Studies on the Copolymerization of Methyl Methacrylate with N-(*O/M/P*-Chlorophenyl) Itaconimides

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ABSTRACT: The article describes the synthesis and characterization of N-aryl itaconimide monomers such as: N-(*p*-chlorophenyl) itaconimide (PI)/N-(*m*-chlorophenyl) itaconimide (MI)/N-(*o*-chlorophenyl) itaconimide (OI) and its copolymerization behavior with MMA. The homopolymers and copolymers of N-aryl itaconimides and methyl methacrylate (MMA, M_2) were synthesized by varying the mol fraction of N-aryl itaconimides in the initial feed from 0.1 to 0.5 using azobisisobutyronitrile (AIBN) as an initiator and tetrahydrofuran (THF) as the solvent. Copolymer composition was determined using ^{1}H-NMR spectroscopy [by taking the ratio of intensities of signals due to —OCH$_3$ of MMA (δ = 3.59 ppm) and the aromatic proton (δ = 7.2–7.5 ppm) of N-aryl itaconimides] and percent nitrogen content. The reactivity ratios were found to be r_1 = 1.33 and r_2 = 0.36 (PI-MMA) r_1 = 1.15 and r_2 = 0.32 (MI-MMA) and r_1 = 0.81 and r_2 = 0.35 (OI-MMA). Molecular weight as determined using high-performance liquid chromatography decreased with increasing mol fraction of itaconimides in copolymers. All the polymers had a polydisperstivity index in the range of 1.5–2.6.Thermal characterization was done using differential scanning calorimetry and dynamic thermogravimetry in nitrogen atmosphere. Incorporation of these N-aryl itaconimides in PMMA backbone resulted in an improvement in glass transition temperature (T_g) and thermal stability. Percent char increased with the increase of PI/MI/OI content in the copolymers. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 2078–2086, 2001

Key words: methyl methacrylate; copolymerization; N-aryl itaconimide; thermal stability; reactivity ratio; addition polymerization; radical polymerization

INTRODUCTION

In our earlier articles[1–8] we have reported the homopolymerization and copolymerization of N-aryl substituted maleimides having electron releasing/or electron withdrawing substituents with methyl methacrylate (MMA). Maleimides contain 1,2 disubstituted double bonds, which has a low tendency to homopolymerize due to kinetic considerations. The propagation step is extremely slow due to the steric interactions between the β-substitutent of the propagating species and the two substituents of the incoming monomer molecule.[9]

Itaconimides, on the other hand contain 1,1-disubstituted double bond outside the ring, which

is considered to be more reactive than the maleimide double bond that is present inside the ring. Copolymerization of maleimides have been well reported in the literature, whereas very few reports are available on the homopolymerization or copolymerization of N-aryl/alkyl itaconimides with MMA/styrene.[10–13] Copolymerization of N-[4-(cholesteroxycarbonyl)phenyl] itaconimide/N-[4-N'-(α-methylbenzyl)aminocarbonylphenyl] itaconimides with MMA has also been reported to prepare optically active materials.[14,15] However, no systematic studies are reported investigating the effect of substituent position in N-(chlorophenyl) itaconimides on the copolymerization behavior with MMA and thermal behavior. It was, therefore considered of interest to systematically investigate the effect of structure of N-aryl itaconimides (the position of chloro substituent, *o/m/p*) on the copolymerization behavior with MMA and its comparison with the corresponding maleimides having a similar structure.

The present article describes the synthesis and characterization of N-(*o/m/p*-chlorophenyl) itaconimide monomers. Homopolymerization and copolymerization of these monomers with varying amounts of MMA was carried out in solution using THF as solvent and AIBN as initiator. Structural and molecular characterisation of these polymers was done using ^{1}H-NMR, elemental analysis, and HPLC. Glass transition temperature was determined using differential scanning calorimetry (DSC). Thermal stability of the polymers in nitrogen atmosphere was determined using dynamic thermogravimetry.

EXPERIMENTAL

Materials Used

Itaconic Acid (Merck), *p*-chloroaniline (Merck), methanol (s.d. fine chem.), chloroform (s.d. fine chem.), phosphorus pentoxide (Qualigens), and silica gel for column chromatography (CDH) were used as supplied. *m*-Chloroaniline (Merck) and *o*-chloroaniline (Merck) were distilled under reduced pressure before use. 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.

Tetrahydrofuran (THF) (CDH) was purified by passing it through an alumina column. It was then 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 sulphate overnight and distilled under reduced pressure.

Preparation of Itaconic Anhydride

Itaconic acid (1.0 mol) and 0.75 mol (excess) of phosphorus pentoxide were taken in a 2-L reaction flask containing 1 L of chloroform. The mixture was allowed to reflux with stirring for 24 h. After refluxing the chloroform solution was decanted from the viscous brown residue at the bottom of the flask, and the solution was concentrated to a half litre by removing chloroform. A rotary vacuum evaporator was used for this purpose. On cooling the remaining solution to −10°C, itaconic anhydride crystallizes out, which was separated by filteration followed by drying in vacuum oven for 2 h at 40°C. Purity of the crystal was checked by DSC (m.p. 69°C) and structural characterization was done by ^{1}H-NMR. Three crops of white crystals were obtained. Yield was found to be about 80%.

In the ^{1}H-NMR spectrum of itaconic anhydride resonance signal due to methylene protons (2H,S) was observed at δ= 3.6 ppm, while the vinylidene protons were observed at δ = 6.5 ppm (1H,S) and δ = 5.9 ppm (1H,S), respectively. This is due to the different environment around the two hydrogen atoms.

Preparation of N-Aryl Itaconimide Monomers

The preparation of N-*o/m/p*-chlorophenyl itaconimide monomers was carried out according to the procedure reported by Searle[16] using acetone as a solvent. A typical procedure for preparation of itaconimides is described below.
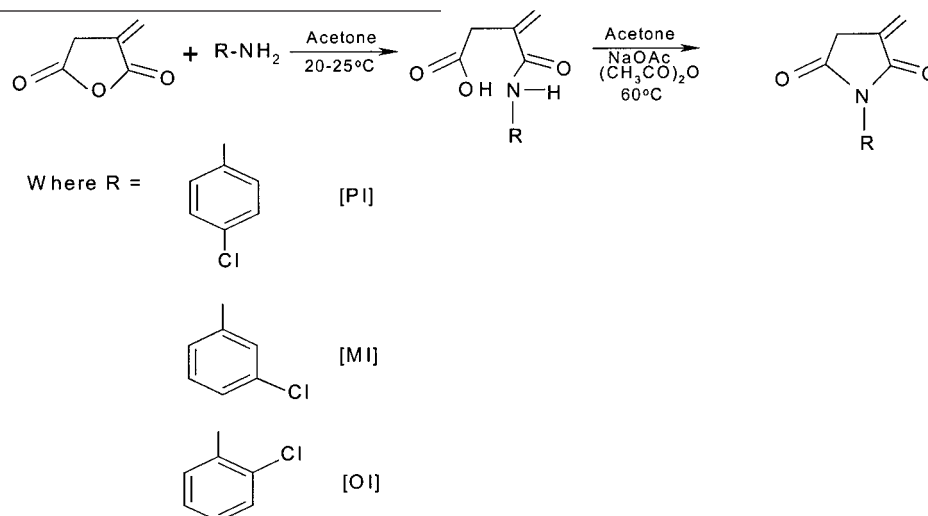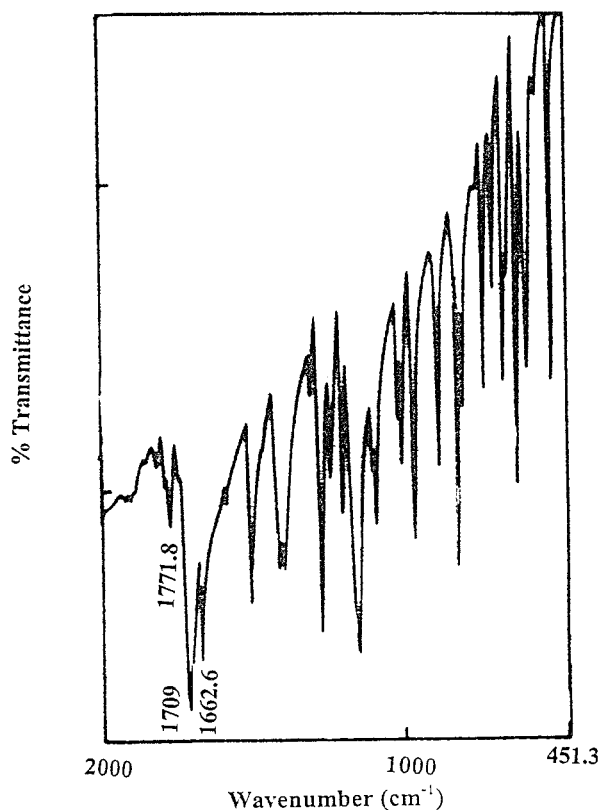
Figure 1 IR spectrum of N-(*p*-chlorophenyl) itaconimide monomer.

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

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. Amine (0.25 mol) dissolved in a minimum amount of dry acetone was added slowly with vigorous stirring. The reaction was carried out at 20–25°C. The amic-acid precipitated out from the solution. Cyclization reaction was carried out by addition of 75 mL of dry acetone, 40 mL of acetic anhydride, and about 4 g of anhydrous sodium acetate (obtained by fusion). 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. A white precipitate of N-substituted itaconimide was separated by filteration. It was then washed with cold distilled water several times. Unreacted amic acid and itaconic anhydride were neutralized by dilute sodium bicarbonate solution and washed repeatedly with cold distilled water

until it becomes neutral. Purification was done by passing a chloroform solution of the monomer through silica gel column and then precipitated by adding hexane. The yield of N-aryl itaconimides was in the range of 40–45%.

The monomers prepared were characterized by DSC, FTIR, and ^{1}H-NMR. In the DSC scans of the itaconimide monomers, an endothermic transition due to melting was observed. The melting points noted from the endothermic peak position were found to be 127.4, 115, and 90°C for PI, MI, and OI, respectively. The position of chloro-substituent in N-aryl maleimides also showed an effect on the melting point.[6]

In the IR spectrum of the monomers, the characteristic absorption bands due to imide groups were observed at 1709 ± 3 cm^{-1} and 1770 ± 3 cm^{-1}. The absorption band due to —C=C— stretch was observed at 1662 cm^{-1}. A typical IR spectrum of N-(*p*-chlorophenyl) itaconimide is shown in Figure 1.

In the ^{1}H-NMR spectrum of N-aryl itaconimide monomers, the proton resonance signals due to aryl group was observed at $\delta = 7.2$–7.6 ppm, the vinylidene protons were observed at $\delta = 6.5 \pm 0.03$ ppm (1H,S) and $\delta = 5.76 \pm 0.03$ ppm (1H,S) and methylene protons (2H,S) at $\delta = 3.5 \pm 0.03$ ppm. The integration was used to calculate the number of protons. A proton resonance signal was also observed at $\delta = 2.17 \pm 0.03$ ppm. This may be attributed to the methyl group of citraconimide. The isomerization of itaconimide to citraconimide may be responsible for this signal. Such isomerization has been earlier reported in itaconic anhydride.[17] The mol fraction of citracon-
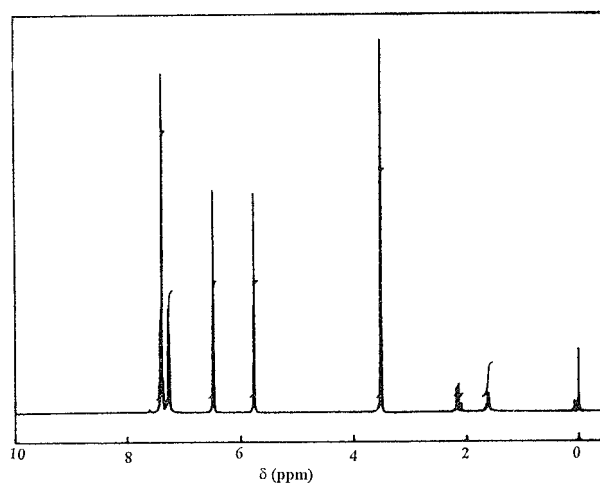

Figure 2 ^{1}H-NMR spectrum of N-(*m*-chlorophenyl) itaconimide monomer.

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

| Sample Designation | Mole Fraction of *N*-Aryl Itaconimides | | % Coversion/min. | % Nitrogen | Mol Fraction of *N*-Aryl Itaconimides in copolymers (From % N) |
	Feed	Copolymers			
PPI	1.000	—	0.2	—	—
PPI-1	0.1002	0.213	0.2	2.22	0.196
PPI-2	0.2004	0.358	0.3	3.46	0.353
PPI-3	0.301	0.460	0.3	4.46	0.519
PPI-4	0.399	0.548	0.4	4.56	0.539
PPI-5	0.500	0.618	0.3	4.95	0.620
PMI	1.000	—	0.5	—	—
PMI-1	0.102	0.219	0.9	2.48	0.226
PMI-2	0.201	0.368	0.8	3.52	0.362
PMI-3	0.301	0.462	0.7	4.06	0.448
PMI-4	0.399	0.536	0.7	—	—
PMI-5	0.499	0.621	0.6	4.95	0.620
POI	1.000	—	0.8	—	—
POI-1	0.101	0.208	0.5	2.50	0.222
POI-2	0.200	0.341	0.8	3.63	0.378
POI-3	0.301	0.421	0.9	4.20	0.472
POI-4	0.402	0.499	0.8	—	—
POI-5	0.490	0.648	0.8	—	—

imide in various samples was calculated from the ratio of intensity of protons at $\delta = 2.17 \pm 0.03$ ppm (citraconimide) to the protons at $\delta = 5.76 \pm 0.03$ ppm (vinylidene) and was found to be in the range of 0.06–0.08. A typical ^{1}H-NMR spectrum of N-(*m*-chlorophenyl) itaconimide is shown in Figure 2.

Preparation of Homopolymers and Copolymers of N-(*o/m/p*-chlorophenyl) Itaconimde with MMA

Homopolymerization and copolymerization of N-(*o/m/p*-chlorophenyl) itaconimides with MMA was carried out in THF using AIBN as initiator at 60°C under nitrogen atmosphere. The mol fraction of N-(*o/m/p*-chlorophenyl) itaconimide in the initial feed was varied from 0.1 to 0.5. A 30% (w/v) solution of monomers in THF was placed in a three-necked round-bottom flask equipped with a reflux condenser, $CaCl_2$ drying tube and a 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 temperature was raised to 60°C. The polymerization was initiated by adding 0.5% AIBN (w/w) as initiator. The reaction was stopped at low conversion ($\leq$15%) by pouring the contents of the flask into large excess of methanol. The precipitated poly-

mer was washed repeatedly with hot methanol to remove unreacted monomers, and was dried in vacuum oven.

Copolymers have been designated by adding a prefix P to the monomer designation of N-aryl itaconimides followed by a numerical suffix indicating the mol fraction of itaconimides multiplied by 10. For example, a copolymer prepared by taking 0.2 mol fraction of PI and OI has been designated as PPI-2 and POI-2, respectively. Homopolymers have been designated by adding a prefix P to the monomer designation of N-aryl itaconimides.

Characterization

^{1}H-NMR and FTIR spectroscopic techniques were used for the structural characterization of monomers and copolymers. ^{1}H-NMR spectrum of the monomers and copolymers were recorded on a Bruker Spectrospin DPX 300 spectrometer using $CDCl_3$ as solvent and tetramethyl silane as an internal standard. FTIR spectra of the monomers were recorded in KBr pellets using Biorad Digilab FTS-40 FTIR spectrophotometer. Elemental analysis was also done to determine the copolymer composition.

Waters HPLC was used to determine the molecular weights and molecular weight distribution
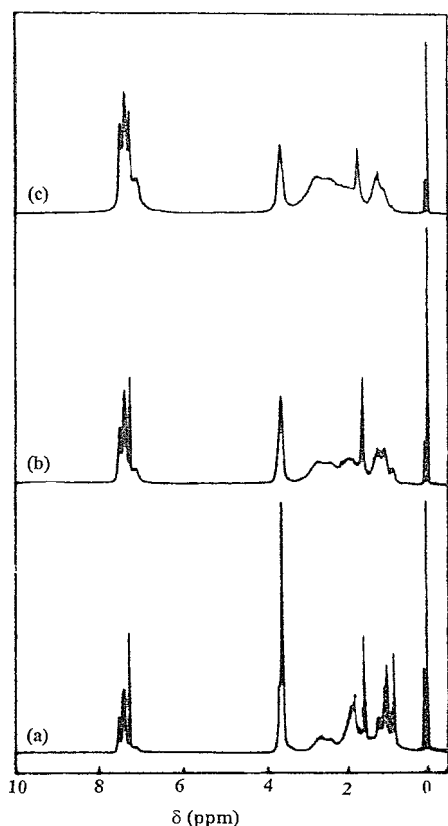
Figure 3   ^{1}H-NMR spectra of MMA-N-Aryl itaconimide copolymers (a) PMI-1, (b) PMI-3, and (c) PMI-5.

in homopolymers and copolymers. The calibration was done using polystyrene standards.

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°C/min by using 5 ± 1 mg of powdered samples. Thermal stability was determined by recording TG/DTG traces in nitrogen atmosphere (flow rate $= 60$ cm^3/min) using a DuPont 9900 thermal analyzer having a 951 TG module. A heating rate of 10°C/min and a sample size of 10 ± 1 mg was used in each experiment.

RESULTS AND DISCUSSION

In the copolymerization of MMA with N-aryl itaconimides, the position of substituent affected the percent conversion per unit time. In all the POI and PMI copolymers, precent conversion per minute was in the range of 0.5 to 0.9. On the other hand, all PPI copolymers had % conversion of 0.3 $\pm$ 0.1 per min. A similar trend was observed in the case of homopolymers. In our earlier work on the copolymerisation of N-aryl maleimides (having electron releasing substituent) with MMA, it was observed that the polymerization was hindered in the case of *ortho*-tolyl maleimides compared to *para*-tolyl maleimides due to steric hinderance.[4] However, in the case of itaconimides, an opposite trend is observed that is very difficult to explain. The experiments were repeated a number of times to verify this fact. The lower yield in the case of PPI copolymers could be due to the incomplete precipitation or due to the formation of a higher amount of soluble oligomers .The results are summarized in Table I.

^{1}H-NMR spectra of the copolymers are shown in Figure 3. The resonance signals due to the —OCH$_3$ protons of the MMA and aromatic protons of N-aryl itaconimides were observed at δ = 3.59 ppm and at δ = 7.2–7.5 ppm, respectively. The other characteristic signals of MMA observed at δ = 0.8–1.2 ppm and δ = 1.8–2.0 ppm were due to —CH$_3$ and >CH$_2$, respectively. The intensity of the signal due to aromatic protons increased with increasing N-aryl itaconimide content in the copolymers (Fig. 3). The copolymer composition was determined by taking the ratio of the intensity of signals due to methoxy proton of MMA (δ = 3.59 ppm) and aromatic proton of N-aryl itaconimide (δ = 7.2–7.5ppm). The results of copolymer composition thus determined are summarized in Table I. In the copolymerization of MMA with N-aryl itaconimides, an increase in M$_1$ (feed) resulted in an increase in the m$_1$ (copolymer).

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

Method	PI-MMA		MI-MMA		OI-MMA	
	r_1	r_2	r_1	r_2	r_1	r_2
Fineman-Ross	1.33	0.36	1.15	0.32	0.81	0.35
Kelen Tüdos	1.29	0.35	1.14	0.32	0.74	0.33
Average	1.31	0.355	1.145	0.32	0.775	0.34
Q	3.12		3.64		3.64	
e	1.27		1.4		1.55	

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

Sample Designation	M_n $\times 10^{-3}$	M_w $\times 10^{-3}$	Polydispersity Index
PPI-1	7.08	15.96	2.25
PPI-2	14.89	29.29	1.97
PPI-3	8.62	15.73	1.83
PPI-4	7.49	15.19	2.03
PPI-5	4.67	8.84	1.89
PPI	2.64	4.18	1.58
PMI-1	6.86	13.02	1.9
PMI-2	5.45	11.02	2.02
PMI-3	2.66	7.01	2.6
PMI-4	4.55	7.23	1.59
PMI-5	2.23	5.14	2.3
PMI	1.05	1.56	1.47
POI-1	30.34	63.81	2.1
POI-2	23.70	50.20	2.12
POI-3	8.01	16.40	2.05
POI-4	3.66	7.57	2.07
POI-5	3.14	7.82	2.49
POI	—	—	—

Table IV   Results of DSC Scans of Homopolymers and Copolymers (Heating Rate 10°C/min)

Sample Designation	Mol Fraction of *N*-Aryl Itaconimides	T_e (°C)	T_g (°C)	T_f (°C)
PPI-1	0.213	139.2	142.7	148.8
PPI-2	0.358	144.2	149.3	157.9
PPI-3	0.460	163.9	177.0	185.4
PPI-5	0.618	184.6	190.9	200.5
PPI	—	228.5	238.1	247.2
PMI-1	0.219	119.9	123.6	132.3
PMI-2	0.368	137.4	142.3	143.7
PMI-3	0.462	141.1	144.4	155.5
PMI-4	0.536	145.5	151.8	156.8
PMI-5	0.621	152.9	155.3	160.1
PMI	—	221.6	227.5	233.7
POI-1	0.208	157.1	162.0	165.9
POI-2	0.341	176.2	180.3	183.6
POI-3	0.421	186.0	190.8	194.5
POI-4	0.499	194.5	204.9	209.3
POI-5	0.648	224.7	228.0	235.8
POI	—	—	—	—

Copolymer composition was also determined from the % nitrogen content, and the results are given in Table I. There was a good agreement between the values obtained by two different methods in all the copolymers.

The reactivity ratios of the monomers were calculated from the knowledge of copolymer composition using Fineman-Ross and Kelen Tüdos methods. Values of r_1 (N-aryl itaconimides) and r_2 (MMA) are given in Table II. These results show a higher reactivity ratio of N-aryl itaconimides (i.e., PI/MI/OI) compared to MMA thus indicating that N-aryl itaconimides are more reactive (i.e., $\kappa_{11} > \kappa_{12}$ and $\kappa_{21} > \kappa_{22}$) than MMA towards homopropagation and copropagation. On the other hand, maleimides with a similar structure showed much lower reactivity ratios compared to MMA.[18] Higher values of reactivity ratios for various itaconimide monomers have been reported in the case of copolymerizations with styrene.[11–15,19] It was not possible to incorporate higher amounts of maleimides, whereas the amounts of itaconimides incorporated are higher than the feed compostion, thereby indicating that the itaconimides are more reactive compared to maleimides.[6,7]

The Q and e values for the N-aryl itaconimide monomers were also calculated using the Alfrey and Price equation by taking Q and e values for MMA as 0.78 and 0.4, respectively.[20] The results

are summarized in Table II. The Q values were similar in all the copolymers and e values are highest for OI monomer and lowest in case of the PI monomer.

The M_n, M_w, and molecular weight distribution of the copolymers were calculated by HPLC using polystyrene as calibration standards. All the copolymers had molecular weight in the range of 2.2×10^3–30.3×10^3 (M_n) and 5.1×10^3–63.8×10^3
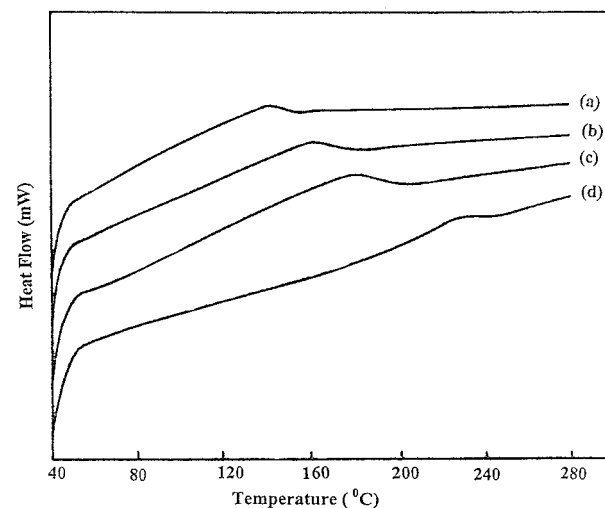

Figure 4   DSC scans of PPI homopolymer and copolymers: (a) PPI-1, (b) PPI-3, (c) PPI-5, and (d) PPI.

Table V Results of Thermogravimetric Analysis in N_2 Atmosphere (Heating Rate 10°C/min)

Sample Designation	T_i (°C)	T_{max} (°C)	T_f (°C)	% Weight Loss	% Char Yield at 700°C
PPI-1	260	323	353	12.4	21.4
	364	432	501	56.4	
PPI-2	249	—	400	20.4	22.8
	400	451	587	54.2	
PPI-3	230	—	390	21.1	27.1
	390	444	598	44.4	
PPI-4	228	—	351	11.5	28.7
	351	442	614	57.0	
PPI-5	226	421	617	65.4	34.6
PPI	254	323	345	10.4	35.2
	345	397	454	31.8	
	454	470	593	17.0	
PMI-1	236	—	374	15.1	19.1
	374	449	531	65.8	
PMI-2	236	—	384	19.5	27.2
	384	446	543	53.3	
PMI-3	227	—	348	14.4	28.2
	348	442	613	57.4	
PMI-4	227	447	606	70.3	29.7
PMI-5	232	447	620	70.3	29.7
PMI	276	362	384	17.0	31.6
	384	431	657	51.8	
POI-1	321	372	391	13.8	20.2
	391	447	514	60.9	
POI-2	307	377	397	20.7	24.2
	397	444	562	48.1	
POI-3	234	354	397	24.4	27.6
	397	444	606	45.2	
POI-4	248	449	613	71.2	28.8
POI-5	259	435	613	68.4	31.0
POI	192	268	306	2.96	35.4
	318	414	590	61.85	

(M_w) with a polydispersity index in the range of 1.5–2.6. 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 the copolymer structure and composition on the glass transition temperature of the copolymers. To have a similar thermal history second heating scans were used to determine the glass transition temperature. The powdered samples were first heated to 120°C and then quench cooled and rerecorded the DSC scans 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); and T_f = extrapolated end set temperature.

The results of DSC traces are summarized in Table IV. Typical DSC scans for PPI homopolymer and copolymers are shown in Figure 4. The T_g of the copolymers increased with an increasing amount of the N-aryl itaconimides in the copolymers. The position of the substituent ($o/m/p$-chloro) in the N-aryl itaconimides also affected the T_g. On comparing the T_g of copolymers (MMA-PI, MMA-MI, and MMA-OI) having an equal mol fraction of N-aryl itaconimides (i.e., PPI-1, PMI-1, and POI-1), highest T_g was observed in the case of POI-1(162°C) and lowest in the case of PMI-1 (123.6°C) (Table IV). The same is true in the case of copolymers having the highest mol fractions of N-aryl itaconimides (i.e., PPI-5, PMI-5, and POI-5). Higher T_g values observed in the case of MMA-OI copolymers could be explained on the basis of

steric hindrance caused by the presence of chloro-substituent at the *ortho* position, which may hinder the mobility of the main chain, whereas higher values of T_g in the case of MMA-PI copolymers than MMA-MI copolymers could be explained on the basis of enhanced polar–polar intermolecular interactions due to the presence of polar substituents at the *para* position. A similar trend has been reported in the case of MMA–N-(*o/m/p*-chlorophenyl) maleimide copolymers.[6,7] A significant increase in T_g (i.e., 18–57°C) was observed upon incorporation of very low mol fractions (i.e., 0.2) of itaconimides. As expected, T_g of MMA–itaconimide copolymers was lower than their corresponding MMA–maleimide copolymers of similar structure and copolymer composition.[6,7,18]

In the case of homopolymers, the position of the substituent on the phenyl ring also affected the T_g (Table IV). The PPI homopolymer had a higher T_g than the PMI homopolymer, whereas no T_g transition was observed in the case of the POI homopolymer.

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

POI homopolymer showed a single-step degradation, whereas PMI and PPI homopolymer showed two- and three-step degradation, respectively. In the case of PMMA, a three-step degradation has been reported.[21–24] The first-step degradation (150–250°C) is attributed to head-to-head linkages; the second step (250–350°C) was due to end unsaturation, and the third step (350–500°C) was due to depropagation. Char yield in the case of POI and PPI copolymers was similar, i.e., 35%, whereas it was lower in the case of the PMI homopolymer (31.6%). In the case of the POI and PPI homopolymers, 1–3% weight loss was observed in the temperature range of 200 to 300°C.

Copolymers having low mol fractions of N-aryl itaconimides showed two-step degradation, whereas copolymers having higher mol fraction of itaconimides showed a broad one-step degradation. In PPI-1, ~2 weight loss was observed in the temperature range of 180–250°C, whereas all the copolymers were stable up to 230 ± 20°C. The results of thermogravimetric analysis along with
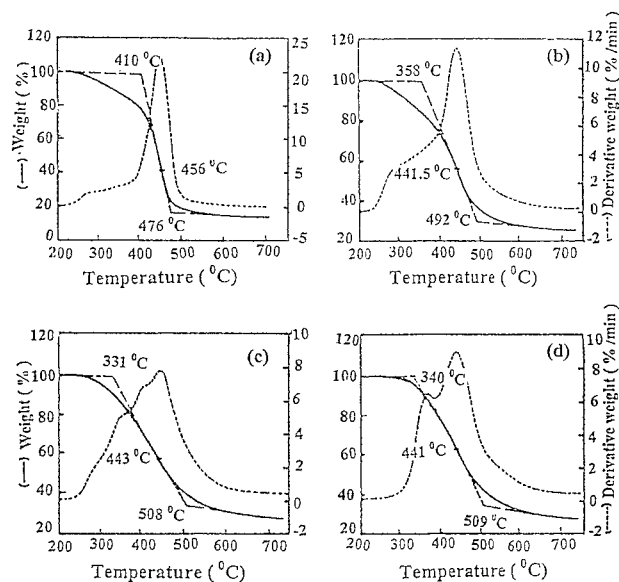

Figure 5 TG/DTG scans of PMI homopolymer and copolymers; (a) PMI-1, (b) PMI-3, (c) PMI-5, and (d) PMI.

the weight loss in each step are summarized in Table V. A significant improvement in the char yield was observed upon the incorporation of N-aryl itaconimides in the PMMA backbone, and it showed an increase with increasing amounts of itaconimides. Improvement in the char yield was more compared to the copolymers obtained by incorporating N-chlorophenyl maleimides in the PMMA backbone.

CONCLUSION

From these results it can be concluded that

1. N-aryl itaconimides can be successfully copolymerized with MMA, and the reactivity of these monomers is higher than their maleimide counterparts. Higher amounts of itaconimides could be incorporated into the copolymers, which was difficult to attain with maleimides.
2. The position of chloro-substituent on the phenyl ring (*o*-,*m*-,or *p*-) in N-aryl itaconimides affected the glass transition temperature. A significant improvement in the glass transition temperature is observed upon incorporation of very low mol fractions of these N-aryl itaconimides. The presence of *o*-/ or *p*-chloro-substituent was more effective in increasing T_g.

3. Copolymerization of MMA with N-aryl itaconimides resulted in a significant increase in the thermal stability.

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