

# Copolymerization and Thermal Behavior of Methyl Methacrylate with *N*-(Phenyl/*p*-tolyl) Itaconimides

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Received 8 January 2002; accepted 21 January 2002

**ABSTRACT:** This study describes the synthesis, characterization, and thermal behavior of copolymers of methyl methacrylate (MMA) and *N-p*-tolyl itaconimide (PTI)/*N*-phenyl itaconimide (I). Homopolymerization and copolymerization of *N*-(phenyl/*p*-tolyl) itaconimide with MMA was carried out by use of various mole fractions of *N*-aryl itaconimide in the initial feed from 0.1 to 0.5, using azobisisobutyronitrile as an initiator and tetrahydrofuran as the solvent. The copolymer composition was determined by <sup>1</sup>H-NMR spectroscopy using the proton resonance signals attributed to -OCH<sub>3</sub> of MMA ( $\delta = 3.5\text{--}3.8$  ppm) and the aromatic protons ( $\delta = 7.0\text{--}7.5$  ppm) of *N*-aryl itaconimide. The reactivity ratios of the monomers were found to be  $r_1$

(PTI) =  $1.33 \pm 0.05/r_2$  (MMA) =  $0.24 \pm 0.03$  and  $r_1$  (I) =  $1.465 \pm 0.035/r_2$  (MMA) =  $0.385 \pm 0.005$ . The molecular weight of the copolymers decreased with increasing mole fraction of *N*-aryl itaconimide in the copolymers. Glass-transition temperature ( $T_g$ ) and thermal stability of PMMA increased with increasing amounts of itaconimides in the polymer backbone. A significant increase in the percentage char yield at 700°C was observed on incorporation of a low mole fraction of *N*-aryl itaconimides. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1195–1202, 2003

**Key words:** methyl methacrylate; copolymerization; *N*-aryl itaconimide; reactivity ratio; thermal stability

## INTRODUCTION

The copolymerization of alkyl methacrylates with *N*-substituted aryl maleimides, using free-radical initiators, is well documented in the literature.<sup>1–9</sup> Maleimides have a very low tendency for homopolymerization because of the presence of a 1,2-disubstituted double bond. Itaconimides, on the other hand, contain the 1,1-disubstituted double bond, thereby rendering it more reactive. Moreover, maleimides are prepared from anhydride based on petrochemical resources, whereas itaconimides are prepared from itaconic acid obtained from easily renewable resources such as corn starch by a fermentation process using *Aspergillus itaconicus* or *Aspergillus terreus* fungi.<sup>10,11</sup> The dwindling petrochemical feed stocks have necessitated the need to focus attention on developing polymers based on annually renewable resources. It was therefore considered of interest to evaluate the copolymerization behavior of methyl methacrylate (MMA) with *N*-aryl itaconimides, which can be obtained from renewable resources.

In our earlier study<sup>12</sup> we reported the copolymerization of MMA with *N*-(*o*/*m*/*p*-chlorophenyl) itaconimides. The position of the substituent as well as the nature of the substituent (i.e., electron-withdrawing or -releasing group) affected the copolymerization and thermal behavior of MMA–maleimide<sup>5–9</sup>/itaconimide<sup>12</sup> copolymers. The present studies were thus carried out with the aim of investigating the copolymerization behavior of *N*-phenyl itaconimide (I) and *N-p*-tolyl itaconimide (PTI) with MMA. The effects of comonomer structure and copolymer composition on the glass-transition temperature and thermal stability were also evaluated.

## EXPERIMENTAL

### Materials

Itaconic acid (Aldrich Chemicals, Milwaukee, WI), *p*-toluidine, phosphorus pentoxide (P<sub>2</sub>O<sub>5</sub>; Qualigens, Delhi, India), methanol, chloroform (s.d. fine chem., Mumbai, India), 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. Aniline (Merck, Darmstadt, Germany) was distilled under reduced pressure before use.

Tetrahydrofuran (THF; CDH) was purified by passing it through an alumina column. It was then dried by

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Contract grant sponsor: Council of Scientific and Industrial Research (CSIR).

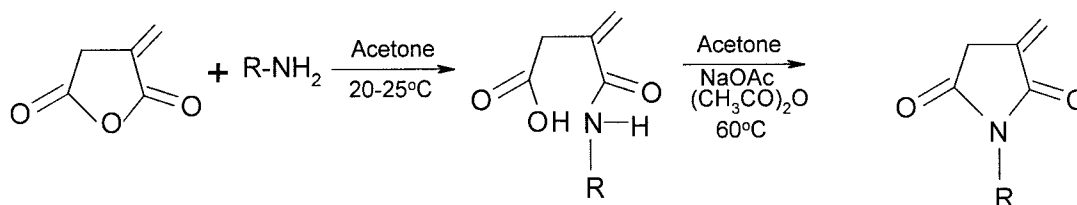
refluxing with metallic sodium and benzophenone followed by distillation. Azobisisobutyronitrile (AIBN; High Polymer Labs, Faridabad, India) was recrystallized using chloroform. Methyl methacrylate (MMA; Merck) was washed with dilute sodium hydroxide to remove the inhibitor, followed by repeated washing with distilled water until neutral. It was dried over anhydrous sodium sulfate overnight and then distilled under reduced pressure.

Itaconic anhydride was obtained by refluxing (24 h) one mole of itaconic acid with 0.75 mol (excess) of phos-

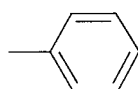
phorus pentoxide using chloroform as a solvent. The detailed procedure for the preparation and characterization of itaconic anhydride is reported in our earlier study.<sup>12</sup>

### Synthesis of *N*-aryl itaconimides

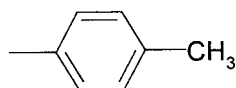
The preparation of *N*-aryl itaconimide monomer was carried out according to the procedure reported by Searle<sup>13</sup> using acetone as a solvent. The reaction scheme for synthesis of itaconimides is given below:



where R =



(I)



(PTI)

The letters within parentheses represent the designation for the itaconimide monomers.

### Procedure

Amine (0.25 mol) dissolved in a minimal amount of dry acetone was added slowly with vigorous stirring to the acetone solution of itaconic anhydride (0.25 mol). The reaction was carried out at 20–25°C. The itaconamic acid precipitated out from the solution. Cyclodehydration of the itaconamic acid was done using acetic anhydride and anhydrous sodium acetate as cyclodehydrating agents. The mixture was refluxed for 2–3 h until a clear solution was obtained. The solution was cooled to room temperature and imide was obtained by pouring the solution into ice-cold water. Purification of monomers was done by passing a chloroform solution of the monomer through a silica gel column and the solution was concentrated under reduced pressure and imide crystallized out on cooling. The yield of *N*-aryl itaconimides was in the range of 30–35%.

The monomers prepared were characterized by DSC, FTIR, <sup>1</sup>H-NMR, and elemental analysis. In the DSC scans [recorded using a TA 2100 thermal analyzer (TA Instruments, New Castle, DE) having 910 DSC module at a heating rate of 10°C/min] of the

itaconimide monomers, an endothermic transition attributed to melting was observed. The melting points noted from the endothermic peak position were found to be 114 and 117.9°C for I and PTI monomers, respectively. The results of elemental analysis in I and PTI were as follows:

### Experimental

(I) C = 69.83%, H = 5.67%, N = 7.71%  
(PTI) C = 70.95%, H = 6.06%, N = 7.14%

### Theoretical

(I) C = 70.59%, H = 4.81%, N = 7.49%  
(PTI) C = 71.64%, H = 5.47%, N = 6.97%

The experimental values substantially agree with the theoretical values. In the FTIR spectrum of monomers [recorded in KBr pellets using a Bio-Rad Digilab FTS-40 FTIR spectrophotometer (Bio-Rad, Hercules, CA)], characteristic absorption bands attributed to imide groups were observed at  $1710 \pm 3$  and  $1771 \pm 3$   $\text{cm}^{-1}$  and the  $\text{>C=C<}$  stretch was observed at  $1662$   $\text{cm}^{-1}$ .

In the <sup>1</sup>H-NMR spectrum of itaconimide monomers [recorded on a Bruker Spectrospin DPX 300 spectrometer (Bruker Instruments, Billerica, MA) using CDCl<sub>3</sub> as solvent and tetramethyl silane as an internal standard], the proton resonance signals attributed to the aryl group were observed at  $\delta = 7.2$ – $7.5$  ppm, the vinylidene protons at  $\delta = 6.47 \pm 0.02$  ppm (1H, S) and  $5.73 \pm 0.02$  ppm (1H, S), and methylene protons (2H, S) at  $\delta = 3.5 \pm 0.02$  ppm. Methyl protons of PTI monomer were observed at  $\delta = 2.39$  ppm. Integration was used to calculate the number of protons. A proton

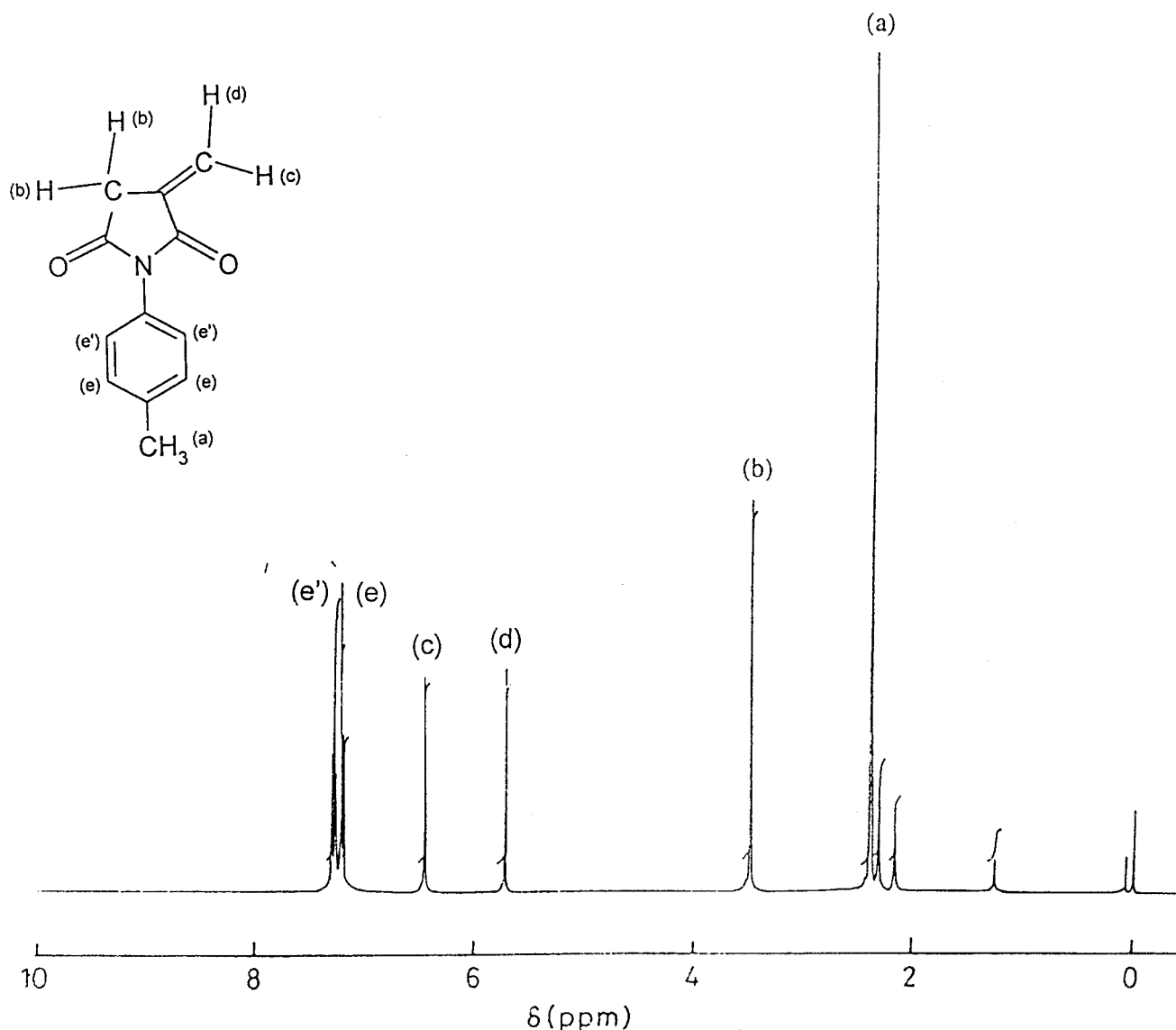


Figure 1  $^1\text{H-NMR}$  spectrum of *N*-(*p*-tolyl) itaconimide (PTI) monomer.

resonance signal was also observed at  $\delta = 2.16 \pm 0.02$  ppm. This may be attributed to the methyl group of citraconimide. The isomerization of itaconimide to citraconimide may be responsible for this signal. The mole fraction of citraconimide in monomer could be calculated from the ratio of protons at  $\delta = 2.16 \pm 0.02$  ppm to the protons at  $\delta = 5.73 \pm 0.02$  ppm and was found to be 0.072 and 0.115 for I and PTI, respectively. A typical  $^1\text{H-NMR}$  spectrum of *N*-(4-tolyl) itaconimide is shown in Figure 1.

#### Preparation of homopolymers and copolymers of *N*-(phenyl/*p*-tolyl) itaconimide with MMA

Homopolymerization and copolymerization of *N*-(phenyl/*p*-tolyl) itaconimide with MMA were carried out in THF using AIBN as an initiator at  $60^\circ\text{C}$

under nitrogen atmosphere. The mole fraction of *N*-(phenyl/*p*-tolyl) itaconimides in the initial feed was varied from 0.1 to 0.5. Polymerization was carried out by taking 30% (w/v) solution of monomers in THF using 0.5% of AIBN as an initiator. The reaction was stopped at low conversion ( $\leq 15\%$ ) 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.

Copolymers have been designated by adding a prefix P to the monomer designation of *N*-aryl itaconimides followed by a numerical suffix, which indicates the mole fraction of itaconimides multiplied by 10. For example, a copolymer prepared by taking 0.2 mol fraction of PTI has been designated as

PPTI-2. Homopolymers have been designated by adding a prefix P to the monomer designation of *N*-aryl itaconimides.

### Characterization

$^1\text{H-NMR}$  and FTIR spectroscopic techniques were used for the structural characterization of copolymers.  $^1\text{H-NMR}$  spectra of copolymers were recorded on a Bruker Spectrospin DPX 300 spectrometer using  $\text{CDCl}_3$  as solvent and tetramethyl silane as an internal standard. Elemental analysis was also done to determine the copolymer composition.

Waters HPLC (Waters Chromatography Division/Millipore, Milford, MA) was used to determine the molecular weight and molecular weight distribution. The calibration curve was obtained using polystyrene standards.

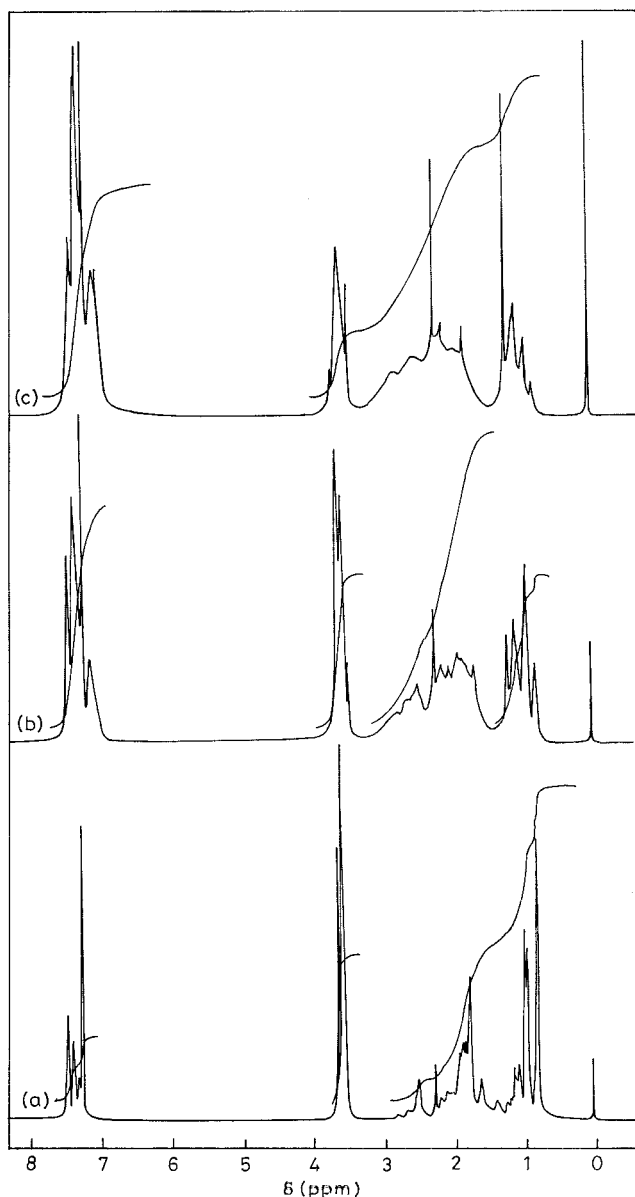
A TA 2100 thermal analyzer with a 910 DSC module and 951 TG module was used for the thermal characterization of copolymers. DSC scans were recorded in a static-air atmosphere at a heating rate of  $10^\circ\text{C}/\text{min}$  by using  $5 \pm 1$  mg of powdered samples. Thermal stability was determined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

## RESULTS AND DISCUSSION

In the copolymerization of MMA with *N*-aryl itaconimides, % conversion  $\text{min}^{-1}$  was found to be higher in *N*-aryl itaconimides having an electron-withdrawing group at either the *m*- or the *o*-position than in monomers having an electron-releasing (PPTI)/electron-withdrawing substituent at the *p*-position (PPI).<sup>12</sup>

In the  $^1\text{H-NMR}$  spectra of copolymers, resonance signals attributed to the  $-\text{OCH}_3$  protons of MMA and aromatic protons of *N*-aryl itaconimides were present at  $\delta = 3.5\text{--}3.8$  ppm and at  $\delta = 7.0\text{--}7.5$  ppm, respectively. The intensity of the signal attributed to aromatic protons increased with increasing *N*-aryl itaconimide content in the copolymers. Figure 2 shows the  $^1\text{H-NMR}$  spectra of PI copolymers. The copolymer composition was determined by taking the ratio of the intensity of signals attributed to methoxy protons of MMA and aromatic protons of *N*-aryl itaconimides. The results of copolymer composition are given in Table I. A plot of mole fraction of *N*-aryl itaconimides in the feed ( $m_1$ ) versus mole fraction of *N*-aryl itaconimides in the copolymer ( $M_1$ ) is shown in Figure 3. In the copolymerization of MMA with *N*-aryl itaconimides an increase in  $m_1$  did not show a linear increase in  $M_1$ .

Copolymer composition was also determined from the % nitrogen content in the copolymers and the



**Figure 2**  $^1\text{H-NMR}$  spectra of PI copolymers (a) PI-1, (b) PI-3, and (c) PI-5.

results are given in Table I. A good correlation was observed between the values obtained by  $^1\text{H-NMR}$  and elemental analysis. It was not possible to incorporate higher amounts of maleimide, whereas the amount of itaconimides incorporated were higher than the feed composition. Similar behavior was observed in the copolymerization of MMA with *N*-(*o/m/p*-chlorophenyl) itaconimides.<sup>12</sup>

The reactivity ratios of the monomers calculated using Fineman–Ross and Kelen–Tüdös methods are given in Table II. From the reactivity ratio  $r_1$  (*N*-aryl itaconimides) and  $r_2$  (MMA) it is clear that *N*-aryl itaconimides (i.e., I and PTI) are more reactive than MMA (i.e.,  $\kappa_{11} > \kappa_{12}$  and  $\kappa_{21} > \kappa_{22}$ ) toward homopropagation and cross-propagation. On the other

TABLE I  
Polymerization Conditions and Results of Copolymer Composition in Case of MMA-*N*-Aryl Itaconimides Copolymers

Sample designation	Mole fraction of <i>N</i> -aryl itaconimides (from <sup>1</sup> H-NMR)		Percentage conversion/min	Percentage nitrogen	Mole fraction of <i>N</i> -aryl itaconimides in copolymers (from % N)
	Feed	Copolymers			
PI-1	0.101	0.217	0.22	2.65	0.227
PI-2	0.199	0.344	0.25	3.80	0.355
PI-3	0.299	0.461	0.28	4.95	0.510
PI-4	0.403	0.531	0.20	5.13	0.538
PI-5	0.500	0.658	0.21	6.05	0.692
PI	1.000	—	0.17	—	—
PPTI-1	0.0997	0.287	0.20	2.71	0.241
PPTI-2	0.1998	0.346	0.20	3.70	0.361
PPTI-3	0.2999	0.487	0.15	4.54	0.482
PPTI-4	0.4018	0.603	0.11	5.20	0.594
PPTI-5	0.5003	0.654	0.23	5.70	0.692
PPTI	1.000	—	0.12	—	—

hand, *N*-aryl maleimides with a similar structure showed much lower reactivity ratios compared to those of MMA.<sup>6</sup> Higher values of reactivity ratios for various itaconimides were also previously reported in copolymerizations with styrene.<sup>14-19</sup>

The *Q* and *e* values for the *N*-aryl itaconimide monomers were also calculated using the Alfrey-Price equation by taking *Q* and *e* values for MMA as 0.78 and 0.4, respectively.<sup>20</sup> The results are summarized in Table II. The *Q* and *e* values of the PTI monomer was

greater than those of the I monomer. The *Q* value was found to be higher in itaconimides having an electron-releasing group and lower in *N*-phenyl itaconimide compared to that of *N*-(*o*/*m*/*p*-chlorophenyl) itaconimides.

$M_n$ ,  $M_w$ , and molecular weight distribution of the copolymers were calculated by HPLC using polystyrene as calibration standards. All the homopolymers and copolymers had molecular weights in the range of 4600-48600 ( $M_n$ ) and 9500-106,300 ( $M_w$ ), with a poly-

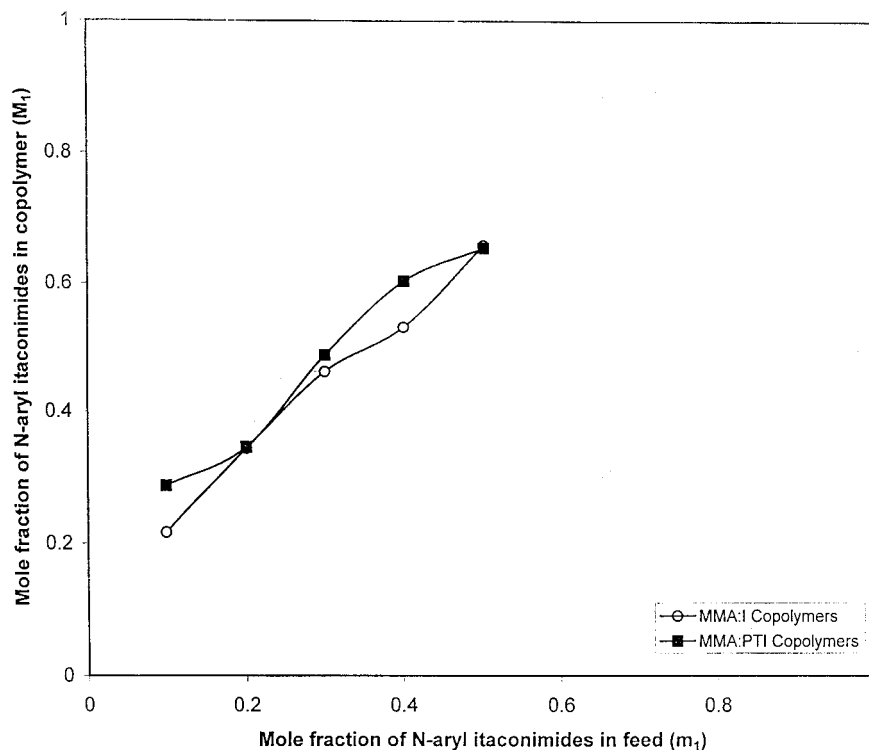


Figure 3 Plot of mole fraction of *N*-aryl itaconimides in the feed ( $m_1$ ) versus mole fraction of *N*-aryl itaconimides in copolymer ( $M_1$ ).

TABLE II  
Reactivity Ratio of *N*-Aryl Itaconimides ( $r_1$ ) and MMA ( $r_2$ )

Method	PTI-MMA		I-MMA	
	$r_1$	$r_2$	$r_1$	$r_2$
Fineman-Ross	1.28	0.21	1.50	0.39
Kelen Tüdös	1.38	0.27	1.43	0.38
Average	$1.33 \pm 0.05$	$0.24 \pm 0.03$	$1.465 \pm 0.035$	$0.385 \pm 0.005$
Q		4.98		2.74
e		1.47		1.16

dispersity index in the range of 1.5–3.0. The molecular weight of the copolymers decreased as the amount of *N*-aryl itaconimides increased in the copolymers. The results of molecular weights and polydispersity index are summarized in Table III.

DSC scans of various copolymers were recorded to study the effect of copolymer structure and composition on the glass-transition temperature ( $T_g$ ) of the copolymers. To have a similar thermal history, second-heating scans were used to determine the  $T_g$ . The powdered samples were first heated to 120°C and then quench-cooled, and the DSC scans were recorded at a heating rate of 10°C/min. The glass-transition region was characterized by noting the following temperatures:

$T_e$  = extrapolated onset temperature  
 $T_g$  = midpoint temperature (inflection point)  
 $T_f$  = extrapolated end-set temperature

The results of DSC traces are summarized in Table IV.  $T_g$  values of the copolymers increased with an increasing amount of the *N*-aryl itaconimides in the polymer backbone. DSC scans for PI homopolymer and copolymers are shown in Figure 4. PPTI homopolymer (232.2°C) and copolymers had higher  $T_g$  values compared to those of PI homopolymer (220.2°C) and copolymers. A significant increase in  $T_g$  (i.e., 42–45°C)

was observed on incorporation of very low mole fractions (i.e., 0.2) of itaconimides. The copolymer richer in itaconimides (i.e., PPTI-5) had a 20°C higher  $T_g$  value compared to that of PI-5, which has an almost identical copolymer composition. No such effect of comonomer structure on  $T_g$  value was observed in other copolymer samples having 0.2 to 0.6 mol fraction of itaconimide in the copolymer. The homopolymer of *N*-aryl itaconimides having an electron-withdrawing group (–Cl) at the *p*-position showed higher  $T_g$  compared to that of the PI and PPTI homopolymers. The following trend in  $T_g$  was observed in homopolymers: PPI > PPTI > PI.

Thermal stability of the copolymers was determined by recording TG/DTG traces in a nitrogen atmosphere. The relative thermal stability of the copolymers was determined by comparing the initial decomposition temperature ( $T_i$ ), temperature of maximum rate of weight loss ( $T_{max}$ ), final decomposition temperature ( $T_f$ ), and percentage char yield at 700°C. Typical TG/DTG traces for PPTI copolymers are shown in Figure 5.

All copolymers showed a broad one-step degradation, whereas copolymers having a lower mole fraction of *N*-aryl itaconimides (i.e., PPTI-1 and PI-1) showed a two-step degradation. Homopolymer PPTI also showed two-step degradation, whereas PI ho-

TABLE III  
Results of Molecular Weights and Polydispersity Index of Homopolymers and Copolymers

Sample designation	$M_n (\times 10^{-4})$	$M_w (\times 10^{-4})$	Polydispersity
PI-1	4.86	10.63	2.19
PI-2	4.60	10.82	2.35
PI-3	4.33	11.7	2.70
PI-4	2.21	5.51	2.49
PI-5	2.33	6.94	2.98
PI	0.46	0.95	2.08
PPTI-1	4.46	6.81	1.52
PPTI-2	6.18	10.02	1.62
PPTI-3	3.57	7.26	2.03
PPTI-4	2.71	5.60	2.07
PPTI-5	1.97	4.18	2.12
PPTI	0.87	1.87	2.15

TABLE IV  
Results of DSC Scans of Homopolymers and Copolymers<sup>a</sup>

Sample designation	Mole fraction of <i>N</i> -aryl itaconimides	$T_e$ (°C)	$T_g$ (°C)	$T_f$ (°C)
PI-1	0.217	136.1	147.2	151.6
PI-2	0.344	153.5	165.9	168.3
PI-3	0.461	168.6	172.5	176.5
PI-4	0.531	181.0	185.3	190.4
PI-5	0.658	183.5	185.8	191.7
PI	—	209.5	220.2	223.2
PPTI-1	0.287	145.6	150.7	154.7
PPTI-2	0.346	159.9	167.2	171.9
PPTI-3	0.487	162.5	167.7	173.3
PPTI-4	0.603	178.6	187.6	192.7
PPTI-5	0.654	198.2	204.5	208.7
PPTI	—	212.9	232.2	236.3

<sup>a</sup> Heating rate of 10°C/min.

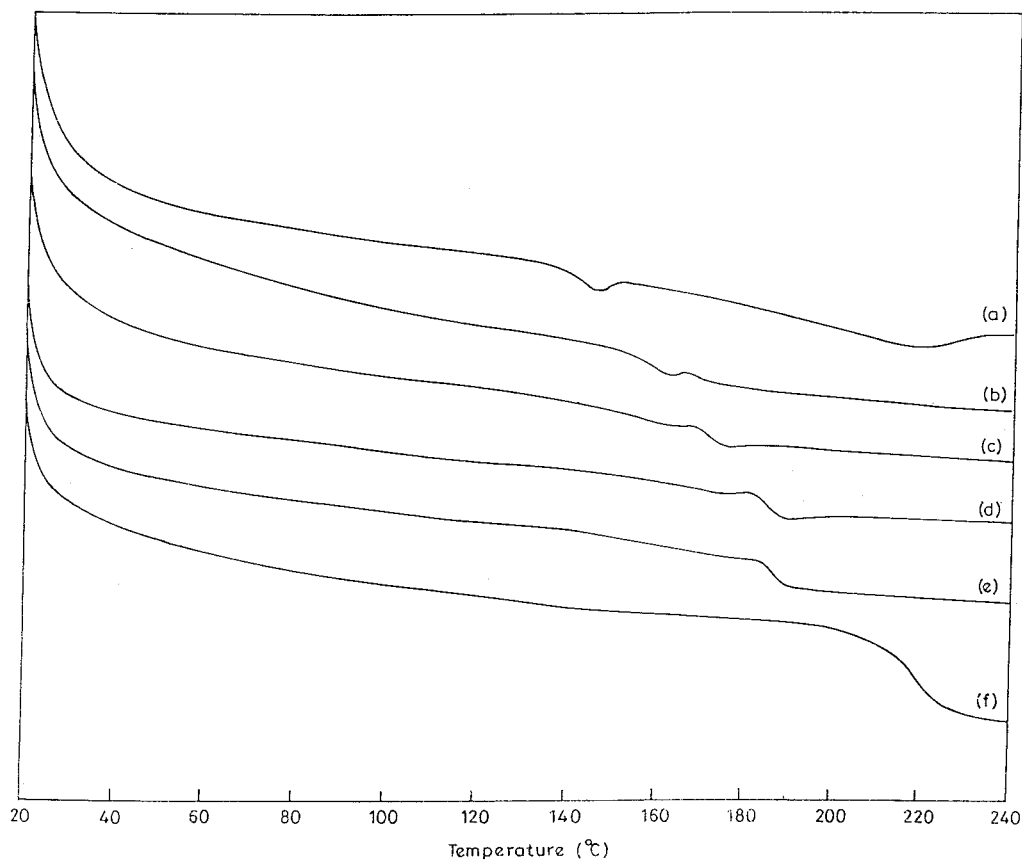


Figure 4 DSC scans of (a) PI-1, (b) PI-2, (c) PI-3, (d) PI-4, (e) PI-5, and (f) PI.

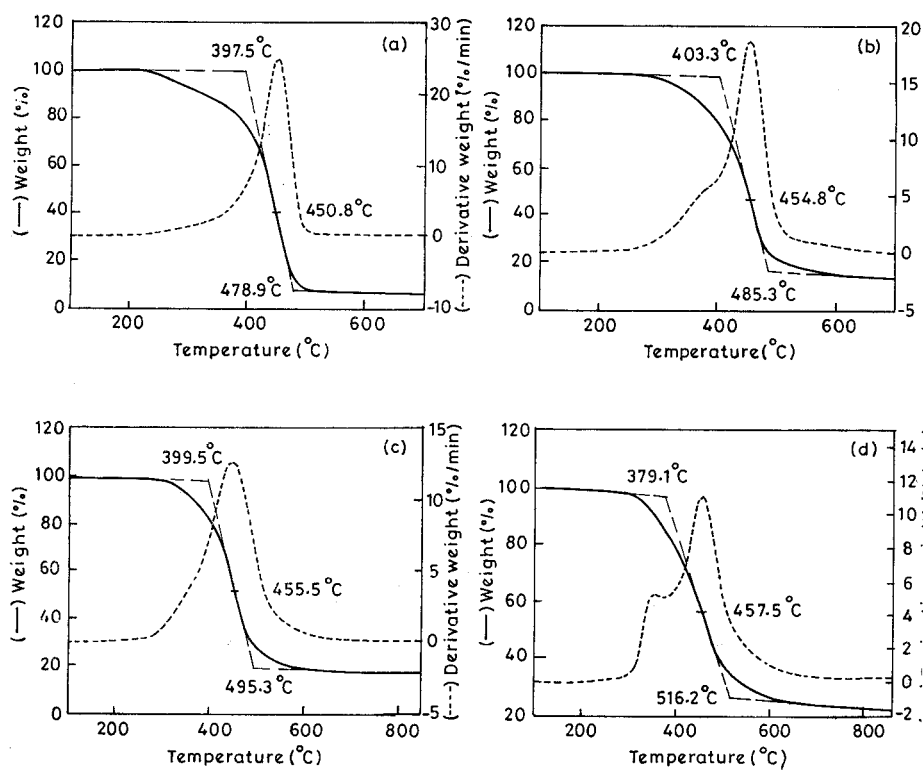


Figure 5 TG/DTG scans of (a) PPTI-1, (b) PPTI-3, (c) PPTI-5, and (d) PPTI.

**TABLE V**  
**Results of Thermogravimetric Analysis**  
**in N<sub>2</sub> Atmosphere<sup>a</sup>**

Sample designation	$T_i$ (°C)	$T_{max}$ (°C)	$T_f$ (°C)	Percentage weight loss	Percentage char yield at 700°C
PI-1	203.0	223.7	251.9	3.5	4.1
	251.9	428.4	500.0	90.8	
PI-2	265.3	429.8	600.0	87.9	11.7
PI-3	257.8	426.4	600.0	84.1	14.8
PI-4	274.2	428.3	600.0	82.5	16.5
PI-5	268.2	426.4	633.0	80.3	18.9
PI	307.5	447.5	700.0	76.9	23.1
PPTI-1	213.8	258.6	310.3	7.0	7.0
	334.5	443.1	500.0	84.2	
PPTI-2	258.6	434.5	610.4	88.9	10.2
PPTI-3	255.1	441.4	618.2	84.5	14.9
PPTI-4	239.1	434.8	636.4	81.4	17.8
PPTI-5	260.9	439.1	652.1	80.5	18.9
PPTI	304.3	352.2	373.9	12.6	25.5
	373.9	450.0	654.5	60.7	

<sup>a</sup> Heating rate of 10°C/min.

mopolymer showed one-step degradation. In PI-1 and PPTI-1 a weight loss of 3.5 and 7%, respectively, was observed in the temperature range of 200–310°C. All other copolymers were stable up to 280 ± 25°C. The results of thermogravimetric analysis along with the weight loss in each step are summarized in Table V. A significant improvement in the char yield was observed on the incorporation of *N*-aryl itaconimides in the PMMA backbone and it showed an increase with increasing amounts of itaconimides. The percent char yield was in the range of 4–19% at 700°C for copolymer samples having a mole fraction of itaconimide in the range of 0.2–0.65 in the copolymers. Char yield in PI and PPTI homopolymers was found to be 23.1 and 25.5%, respectively. As expected, char yield in PI and PPTI homopolymers and copolymers was lower compared to that of *N*-(*p*-chlorophenyl) itaconimide homo/copolymers.<sup>12</sup> In spite of the ring structure present in the main chain of *N*-aryl maleimide homopolymers and copolymers, % char yield was much lower compared to that of *N*-aryl itaconimide homopolymers and copolymers. Char yield for *N*-(phenyl/*p*-tolyl/*p*-chlorophenyl) maleimide : MMA copolymers having mole fraction of maleimide in the range of 0.1–0.36 in the copolymers was less than 8% at 500°C,<sup>6,8</sup> whereas in *N*-(phenyl/*p*-tolyl/*p*-chlorophenyl) itaconimide : MMA copolymers, char yield was

found to be 10–30% at 500°C having mole fraction of itaconimide in the range of 0.2–0.35 in the copolymers.

## CONCLUSIONS

Greater amounts of *N*-aryl itaconimides could be incorporated into copolymers, which was difficult to attain with maleimides having a similar structure. A significant increase in  $T_g$  and thermal stability of PMMA was achieved by incorporating a low mole fraction of itaconimide in the backbone.

The financial assistance provided by the Council of Scientific and Industrial Research (CSIR) (to V.A.) is gratefully acknowledged.

## References

- Patel, J. D.; Patel, M. R. *J Macromol Sci Chem* 1983, A19, 801.
- Barrales-Rienda, I. M.; Gonzales, D. E.; La Campa, J. I.; Ganzalez Ramos, I. *J Macromol Sci Chem* 1977, A11, 267.
- Patel, J. D.; Patel, M. R. *J Polym Sci Polym Chem Ed* 1983, 21, 3027.
- Choudhary, L.; Varma, D. S.; Varma, I. K.; Wang, F. W. *J Therm Anal* 1993, 39, 633.
- Bharel, R.; Choudhary, V.; Varma, I. K. *J Appl Polym Sci* 1993, 49, 31.
- Bharel, R.; Choudhary, V.; Varma, I. K. *J Appl Polym Sci* 1994, 54, 2165.
- Bharel, R.; Choudhary, V.; Varma, I. K. *J Appl Polym Sci* 1995, 57, 767.
- Choudhary, V.; Mishra, A. *J Appl Polym Sci* 1996, 62, 707.
- Mishra, A.; Sinha, T. J. M.; Choudhary, V. *J Appl Polym Sci* 1998, 68, 527.
- Radiac, D.; Gargolla, L.; Salamone, J. C., Eds. *Polymeric Materials Encyclopedia*, Vol. 8; CRC Press: Boca Raton, FL, 1996; pp. 6346–6350.
- Yahiro, K.; Shibata, S.; Shi-Ruk, J.; Park, Y.; Okabe, M. *J Ferment Bioeng* 1997, 84, 375.
- Anand, V.; Choudhary, V. *J Appl Polym Sci* 2001, 82, 2078.
- Searle, N. E. U.S. Pat. 2,444,536, 1948; *Chem Abstr* 1948, 42, 7340c.
- Oishi, T.; Momoi, M.; Fujimoto, M.; Kimura, T. *J Polym Sci Polym Chem Ed* 1983, 21, 1053.
- Yamazaki, H.; Matsumoto, A.; Otsu, T. *Eur Polym J* 1997, 33, 157.
- Pyriadi, T. M.; Fraih, M. *J Macromol Sci Chem* 1982, A18, 159.
- Oishi, T.; Nagai, K.; Kawamoto, T.; Tsutsumi, H. *Polymer* 1996, 37, 3131.
- Oishi, T.; Kawamoto, T. *Polym J* 1994, 26, 920.
- Oishi, T.; Seo, I.; Kimura, T. *Technol Rep Yamaguchi Univ* 1979, 2, 199.
- Brandrup, J.; Immergent, E. H., Eds. *Polymer Handbook* 2nd ed.; Wiley-Interscience: New York, 1975.