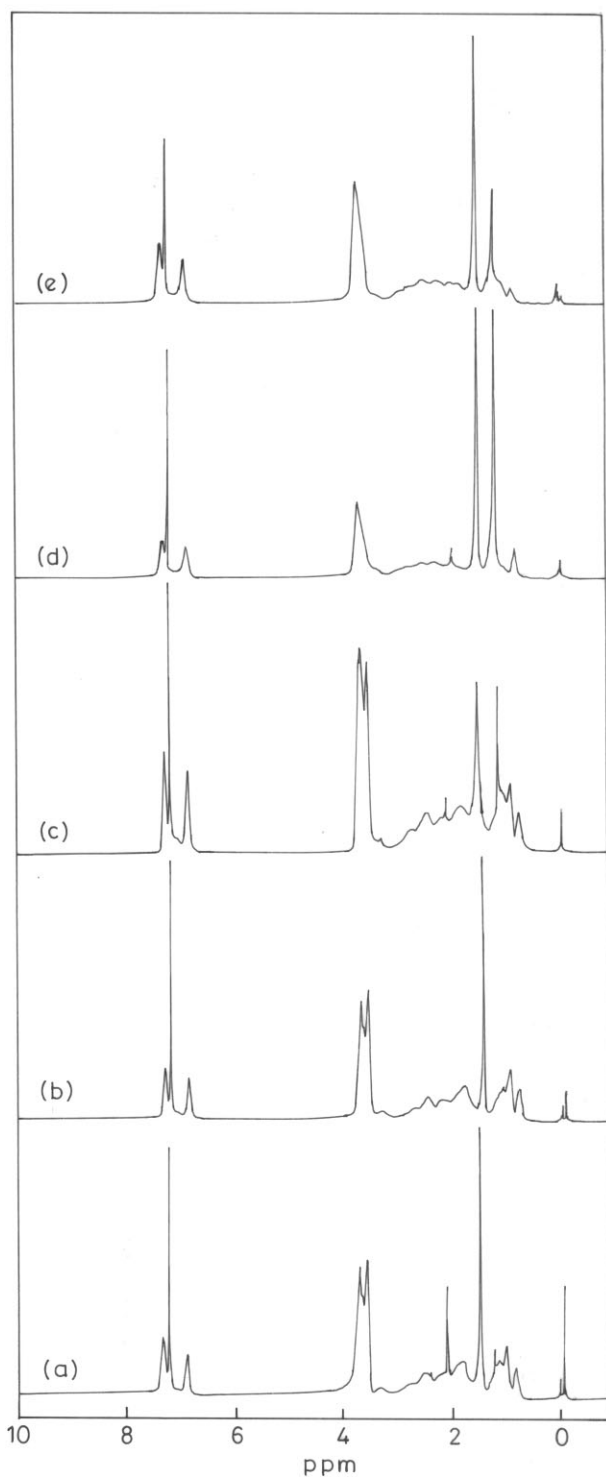
In the  $^1\text{H}$  NMR spectra of MMA-MCPI copolymers, the proton resonance signals corresponding to the aromatic protons were observed in the region of 6.9–7.3 ppm. The methoxy attached to aromatic ring was observed at 3.9 ppm and the methoxy of MMA ( $3.59 \pm 0.05$  ppm) got merged with the resonance signal due to methylene of imide (3.5 ppm). The intensity of the signals due to aromatic protons (6.9–7.3 ppm) and methoxy attached to aromatic ring (3.9 ppm) increased with increasing concentration of MCPI in the initial feed. The other characteristic signals observed at  $\delta = 0.8$ – $2.5$  ppm were due to  $-\text{CH}_2$  and  $-\text{CH}_3$  of MMA, respectively. Similarly, for the copolymers of

MMA and OMCPI, the resonance signals due to  $-\text{OCH}_3$  protons of MMA and  $-\text{OCH}_3$  of aromatic ring were observed in the region of 3.5–3.7 ppm respectively, and aromatic protons of *N*-arylitaconimide were observed at  $\delta = 6.8$ – $7.3$  ppm. The other characteristic signals observed at  $\delta = 2.5$ – $1.7$  and  $1.0$ – $0.7$  ppm were due to  $-\text{CH}_2$  and  $-\text{CH}_3$  proton of MMA, respectively. Here again, the intensity of the signals due to aromatic protons increased with increasing concentration of *N*-aryl-substituted itaconimide in the initial feed (Fig. 2).

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

Copolymer composition data was used to calculate the monomer reactivity ratios of the monomers using Fineman-Ross and Kelen Tüdös methods. The monomer reactivity ratios for MMA-MCPI copolymers were found to be  $r_1$  (MMA) =  $0.32 \pm 0.03$  and  $r_2$  (MCPI) =  $1.54 \pm 0.05$  and that for MMA-OMCPI copolymers were  $r_1$  (MMA) =  $0.15 \pm 0.02$  and  $r_2$  (OMCPI) =  $1.23 \pm 0.18$ , showing that the copolymers are random. As methyl methacrylate shows lower monomer reactivity ratio as compared to itaconimide monomers, the incorporation of *N*-arylsubstituted itaconimides is much higher in the copolymers as compared to MMA. Higher monomer reactivity ratio of *N*-aryl-substituted itaconimide as compared to MMA has already been reported<sup>1,2</sup>

From the knowledge of monomer reactivity ratios,  $Q$  and  $e$  values for the *N*-aryl-substituted itaconimide monomers were also calculated using Alfrey and Price equation. The  $Q$  and  $e$  values for MMA were taken as 0.78 and 0.40, respectively.<sup>9</sup> The  $Q$  and  $e$  values for MCPI and OMCPI were found to be 3.4 and  $1.3 \pm 0.06$ ,



**Figure 2** <sup>1</sup>H NMR spectra of MMA-OMCPI copolymers: (a) MMA-OMCPI-1, (b) MMA-OMCPI-2, (c) MMA-OMCPI-3, (d) MMA-OMCPI-4, and (e) MMA-OMCPI-5.

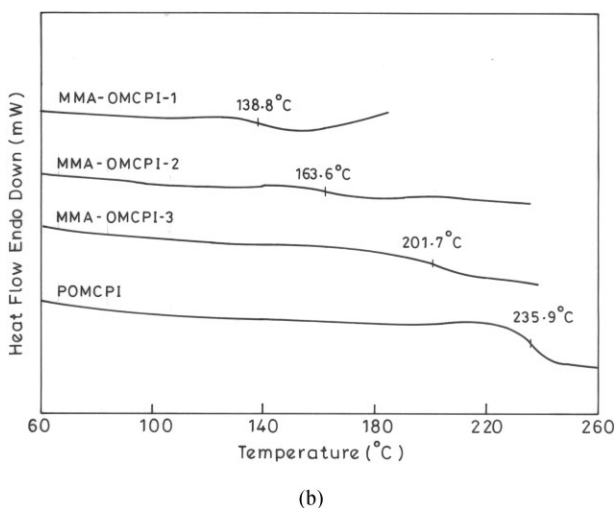
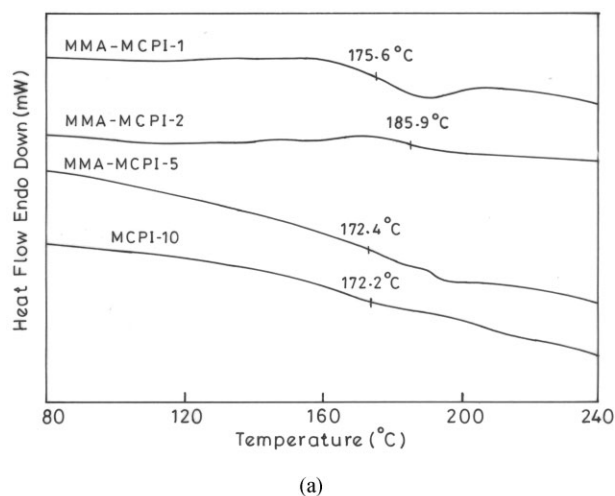
respectively. As expected, the position of the substituents did not show much effect on the values of *Q* and *e*.

**Thermal characterization**

The DSC scans of various copolymers were recorded primarily to study the effect of copolymer structure

**TABLE II**  
Details of Feed Composition and Results of Copolymer Composition Determined from Nitrogen Content in MCPI and OMCPI Copolymers

Sample designation	Mole fraction of MCPI/OMCPI in feed	% nitrogen	Mole fraction MCPI/OMCPI in copolymer
MMA-MCPI-1	0.1	2.26	0.21
MMA-MCPI-2	0.2	3.31	0.37
MMA-MCPI-3	0.3	4.29	0.57
MMA-MCPI-4	0.4	4.01	0.51
MMA-MCPI-5	0.5	5.33	0.58
MMA-OMCPI-1	0.1	3.03	0.32
MMA-OMCPI-2	0.2	3.50	0.40
MMA-OMCPI-3	0.3	4.34	0.58
MMA-OMCPI-4	0.4	4.24	0.56
MMA-OMCPI-5	0.5	4.70	0.68



**Figure 3** DSC scans of copolymers: (a) MMA-MCPI copolymers and (b) MMA-OMCPI copolymers.

TABLE III  
Results of DSC Scans of MMA–MCPI, and MMA–OMCPI Copolymers (Heating Rate, 10°C/min)

Sample designation	Mole fraction of MCPI/OMCPI in copolymers	$T_e$ (°C)	$T_g$ (°C)	$T_f$ (°C)	$T_g$ calculated using Fox Eq. (°C)
MMA–MCPI-1	0.21	164.5	175.6	187.5	120.3
MMA–MCPI-2	0.37	180.0	185.9	195.8	133.9
MMA–MCPI-5	0.58	158.7	172.5	190.0	149.1
MCPI-10	1.00	158.1	172.2	190.2	–
MMA–OMCPI-1	0.32	124.3	138.8	148.6	145.2
MMA–OMCPI-2	0.40	142.8	163.6	182.8	157.0
MMA–OMCPI-5	0.68	160.0	210.7	216.2	193.8
OMCPI-10	1.00	219.5	235.9	244.7	–

$T_e$ : extrapolated onset temperature;  $T_g$ : glass transition temperature;  $T_f$ : extrapolated end set temperature.

and composition on the glass transition temperature ( $T_g$ ) of the copolymers. Figure 3 shows the DSC scans of MCPI and OMCPI copolymers. A shift in the baseline due to glass transition was observed in all the samples. To fully characterize the glass transition region, the following temperatures were noted and the results of the DSC traces are summarized in Table III.

In the DSC scans of MMA–MCPI and MMA–OMCPI copolymers, a single endothermic shift in the baseline corresponding to the glass transition temperature ( $T_g$ ) was observed.  $T_e$ ,  $T_g$ , and  $T_f$  increased with increasing amount of OMCPI in the copolymers. The  $T_g$  of MMA–OMCPI copolymers were obtained in the region 130–215°C. The  $T_g$  of the MMA–MCPI copolymers with low mole fraction of the MCPI in the feed, i.e., MMA–MCPI-1 and MMA–MCPI-2 increased with increasing amount of MCPI in the copolymers. But as the mole fraction of the MCPI in the feed increased beyond 0.2, the  $T_g$  decreased.  $T_g$  is found to be dependent on the various factors i.e., structural rigidity, regularity, interchain attractions, and molecular weight. One would have expected an increase in  $T_g$  with increasing amounts of MCPI, however a decrease observed in the present work could be due to the formation of low molecular weight oligomers. Homopolymerization of MCPI gave oligomer (with  $M_n$  of 700 and  $M_w = 900$  g/mol), whereas homopolymer of OMCPI gave comparatively a high molecular weight oligomer ( $M_n = 5500$ ,  $M_w = 17,800$ ) with a high PDI value. The theoretical values of  $T_g$  calculated using Fox equation,<sup>10</sup> were close for the experimentally obtained values in MMA–OMCPI copolymers but for the MMA–MCPI copolymers, the calculated values were very low as compared to the experimentally obtained values. It could be due to the fact that  $T_g$  value of MCPI homopolymer used for calculation is very low as it has very low molecular weight and has not reached the limit where it is independent of molecular weight.

The glass transition for MMA–MCPI copolymers was higher as compared to MMA–OMCPI copolymers

when low amount of itaconimide was incorporated in the polymer backbone as shown in Figure 4. It could be due to the presence of —OCH<sub>3</sub> at the meta position, which leads to enhanced polar–polar interaction between the chains, whereas this kind of interaction are less in OMCPI in which the —OCH<sub>3</sub> is present at the ortho position and is not available for interaction. Similar effect has already been reported by us in maleimide/itaconimide copolymers.<sup>4</sup> But for copolymers having higher mole fractions of OMCPI, glass transition temperature was higher as compared to the MMA–MCPI copolymers. This could be explained on the basis of molecular weight, which is much higher in case of MMA–OMCPI copolymers as compared to MMA–MCPI. OMCPI homopolymer had much higher  $T_g$  (235.9°C) as compared to MCPI homopolymer (172.2°C). This could be due to the higher molecular weight of OMCPI homopolymer as compared to MCPI homopolymer.

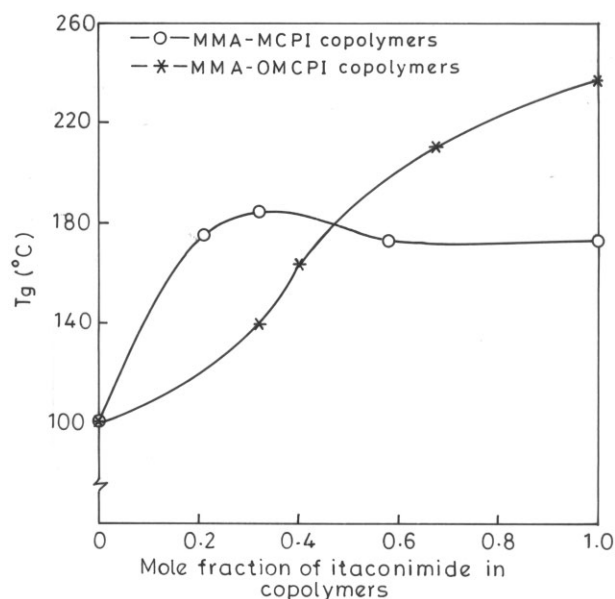
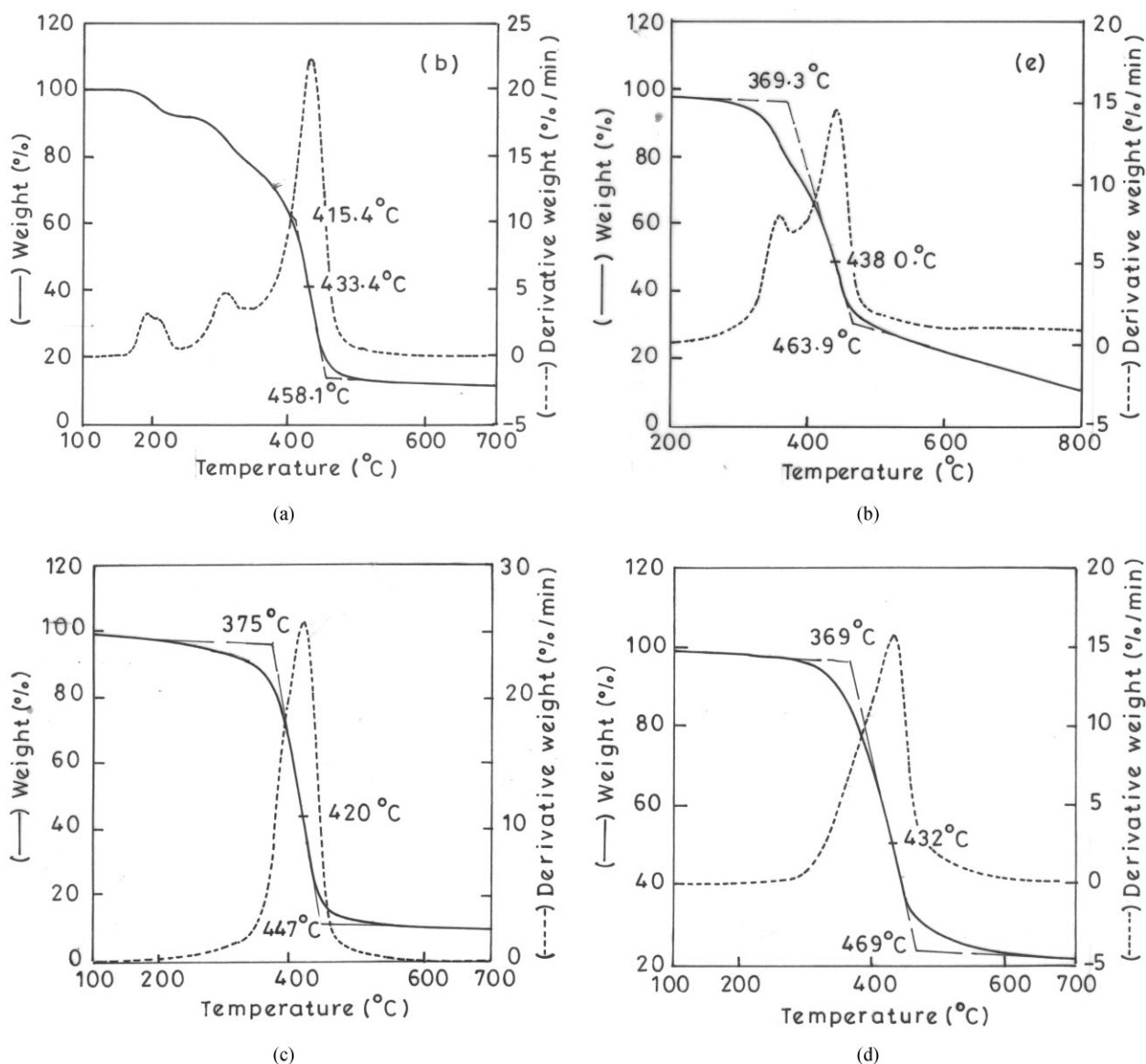


Figure 4 Plot of  $T_g$  versus mole fraction of *N*-aryl-substituted itaconimides in the copolymers.

**TABLE IV**  
Results of Thermogravimetric Analysis in Nitrogen Atmosphere

Sample designation	Percentage mass loss in the temperature range			Char yield at 700°C (%)
	150–250°C	250–350°C	350–700°C	
MMA–MCPI-1	8.2	15.5	61.7	14.6
MMA–MCPI-2	2.7	9.1	73.3	14.9
MMA–MCPI-3	1.8	10.9	65.2	22.1
MMA–MCPI-4	0.9	10.0	69.3	19.8
MMA–MCPI-5	1.5	4.4	71.8	22.3
MCPI-10	1.5	14.8	56.7	27.0
MMA–OMCPI-1	4.5	6.4	79.5	9.6
MMA–OMCPI-2	6.4	7.3	72.4	13.9
MMA–OMCPI-3	4.5	8.2	75.1	12.2
MMA–OMCPI-4	3.0	7.5	68.1	21.4
MMA–OMCPI-5	2.2	3.0	72.3	22.5
OMCPI-10	3.7	2.3	69.0	25.0



**Figure 5** TG/DTG traces of copolymer samples: (a) MMA–MCPI-1, (b) MMA–MCPI-4, (c) MMA–OMCPI-1, and (d) MMA–OMCPI-4.

The relative thermal stability of the copolymers was assessed by comparing the mass loss in the temperature range of 150–250, 250–350, 350–700°C and the char yield at 700°C. The results of the thermal behavior of copolymers are summarized in Table IV. Typical TG/DTG traces for MMA–MCPI-1, MMA–MCPI-4, MMA–OMCPI-1, and MMA–OMCPI-4 are shown in Figures 5(a)–5(d).

In case of PMMA, three-step degradation has been reported.<sup>9,11</sup> The first step degradation (150–250°C) is attributed to head-to-head linkages, the second step (250–300°C) to the end unsaturation, and the third step (350–500°C) due to depropagation.

All the samples were stable upto 250°C and started losing weight above this except for MMA–MCPI-1, which started degrading at 160°C due to lower incorporation of MCPI in the polymer backbone. In all the MMA–MCPI copolymer samples, (1.8 ± 1.0)% mass losses was observed in the temperature range of 150–250°C except in the MMA–MCPI-1, where it showed 8.2% mass loss. Similar behavior was observed in case of MMA–OMCPI copolymers. Mass loss in the temperature range of 150–250°C decreased with increasing mole fraction of OMCPI in the copolymers. Mass loss in the temperature range of 250–350 and 350–700°C also decreased with increasing mole fraction of *N*-aryl-substituted itaconimide monomers leaving behind a large amount of char. Homopolymer of MCPI and OMCPI gave a char yield of (26 ± 1)%. Percent char yield in copolymers (MMA–MCPI/or OMCPI) increased with increasing amounts of MCPI/or OMCPI in the copolymer.

## CONCLUSIONS

From these results, it can be concluded that

1. *N*-(2-methoxy-5-chlorophenyl) itaconimide (OMCPI) and *N*-(4-methoxy-3-chlorophenyl) itaconimide (MCPI) can be successfully copolymerized with MMA and the rate of polymerization was dependent on the structure of the itaconimide monomer.
2. A significant improvement in the  $T_g$  was observed upon incorporation of very low mol fractions of these monomers, however increase was higher for MMA–MCPI copolymers as compared to MMA–OMCPI copolymers at low mole fraction.
3. Copolymerization of MMA with these monomers resulted in a significant increase in the thermal stability. Percent char yield increased with increasing mole fraction of MCPI/or OMCPI in the copolymer.

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