

Copolymerization of Methyl Methacrylate with *N*-(Methoxyphenyl) Itaconimides

Rashmi Chauhan, Veena Choudhary

Centre for Polymer Science and Engineering, Indian Institute of Technology, Delhi, Hauz Khas, New Delhi, India 110016

Received 29 December 2006; accepted 29 December 2007

DOI 10.1002/app.28099

Published online 11 April 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This article describes the synthesis and characterization of *N*-(3-methoxyphenyl) itaconimide (MAI) and *N*-(4-methoxyphenyl) itaconimide (PAI) obtained by the reaction of itaconic anhydride with *m*-anisidine and *p*-anisidine, respectively. Structural and thermal characterization of MAI and PAI monomers was performed with Fourier transform infrared (FTIR), ¹H-NMR, differential scanning calorimetry (DSC), and thermogravimetric analysis. Copolymerization of methyl methacrylate (MMA) with various amounts of MAI or PAI ranging from 0.1 to 0.5 was performed in solution with azobisisobutyronitrile as an initiator. Structural and molecular characterization of copolymers was performed with FTIR, ¹H-NMR, elemental analysis, and gel permeation chromatography. The nitrogen percentage was used to calculate the copolymer composition. The monomer reactivity ratios for MMA–MAI and MMA–PAI copolymers were found to be 1.00 ± 0.01 for MMA and

0.99 ± 0.07 for MAI; those for MMA–PAI copolymers were 0.93 ± 0.02 for MMA and 1.11 ± 0.10 for PAI. The molecular weights of the copolymers were in the range of $0.94\text{--}9.7 \times 10^3$ (number-average molecular weight) and $3.3\text{--}101.8 \times 10^3$ (weight-average molecular weight), with polydispersity indices in the range of 1.5–4.1. The molecular weight decreased with the increasing molar fraction of imide in the polymer backbone. The glass-transition temperature, as determined from DSC scans, increased with increasing amounts of itaconimides in the copolymers. A significant improvement in the char yield, as determined by thermogravimetry, was observed upon copolymerization. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 987–996, 2008

Key words: addition polymerization; calorimetry; glass transition; radical polymerization; thermal properties

INTRODUCTION

In our previous articles,^{1–13} we investigated the copolymerization of methyl methacrylate (MMA) with imide monomers, that is, maleimides or itaconimides having electron-withdrawing or electron-releasing substituents. The nature of the substituents as well as the position of the substituents had a large effect on the physical properties. In our previous studies, we found that the electron-withdrawing group had a large effect on the glass-transition temperature (T_g) as well as the copolymerization behavior.

The aim of this work was to investigate systematically the effect of the methoxy group and its position in *N*-aryl itaconimides on the copolymerization behavior with MMA. This article describes the synthesis, characterization, and radical copolymerization of *N*-(3-methoxyphenyl) itaconimide (MAI) and *N*-(4-methoxyphenyl) itaconimide (PAI) monomers with MMA with tetrahydrofuran (THF) as a solvent. Several copolymer samples were prepared by the varia-

tion of the molar fractions of the itaconimides in the initial feed to investigate the effects of the copolymer composition and structure on the thermal behavior.

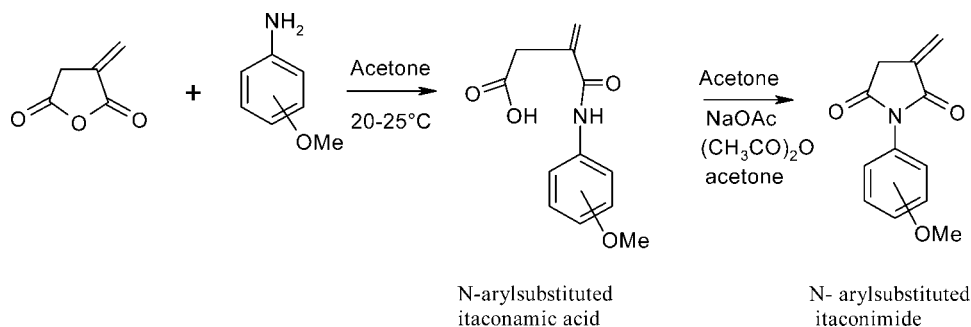
EXPERIMENTAL

Materials

Itaconic acid (Merck, Goa, India), *m*-anisidine (Sigma-Aldrich, Seelze, Germany), *p*-anisidine (Sigma-Aldrich, Seelze, Germany), methanol (S.D. Fine Chemicals, Maharashtra, India), chloroform (S.D. Fine Chemicals, Maharashtra, India), phosphorous 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, and this was followed by distillation. Acetic anhydride (S.D. Fine Chemicals, Maharashtra, India) was used after distillation. Anhydrous sodium acetate (CDH) was obtained by fusion. THF (CDH) (Delhi, India) was dried by refluxing with metallic sodium and benzophenone followed by distillation. Azobisisobutyronitrile (AIBN; High Polymer Labs, India) was recrystallized with chloroform. MMA (Merck, Goa, India) was washed with diluted sodium hydroxide to remove the inhibitor, and this

Correspondence to: V. Choudhary (veenach@hotmail.com).

Contract grant sponsor: Council for Scientific and Industrial Research (to R.C.).



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

was followed by repeated washing with distilled water until neutrality was achieved. It was dried over anhydrous sodium sulfate overnight and distilled under reduced pressure.

Itaconic anhydride was prepared from itaconic acid with an excess of phosphorous pentoxide as a dehydrating agent and chloroform as a solvent. The detailed procedure is reported in our earlier article.³

Preparation of the MAI and PAI monomers

MAI and PAI monomers were synthesized according to the procedure reported by Searle¹⁴ with acetone as the solvent, as shown in Scheme 1.

Procedure

Itaconic anhydride (0.25 mol) was dissolved in the minimum amount of dry acetone in a three-necked, round-bottom flask equipped with a magnetic stirrer and a reflux condenser. *m*-Anisidine (0.25 mol), dissolved in the minimum amount of dry acetone, was added slowly with vigorous stirring. The reaction mixture was vigorously stirred for another 4 h at 40°C. The reaction mixture was then cooled to room temperature and diluted with a saturated sodium bicarbonate solution. A 5% HCl solution was then added to it with continuous stirring of the solution. A white precipitate of *N*-(3-methoxyphenyl) itaconamic acid was obtained. The precipitate was filtered, washed with distilled water until the filtrate was neutral, and dried; this yielded *N*-(3-methoxyphenyl) itaconamic acid (68% yield, mp = 160.6°C), which was characterized with Fourier transform infrared (FTIR; 1708, 1668, and 1598 cm⁻¹) and ¹H-NMR [300 MHz, CDCl₃, δ = 10.0 (1H, s), 7.3 (1H, s), 7.2 (1H, m), 7.1 (1H, m), 6.6 (3H, m), 6.1 (1H, s), 5.7 (1H, s), 3.7 (3H, s), and 2.5 (2H, s)].

In the second step, cyclization was carried out by the addition of 75 mL of dry acetone, 40 mL of acetic anhydride, and 4 g of sodium acetate to *N*-(3-methoxyphenyl) 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 into ice-cold water. The precipitated monomer (MAI) was filtered, washed with a saturated sodium bicarbonate solution and distilled water, dried, and purified by the passage of the solution of the monomer in THF through a silica bed and then concentration of the THF solution to give MAI in a 60% yield.

For the preparation of PAI, *N*-(4-methoxyphenyl) itaconamic acid was precipitated during the refluxing of 4-anisidine (0.25 mol) and itaconic anhydride (0.25 mol) in acetone. The precipitated amic acid was washed with acetone and distilled water and dried to give purified *N*-(4-methoxyphenyl) itaconamic acid (55% yield, mp = 187.7°C), which was characterized with FTIR (1701, 1676, 1596 cm⁻¹) and ¹H-NMR [300 MHz, CDCl₃, δ = 9.8 (1H, s), 7.5 (2H, d), 6.9 (2H, d), 6.2 (1H, s), 5.7 (1H, s), 3.7 (3H, s), and 2.5 (2H, s)]. The procedure for the preparation of PAI was same as that used for the preparation of MAI.

The prepared imide monomers were characterized with differential scanning calorimetry (DSC), FTIR, and ¹H-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 73.1 and 111.6°C for MAI and PAI, respectively. Both monomers were stable up to 200°C and started degrading after that. The thermogravimetry (TG)/differential thermogravimetry (DTG) traces of the monomers are shown in Figure 1.

In the FTIR spectra of the two monomers, the characteristic absorption bands due to the imide group were observed at 1709 ± 3 and 1770 ± 3 cm⁻¹. The absorption band due to —C=C— stretching was observed at 1662 cm⁻¹.

In the ¹H-NMR spectrum of MAI in CDCl₃ [Fig. 2(a)], proton resonance signals due to aromatic protons were observed at δ = 7.3–6.8 ppm. The two singlets corresponding to the vinylidene protons were observed at δ = 6.4 ppm and δ = 5.6 ppm. The resonance signals due to methoxy in the aromatic ring

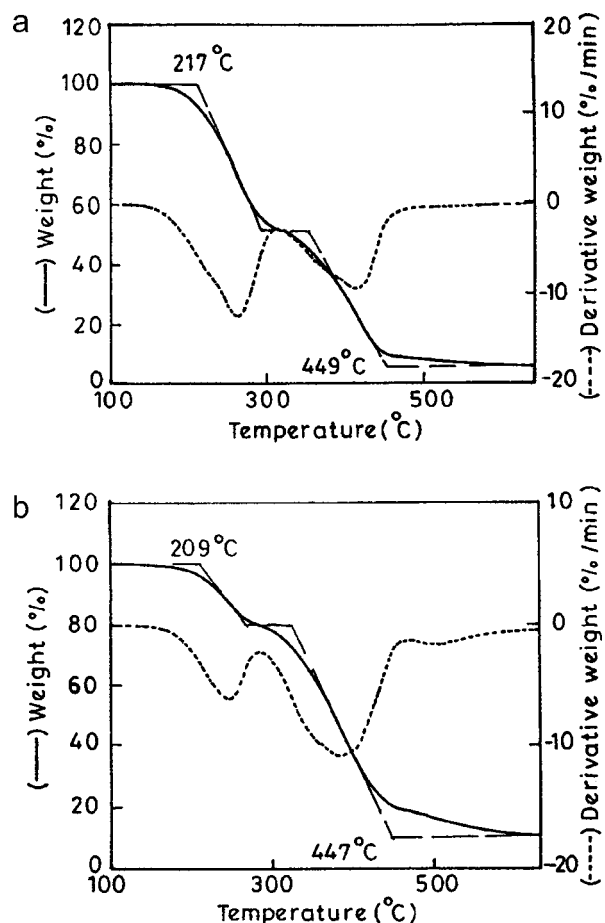


Figure 1 TG/DTG traces of the itaconimide monomers: (a) MAI and (b) PAI.

and due to methylene protons were observed at 3.7 and 3.4 ppm, respectively.

Similarly, in the $^1\text{H-NMR}$ spectrum of PAI in CDCl_3 [Fig. 2(b)], the two doublets corresponding to the aromatic protons were observed at $\delta = 7.0$ and $\delta = 6.8$ ppm. The two singlets corresponding to the vinylidene protons were observed at $\delta = 6.5$ ppm and $\delta = 5.7$ ppm, and those due to methoxy in the aromatic ring and methylene protons were observed at 3.8 and 3.5 ppm, respectively.

Preparation of the homopolymers and copolymers of MAI and PAI

Homopolymerization and copolymerization of *N*-aryl-substituted itaconimides with MMA were carried out at 60°C under a nitrogen atmosphere in solution with THF as a solvent and AIBN as an initiator. A 10–30% (w/v) solution of the monomers in THF was placed in a three-necked, round-bottom flask equipped with a reflux condenser, a CaCl_2 drying tube, and a nitrogen gas inlet tube. The whole assembly was placed in a thermostated bath and

stirred with a magnetic stirrer. The reaction mixture was purged with nitrogen, and the temperature was raised to 60°C . The polymerization was initiated by the addition of 1% AIBN (w/w) to the monomer solution. The reaction was stopped at a low conversion (~ 10 – 15%) by the contents of the flask being poured into a large excess of methanol. The precipitated polymer was washed repeatedly with hot methanol to remove unreacted monomer and was dried *in vacuo*. The homopolymers of MAI and PAI are designated MAI-10 and PAI-10, respectively.

Similarly, the copolymerization of MAI or PAI with MMA was also carried out in a nitrogen atmosphere at 60°C with AIBN as an initiator and THF as a solvent. The molar fraction of imides in the initial feed was varied from 0.1 to 0.5. Copolymers have been designated as MAI or PAI followed by a numerical suffix indicating the molar fraction of the itaconimide in the feed multiplied by 10. For example, a copolymer prepared with a 0.2 molar fraction of MAI or PAI has been designated MAI-2 or PAI-2, respectively.

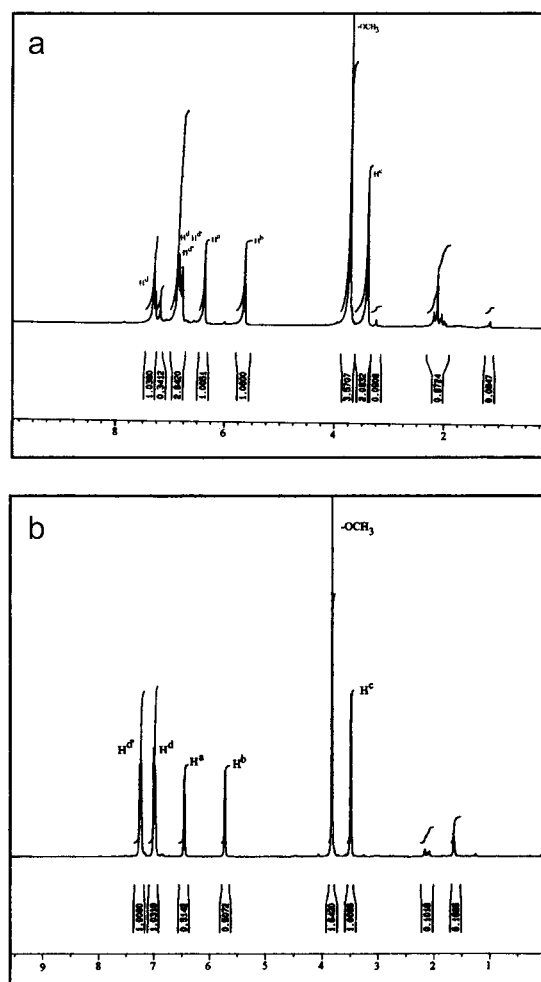


Figure 2 $^1\text{H-NMR}$ spectra of the itaconimide monomers: (a) MAI and (b) PAI.

TABLE I
Sample Designations, Polymerization Conditions, Conversions, and M_n , M_w , and PDI Values of MMA/ *N*-(Methoxyphenyl) Itaconimide Copolymers (Temperature of Polymerization = $60 \pm 5^\circ\text{C}$)

Sample designation	Molar fraction in the feed		Conversion (%/h)	$M_n \times 10^{-3}$ (g/mol)	$M_w \times 10^{-3}$ (g/mol)	PDI
	Itaconimide	MMA				
MAI-1	0.1	0.9	12.0	43.3	76.6	1.7
MAI-2	0.2	0.8	10.2	28.0	101.8	3.6
MAI-3	0.3	0.7	7.8	23.8	43.4	1.8
MAI-4	0.4	0.6	6.6	0.94	3.3	3.5
MAI-5	0.5	0.5	5.4	1.0	4.3	4.1
MAI-10	1.0	0.0	4.2	—	—	—
PAI-1	0.1	0.9	13.2	48.1	84.2	1.7
PAI-2	0.2	0.8	9.6	59.7	92.5	1.5
PAI-3	0.3	0.7	9.0	24.4	58.3	2.3
PAI-4	0.4	0.6	7.2	52.3	83.0	1.6
PAI-5	0.5	0.5	6.0	40.1	67.1	1.7
PAI-10	1.0	0.0	4.8	26.1	78.9	3.0

Characterization

The conversion percentage was determined gravimetrically. For this purpose, known amounts of the monomer and solvent were taken and heated in an inert atmosphere; when it reached a temperature of 60°C , a known amount of the initiator was added, and that was noted as the starting time of the reaction. After the desired time interval, the reaction was terminated by the addition of methanol, and the yield of the polymer was calculated after filtration and purification by repeated washing with hot methanol and drying. The results are reported as the conversion percentage per hour. $^1\text{H-NMR}$ and FTIR spectroscopy techniques were used for the structural characterization of the homopolymers and copolymers. $^1\text{H-NMR}$ spectra of the homopolymers and copolymers were recorded on a Bruker Spectrospin DPX 300 spectrometer (Fallenden, Switzerland) with CDCl_3 as a solvent and tetramethyl silane as an internal standard. FTIR spectra of the polymers were recorded as thin films with a Nicolet FTIR spectrophotometer (Waltham, MA). An Elementar Vario EL (Hanau, Germany) was used for C, H, and N analysis.

A Waters gel permeation chromatograph (Milford, MA) equipped with a high-resolution and high-temperature PLgel 5- μ mixed column ($300 \times 7.5 \text{ mm}^2$) along with a refractive-index detector was used to determine the molecular weights and molecular weight distributions of the polymers. THF was used as an eluent at a flow rate of 1.0 mL/min.

A PerkinElmer Pyris 6 differential scanning calorimeter (Waltham, MA) was used for the thermal characterization of the polymers. DSC scans were recorded in a static air atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$ with $5 \pm 1 \text{ mg}$ of powdered samples. Thermal stability was determined by the recording

of TG/DTG traces in a nitrogen atmosphere (flow rate = $60 \text{ cm}^3/\text{min}$) with a PerkinElmer Pyris 6 thermogravimetric analyzer (Waltham, MA). A heating rate of $20^\circ\text{C}/\text{min}$ and a sample size of $10 \pm 1 \text{ mg}$ were used in each experiment.

RESULTS AND DISCUSSION

Molecular characterization

The details for the feed composition, conversion percentage per hour, and molecular weight of the copolymers are given in Table I. The conversion percentage per hour decreased with the increasing molar fraction of the comonomer (MAI or PAI).

The number-average molecular weight (M_n), weight-average molecular weight (M_w), and molecular weight distribution of the polymers were determined by gel permeation chromatography. The MMA–MAI and MMA–PAI copolymers had molecular weights in the ranges of 0.94×10^3 to 43.3×10^3 (M_n) and 3.3×10^3 to 101.8×10^3 (M_w) and 24.4×10^3 to 59.7×10^3 (M_n) and 58.3×10^3 to 92.5×10^3 (M_w), respectively. The polydispersity index (PDI) of the MMA–MAI and MMA–PAI copolymers was in the range of 1.5–4.1. The MMA–PAI copolymers were obtained with higher molecular weights in comparison with the MMA–MAI copolymers. In the MMA–MAI copolymers, the molecular weight decreased significantly with an increasing amount of itaconimide, whereas in the MMA–PAI copolymers, there was no definite trend as a function of increasing PAI content.

Structural characterization

Figure 3 shows the $^1\text{H-NMR}$ spectra of MMA–MAI and MMA–PAI copolymers. In the $^1\text{H-NMR}$ spectra of MMA–MAI copolymers [Fig. 3(a)], the proton res-



Figure 3 $^1\text{H-NMR}$ spectra of (a) MMA-MAI copolymers and (b) MMA-PAI copolymers.

onance signals corresponding to the aromatic protons were observed in the region of $\delta = 7.3\text{--}6.9$ ppm. The methoxy attached to the aromatic ring and ester was observed at $\delta = 3.8$ and 3.65 ± 0.05 ppm, respectively. The methylene of the imide ring was observed at $\delta = 2.5$ ppm. The intensity of the signals due to aromatic protons ($\delta = 7.3\text{--}6.9$ ppm) and methoxy attached to the aromatic ring ($\delta = 3.8$ ppm) increased with an increasing concentration of MAI in the initial feed. The other characteristic signals observed at $\delta = 2.1\text{--}1.4$ and $\delta = 1.0\text{--}0.8$ ppm were due to $-\text{CH}_2$ and $-\text{CH}_3$ of MMA, respectively.

Similarly, for the copolymers of MMA and PAI, the resonance signals due to $-\text{OCH}_3$ protons on the aromatic ring and $-\text{OCH}_3$ of MMA were observed in the regions of $\delta = 3.7$ ppm and $\delta = 3.6\text{--}3.5$ ppm, respectively, and aromatic protons of *N*-aryl itaconimide were observed at $\delta = 7.2\text{--}6.9$ ppm. The other characteristic signals observed at $\delta = 1.8\text{--}1.3$ ppm and $1.0\text{--}0.7$ ppm were due to $-\text{CH}_2$ and $-\text{CH}_3$ protons of MMA, respectively. Here again, the intensity of the signals due to aromatic protons increased with an increasing concentration of *N*-aryl-substituted itaconimide in the initial feed [Fig. 3(b)].

TABLE II
Details of the Feed Composition and Results for the Copolymer Composition Determined from the Nitrogen Content in MMA/*N*-(Methoxyphenyl) Itaconimide Copolymers

Sample designation	Nitrogen (%)	Molar fraction of MAI/PAI	
		Feed	Copolymer
MAI-1	1.29	0.1	0.10
MAI-2	2.25	0.2	0.20
MAI-3	3.18	0.3	0.31
MAI-4	3.79	0.4	0.40
MAI-5	4.47	0.5	0.51
PAI-1	1.31	0.1	0.11
PAI-2	2.25	0.2	0.20
PAI-3	3.43	0.3	0.34
PAI-4	3.78	0.4	0.39
PAI-5	4.73	0.5	0.56

The nitrogen percentage was used to calculate the molar fraction of itaconimides in the copolymers, and the results are given in Table II. Copolymer

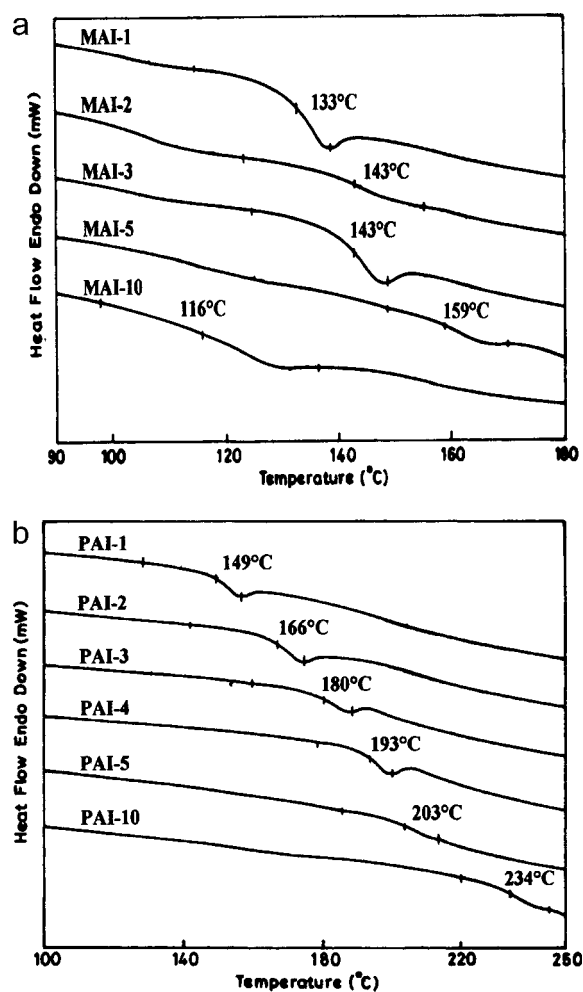


Figure 4 DSC scans of (a) MMA-MAI copolymers and (b) MMA-PAI copolymers.

TABLE III
Results of DSC Scans of MMA/*N*-(Methoxyphenyl) Itaconimide Copolymers (Heating Rate = 10°C/min)

Sample designation	Molar fraction of itaconimides		T_e (°C)	T_g (°C)	T_f (°C)	T_g (°C) ^a
	Feed	Copolymers				
MAI-1	0.1	0.10	125	133	138	107
MAI-2	0.2	0.20	128	143	153	109
MAI-3	0.3	0.31	120	143	147	110
MAI-5	0.5	0.51	152	159	165	113
MAI-10	1.0	1.00	107	116	123	—
PAI-1	0.1	0.11	128	149	156	127
PAI-2	0.2	0.20	149	166	174	142
PAI-3	0.3	0.34	160	180	187	164
PAI-5	0.5	0.56	189	203	211	192
PAI-10	1.0	1.00	220	234	245	—

^a Calculated with the Fox equation.

composition data were used to calculate the monomer reactivity ratios of the monomers with Fineman–Ross and Kelen–Tüdös methods. The monomer reactivity ratios for the MMA–MAI copolymers were found to be 1.00 ± 0.01 for MMA and 0.99 ± 0.07 for MAI, and those for MMA–PAI copolymers were 0.93 ± 0.02 for MMA and 1.11 ± 0.10 for PAI; this showed that the copolymers were close to azeotropic polymerization.

Thermal characterization

DSC studies

The DSC scans of various copolymers were recorded primarily to study the effects of the copolymer structure and composition on T_g of the copolymers. Figure 4 shows the DSC scans of MMA–MAI and MMA–PAI homopolymers and copolymers. A shift in the baseline due to the glass transition was observed in all the samples. To fully characterize the glass-transition region, the following temperatures were noted, and the results of DSC traces are summarized in Table III.

In the DSC scans of MMA–MAI and MMA–PAI copolymers, a single endothermic shift in the baseline corresponding to T_g was observed. The extrapolated onset temperature (T_e), T_g , and extrapolated end-set temperature (T_f) increased with increasing amounts of itaconimides in the copolymers.

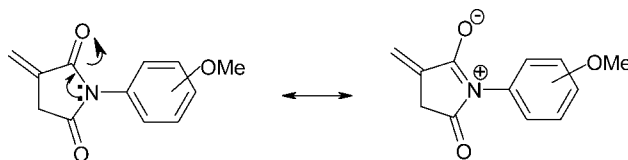
In case of MMA/*N*-aryl-substituted itaconimide copolymers, a significant increase in T_g was observed upon the incorporation of imide into the polymer backbone. An increase in T_g with electron-donating substituents in *N*-aryl-substituted itaconimides can be explained on the basis of the resonance structure, as shown in Scheme 2. Because of the presence of an electron-releasing group, the polarity of the carbonyl increases, and thus T_g increases. This observation is in

accordance with the studies carried out by Oishi et al.,^{15–17} who studied the polymerization of *N*-alkyl-substituted maleimides with styrene and observed that the softening points of *N*-alkyl-substituted maleimides increased with an increase in the polarization of carbonyl groups.

Also, in the homopolymer of PAI, that is, PAI-10, having $-\text{OCH}_3$ at the *p*-position, T_g was higher than that of the corresponding homopolymer having $-\text{OCH}_3$ at the *m*-position, that is, MAI-10. This shows the effect of the position of the same substituent on the aromatic ring. In PAI-10, the presence of a methoxy group at the *p*-position in the aromatic ring gives a more symmetrical structure in comparison with MAI-10, in which the $-\text{OCH}_3$ is at the *m*-position. This is in accordance with the fact that T_g increases with an increase in symmetry.¹⁸

The theoretical values of T_g , calculated with the Fox equation,¹⁹ were close to the experimentally obtained values for the MMA–PAI copolymers, but for the MMA–MAI copolymers, the calculated values were very low in comparison with the experimentally obtained values. This could be due to the fact that the T_g value of the MAI homopolymer (i.e., MAI-10) used for the calculation was very low as it had a very low molecular weight and had not reached the limit at which it was independent of the molecular weight.

Figure 5 shows the variation of T_g as a function of the imide content in the polymer backbone for MMA/*N*-aryl-substituted itaconimide copolymers. As expected, the copolymers containing MAI in the



Scheme 2 Resonance in *N*-aryl-substituted itaconimides.

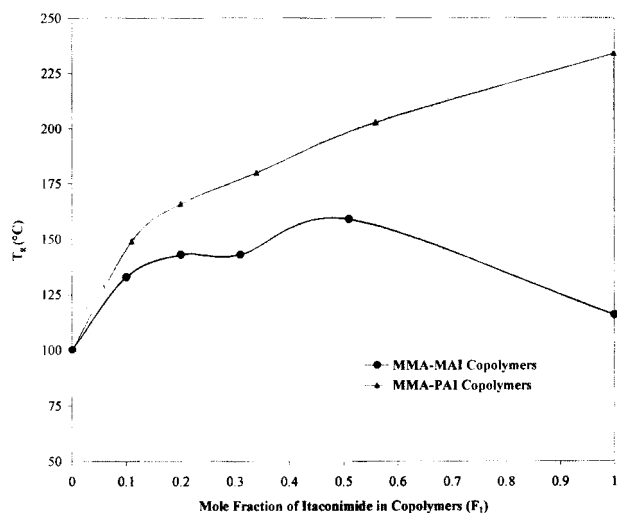


Figure 5 Variation of T_g with the molar fraction of *N*-aryl-substituted itaconimides in the copolymers.

polymer backbone showed lower T_g values than MMA-PAI copolymers of a similar composition.

Thermal stability

The thermal stability of the homopolymers and copolymers was determined by the recording of TG/DTG traces in a nitrogen atmosphere. TG/DTG traces of homopolymers and copolymers are shown in Figures 6-8, and the results are summarized in Table IV.

In the case of poly(methyl methacrylate) (PMMA), three-step degradation was observed for samples obtained under similar polymerization conditions, and this is well reported in the literature.^{20,21} The relative thermal stability of the copolymers was assessed by a comparison of the mass loss in the temperature ranges of 150-250, 250-350, and 350-700°C and the char yield percentage at 700°C and by the calculation of the integral procedural decomposition temperature (IPDT) according to the procedure of Doyle with eq. (1). IPDT values for the homopolymers and copolymers were determined in the temperature range of 100-700°C:

$$IPDT = A^*(T_f - T_i) + T_i$$

where A^* is the ratio of the area under the TG trace to the area of the rectangular plot bounded by the TG trace, T_f is the final temperature (700°C), and T_i is the initial temperature (100°C).

MAI-10 was stable up to 200°C, whereas PAI-10 was stable up to 300°C and started degrading after that. Both homopolymers degraded in two steps above this temperature and showed higher thermal stability than PMMA. The formation of head-to-head linkages is negligible in such homopolymers. This

could be due to the steric hindrance caused by bulky side groups. IPDT values for the imide homopolymers were higher than that for PMMA, and the observed trend was as follows:

$$PAI-10 > MAI-10 > PMMA$$

The char yield at 700°C, on the other hand, showed a different trend:

$$MAI-10 > PAI-10 >>>> PMMA$$

Similarly to MMA-MAI and MMA-PAI copolymers, the thermal stability of PMMA increased upon

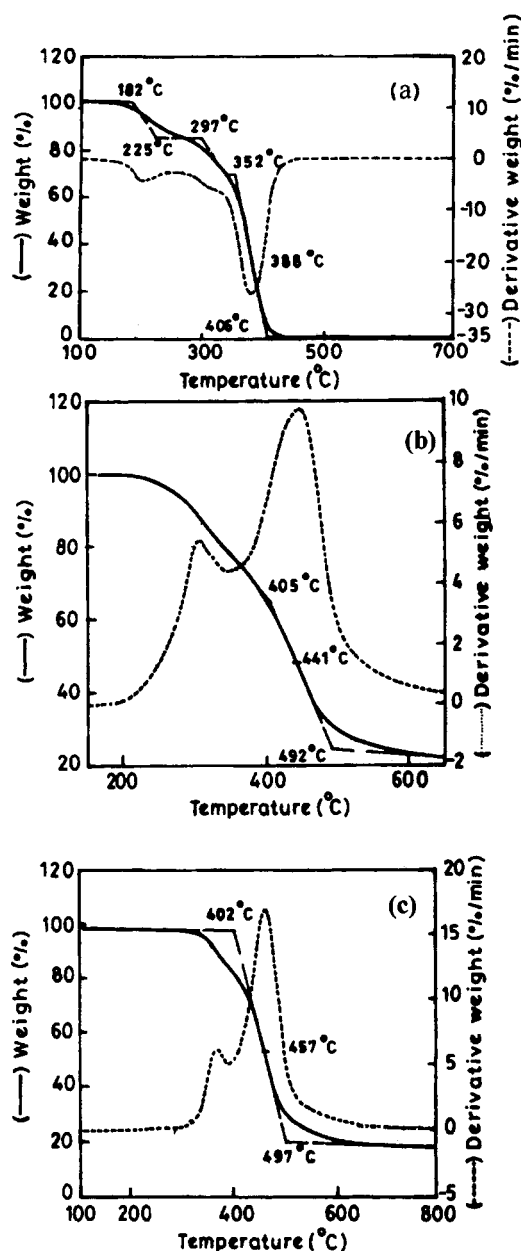


Figure 6 TG/DTG traces of the homopolymers: (a) PMMA, (b) MAI-10, and (c) PAI-10.

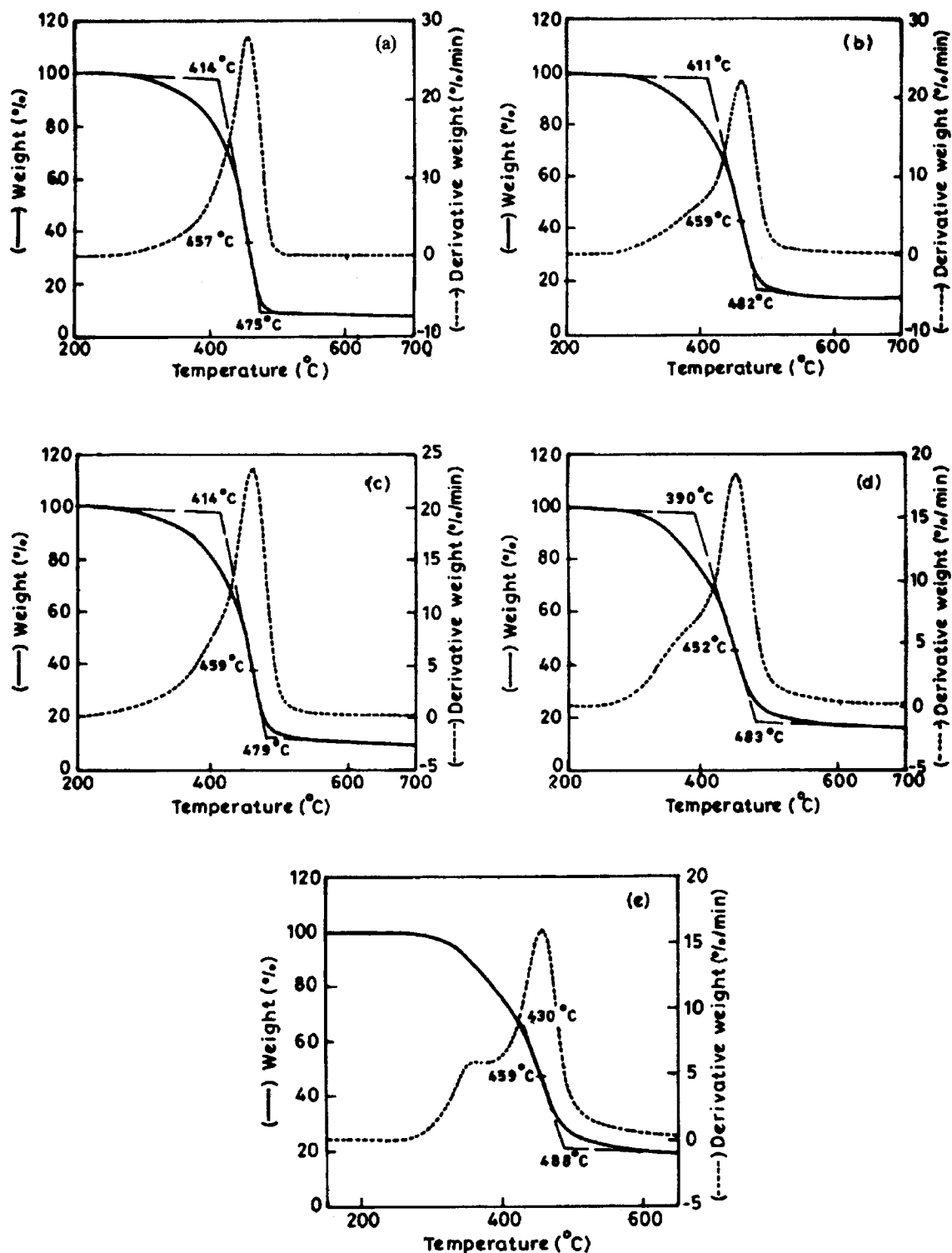


Figure 7 TG/DTG traces of the MMA-MAI copolymers: (a) MAI-1, (b) MAI-2, (c) MAI-3, (d) MAI-4, and (e) MAI-5.

copolymerization with *N*-aryl-substituted itaconimides, and it showed higher thermal stability for MMA-PAI copolymers than MMA-MAI copolymers.

Also, the IPDT values calculated for MMA/*N*-aryl-substituted itaconimide copolymers (435–512°C) were found to be higher than that for PMMA (341°C), showing an increase in the thermal stability

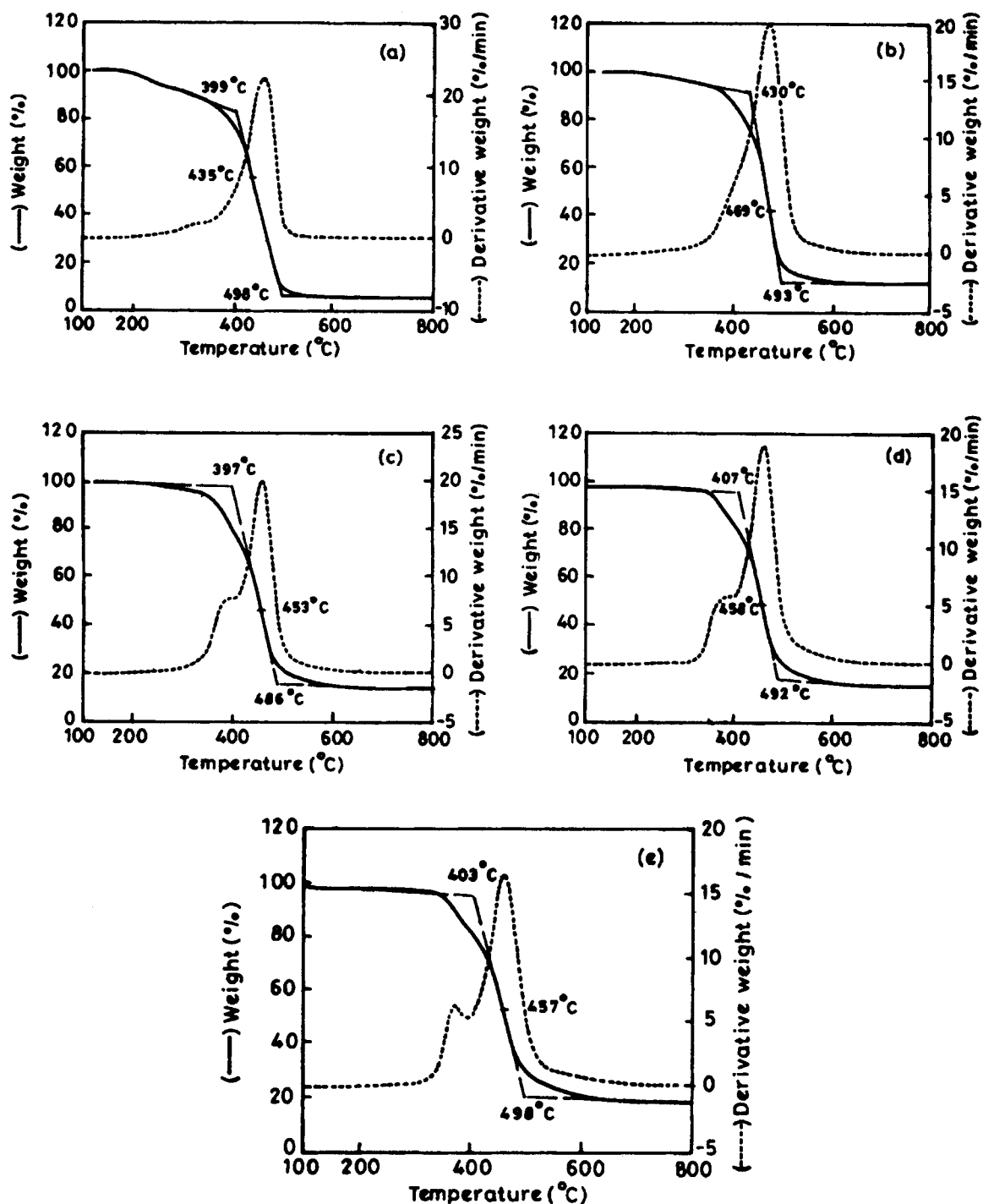


Figure 8 TG/DTG traces of the MMA-PAI copolymers: (a) PAI-1, (b) PAI-2, (c) PAI-3, (d) PAI-4, and (e) PAI-5.

upon the incorporation of *N*-aryl-substituted itaconimides into the backbone.

PAI-1 and PAI-2 copolymers also degraded in single steps with a major mass loss in the temperature range of 350–700°C. The weight loss in the temperature range of 250–350°C (due to end unsaturation) showed a decrease when lower amounts of imide were incorporated into the copolymer, but it increased when higher amounts of the imides were

incorporated. This could be due to the formation of low-molecular-weight polymers at a higher feed ratio of imide; this meant more chain ends per unit of weight of the copolymer.

CONCLUSIONS

MAI and PAI were successfully synthesized and copolymerized with MMA. A significant increase in

TABLE IV
Results of Thermogravimetric Analysis of MMA/N-(Methoxyphenyl) Itaconimide Copolymers in a Nitrogen Atmosphere (Heating Rate = 20°C/min)

Sample designation	Mass loss (%)			Char yield at 700°C (%)	IPDT (°C)
	50–250 (°C)	250–350 (°C)	350–700 (°C)		
PMMA	13.3	22.6	64.1	0	341
MAI-1	8.2	15.5	61.7	14.6	449
MAI-2	2.7	9.1	73.3	14.9	459
MAI-3	1.8	10.9	65.2	22.1	458
MAI-4	0.9	10.0	69.3	19.8	500
MAI-5	1.5	4.4	71.8	22.3	484
MAI-10	1.7	23.5	52.2	22.6	408
PAI-1	4.5	6.4	79.5	9.6	435
PAI-2	6.4	7.3	72.4	13.9	475
PAI-3	4.5	8.2	75.1	12.2	512
PAI-4	3.0	7.5	68.1	21.4	466
PAI-5	2.2	3.0	72.3	22.5	498
PAI-10	1.7	1.7	77.9	18.7	484

the T_g values and thermal stability was observed upon the copolymerization of these monomers with MMA. It was observed that the T_g values and thermal stability were higher for the *p*-substituted itaconimide than the corresponding *m*-substituent.

References

1. Chauhan, R.; Choudhary, V. *J Appl Polym Sci* 2005, 98, 1909.
2. Chauhan, R.; Choudhary, V. *J Appl Polym Sci* 2006, 101, 2391.
3. Anand, V.; Choudhary, V. *J Appl Polym Sci* 2001, 82, 2078.
4. Anand, V.; Choudhary, V. *J Appl Polym Sci* 2001, 89, 1195.
5. Solanki, A.; Anand, V.; Choudhary, V.; Varma, I. K. *J Macromol Sci Polym Rev* 2001, 41, 253.
6. Anand, V.; Kumar, R.; Choudhary, V. *J Appl Polym Sci* 2004, 91, 2016.
7. Anand, V.; Choudhary, V. *Macromol Chem Phys* 2001, 202, 943.
8. Anand, V.; Agarwal, S.; Greiner, A.; Choudhary, V. *Polym Int* 2005, 54, 823.
9. Mishra, A.; Sinha, T. J. M.; Choudhary, V. *J Appl Polym Sci* 1998, 68, 527.
10. Choudhary, V.; Mishra, A. *J Appl Polym Sci* 1996, 62, 707.
11. Bharel, R.; Choudhary, V.; Varma, I. K. *J Appl Polym Sci* 1993, 49, 31.
12. Bharel, R.; Choudhary, V.; Varma, I. K. *J Appl Polym Sci* 1995, 57, 767.
13. Bharel, R.; Choudhary, V.; Varma, I. K. *J Appl Polym Sci* 1994, 54, 2165.
14. Searle, N. E. U.S. Pat. 2,444,536 (1948).
15. Oishi, T. *Polym J* 1980, 12, 719.
16. Oishi, T.; Kimura, T. *Kobunshi Ronbunshu* 1975, 84, 60054.
17. Oishi, T.; Kimura, T. *Kobunshi Ronbunshu* 1976, 85, 33463.
18. Odian, G. *Principles of Polymerization*, 4th ed.; Wiley: New York, 2004; p 480.
19. Fox, T. G., Jr. *Bull Am Phys Soc* 1956, 1, 123.
20. Manring, L. E. *Macromolecules* 1989, 22, 2673.
21. Song, J. *Polym Degrad Stab* 1992, 36, 261.