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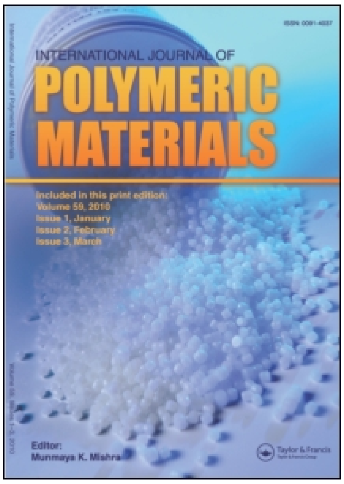

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Copolymerization of Methyl Methacrylate, Ethyl Acrylate, and Butyl Acrylate with N-2-Anisylmaleimide and Characterization of the Copolymers

Shantilal Oswal[a]; Mahesh H. Patel[a]; Suresh G. Patel[b]
[a] Department of Chemistry, V. N. South Gujarat University, Surat, India [b] Department of Chemistry, B. K. G. Science College, Valsad, India

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Copolymerization of Methyl Methacrylate, Ethyl Acrylate, and Butyl Acrylate with N-2-Anisylmaleimide and Characterization of the Copolymers

Shantilal Oswal
Mahesh H. Patel
Department of Chemistry, V. N. South Gujarat University, Surat, India

Suresh G. Patel
Department of Chemistry, B. K. G. Science College, Valsad, India

The free radical copolymerizations of methyl methacrylate (MMA), ethyl acrylate (EA), and butyl acrylate (BA) with N-2-Anisylmaleimide (AMI), initiated by AIBN, were performed in THF solvent at 65°C. A series of copolymers of AMI-MMA, AMI-EA, and AMI-BA were prepared using different feed ratios of comonomers. The polymer samples have been characterized by solubility tests, intrinsic viscosity measurements, FT-IR, and ^{1}H-NMR spectral analysis, and thermo-gravimetric analysis. The values of monomer reactivity ratios r_1 and r_2 determined by Fineman-Ross and Kelen-Tudos methods are 0.43 and 0.42 in AMI/MMA, 0.72 and 0.62 in AMI/EA and 0.76 and 0.72 in AMI/BA systems. Alfrey-Price Q-e values for AMI are $Q = 3.13$ and $e = 1.71$ in AMI/MMA, $Q = 1.10$ and $e = 1.46$ in AMI/EA and $Q = 1.02$ and $e = 1.63$ in AMI/BA systems. It was found that the initial and final decomposition temperature increased with increasing the component of AMI in the copolymer.

Keywords: acrylate-maleimide copolymers, 4-anisylmaleimide, reactivity ratios, thermo-gravimetry

INTRODUCTION

Polymers are widely used in several technological applications. The high demand for new materials requires the preparation of new

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Address correspondence to Shantilal Oswal, Department of Chemistry, V. N. South Gujarat University, Surat, 395 007, India. E-mail: oswalsl@satyam.net.in

polymers with enhanced mechanical and thermal properties and the copolymerization technique has been widely used to achieve this target. It has been found that N-substituted maleimide could polymerize with many vinyl monomers [1–2], therefore they became interesting monomers to copolymerize with other monomers in order to obtain heat resistant resins. The incorporated five-member planar ring in the backbones of the copolymer ensures higher glass transition temperature, T_g, and higher thermal degradation temperature. So N-substituted maleimides are widely used to enhance the heat resistance of polymers such as polystyrene, poly(alkyl methacrylate), poly(vinyl acetate), poly(vinyl chloride), and so on [3–16]. Moreover, the maleimides-based copolymers have been found to have versatile applications in industries ranging from aerospace to the medical and microelectronics fields [17–18]. These materials are also used as photo-resist with high T_g [19–20], flexibilizer for thermosetting polymers [21–22], nonlinear polymer with high T_g and flame retardant [23], and so on.

The authors have initiated studies on the synthesis and characterization of polymers and copolymers of substituted-phenyl maleimide [24–27]. This article presents investigation on copolymerization of methyl methacrylate (MMA), ethyl acrylate (EA), and butyl acrylate (BA) with N-2-anisylmaleimide (AMI) initiated by AIBN in THF solvent. The effect of different feed ratios of monomers on the properties of copolymers has been examined. The physical, spectral, and thermal properties have been studied in order to characterize the polymer samples.

EXPERIMENTAL

Materials

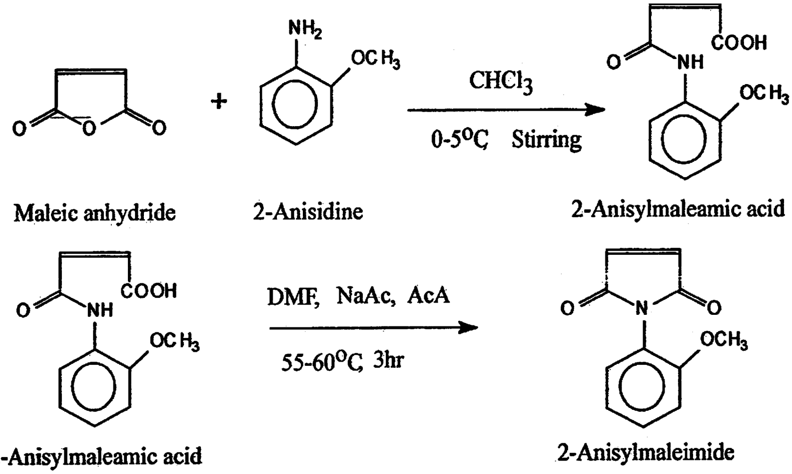
Maleic anhydride (SRL, extra pure) was first recrystallized from chloroform and then was further purified by sublimation at 54 ± 2°C. 2-Anisidine (Atul Industries Ltd. Extra pure) was used as received. MMA (BDH, AR), EA and BA (SISCO, AR) were shaken two to three times with 5% NaOH to eliminate hydroquinone inhibitor, then dried over anhydrous $CaCl_2$ for 6 h and distilled. The head and tail fractions were discarded. AIBN [2,2′-azobis-isobutironitrile (Wilson Lab.)] was recrystallized twice from methanol prior to use. THF (Qualigen Fine Chemicals, Mumbai, AR) was purified by distillation after being refluxed for 2 h in the presence of sodium. Acetic anhydride (AcA), anhydrous sodium acetate (NaAc), chloroform, DMF, methanol, and so on used in the present work were of analytical grade and used as received.

Measurements

^{1}H-NMR spectra of monomer and polymer samples were taken in DMSO-d_6 on a Bruker DPX-200/DRX-300 Spectrometer at 200 or 300 MHz (RSIC CDRL Lucknow). The internal reference used was TMS. FT-IR spectra of the monomer and polymer samples were recorded on a Perkin Elmer IR Spectrometer, using a KBr pellet technique. The viscosity measurements were carried out in DMF at 30 ± 0.2°C, using an Ubbelohde suspended-level viscometer. The intrinsic viscosities were calculated by means of Huggins equation [28] and Kraemer equation [29]. Elemental analysis was made on the Carlo Erba Model NA 1106 series analyzer. The thermograms in air/nitrogen atmosphere were obtained on a Mettler TA-4000 system, at a heating rate of 10°C/min.

Preparation of N-2-Anisylmaleimide

AMI was synthesized by condensation of maleic anhydride with 2-anisidine followed by cyclodehydration using AcA and NaAc [30–31] as shown in Scheme 1. 2-Anisidine (12.315 g, 0.1 mol) in chloroform was added dropwise to a well stirred chloroform solution of maleic anhydride (9.88 g, 0.1 mol) in a round bottom flask. The entire reaction mixture was cooled externally. The greenish yellow solids of N-2-anisylmaleimic acid (AMA) were filtered and then dried at 55 ± 5°C. AMA was purified by recrystallization from



SCHEME 1

chloroform. Yield 94%, mp 161–162°C, FT-IR (in cm^{-1}) at 3300–2500 (carboxylic acid O-H), 3330, 1542, 1504 (amide N-H), 1715 (carboxylic acid and amide), 1625 alkene (C=C), 860 (CH=CH), and 660 (C−H bending).

Cyclodehydration of the AMA to maleimide was carried out by reacting 22.1 g (0.1 mol) AMA, 16.4 g (0.2 mol) NaAc and 115 ml AcA in 200 ml DMF for 3 h at 55–60°C. The cooled reaction mixture was poured into crushed ice. Yellow needles of AMI were filtered, washed with 10% $NaHCO_3$ solution, and dried at 55 ± 5°C for several hours. AMI was further recrystallized from hot water. Yield 62%, mp 129°C. Elemental analysis ($C_{11}H_9NO_3$) calcd. (C 65.02; H 4.43; N 6.89%); found (C 65.01; H 4.36; N 6.85%), FT-IR (in cm^{-1}) 3150, 3040 (C-H, alkene and aromatic), 1778 and 1702 (C=O symmetric and asymmetric stretch in a five-member imide ring [32–33]), 1598, 1502, (C=C, aromatic), 1298 (C−N), 1255, 1020 (C−O−C), 958 (CH=CH), 760 (1,2-disubstituted benzene), and 698 (cis −CH=CH−). ^{1}H-NMR (200 MHz, TMS, DMSO-d_6, δ ppm, Figure 1) 7.154 (s, 2H, CH=CH); 7.023(td), 7.205(dd), 7.171(dd), and 7.436(td) Ar-H at b_3, b_4, b_5, and b_6 in phenyl ring, 3.717 [s, 3H ($-OCH_3$)].

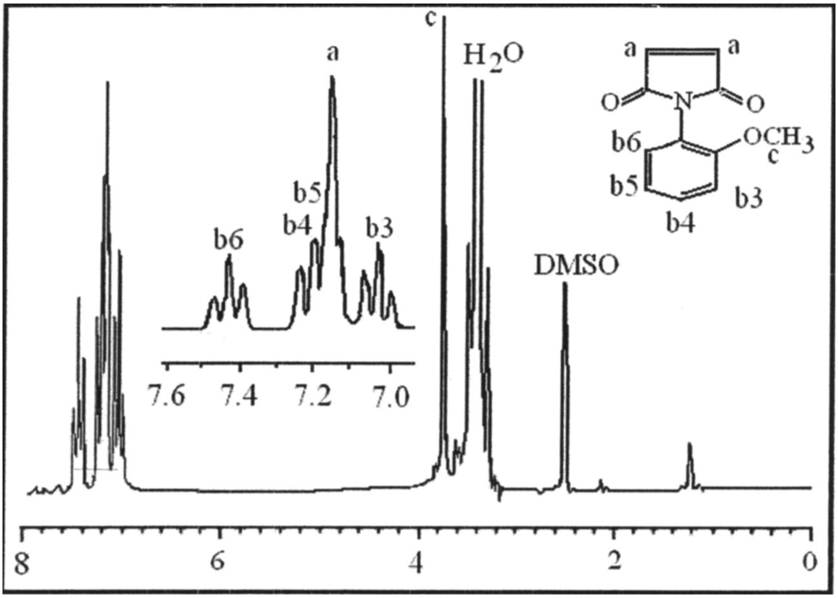


FIGURE 1 ^{1}H-NMR spectrum of N-2-Anisylmaleimide at 200 MHz in DMSO-d_6.

Polymerization Procedure

In a round bottom flask, fitted with a reflux condenser, calculated amounts of monomers MMA/EA/BA and AMI in 35 ml THF solvent were refluxed after adding 100 mg AIBN at 65°C for 12 h with occasional shaking. The copolymer samples were isolated in excess quantity of methanol containing 5% water. After dissolving the crude copolymer in THF, it was reprecipitated from an excess quantity of methanol–water mixture. The process was repeated three times to purify the copolymer samples. The precipitated copolymer was washed with methanol several times and dried at 60°C under vacuum.

The series of copolymer samples each of MMA with AMI (CMIMA1 to CMIMA9), of EA with AMI (CMIEA1 to CMIEA9), and of BA with AMI (CMIBA1 to CMIBA9) listed in Table 1 were synthesized by the same procedure and identical reaction conditions as described in the preceding paragraph.

Polyanisylmaleimide (PAMI) was synthesized by refluxing AMI (2.032 g, 0.01 mol) in 35 ml THF with 100 mg AIBN at 65°C for 24 h, with occasional shaking. The polymer PAMI was isolated by using an excess quantity of methanol–water. The crude PAMI was purified by dissolving in THF and reprecipitating from a methanol–water mixture. It was dried under vacuum at 60°C, obtaining PAMI in 58% yield. The yield depends on duration of reaction. MMA, EA, and BA were polymerized under identical condition to that employed for the polymerization of AMI, except reducing the reaction to only 6 h. The PMMA, PEA, and PBA were isolated in water containing small amount of methanol.

RESULTS AND DISCUSSION

The polymers of varying compositions were synthesized by the free radical copolymerization of MMA or EA or BA with AMI in a THF solution using AIBN as an initiator as shown in Scheme 2. Basic properties of different polymer samples are given in Table 1.

Intrinsic Viscosity

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 a given solution. The values of intrinsic viscosity were calculated in combination with Huggins [28] and Kraemer [29] equations. The values of $[\eta]$ obtained in DMF solution at 30°C are listed in VI column of Table 1. The value of $[\eta]$ depends on composition of copolymers and

TABLE 1 Radical Polymerization and Copolymerization in THF at 65°C

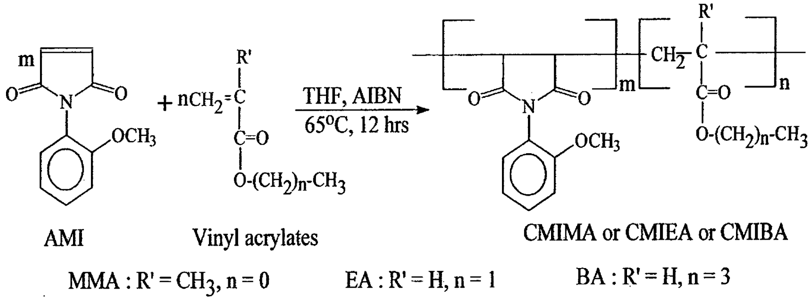
Polymer code	Feed mol fraction of AMI (X_1)	Poly time (h)	Yield (%)	Appearance*	[η] dl/g	%N	Copolym. from N%	Comp from NMR
PMMA	0.0	06	80	Wh-S	0.304	0.00	0.0	
CMIMAl	0.1	12	64	LY-S	0.238	1.96	0.165	0.143
CMIMA2	0.2	12	62	LY-S	0.230	3.12	0.292	
CMIMA3	0.3	12	56	LY-S	0.225	3.79	0.379	0.382
CMIMA4	0.4	12	54	LY-S	0.210	4.34	0.460	
CMIMA5	0.5	12	49	LY-S	0.198	4.67	0.513	0.502
CMIMA6	0.6	12	47	LY-S	0.193	4.91	0.555	
CMIMA7	0.7	12	34	LY-S	0.174	5.26	0.620	0.629
CMIMA8	0.8	12	27	LY-S	0.159	5.73	0.716	
CMIMA9	0.9	12	24	LY-S	0.136	6.18	0.820	0.761
PAMI	1.0	24	21	LY-S	0.151	6.86	1.0	
PEA	0.0	06	70	Cl-VL	0.321	0.00	0.0	
CMIEA1	0.1	12	67	LY-L	0.228	1.71	0.141	
CMIEA2	0.2	12	64	LY-L	0.208	2.88	0.263	
CMIEA3	0.3	12	59	LY-S	0.205	3.51	0.341	0.344
CMIEA4	0.4	12	54	LY-S	0.195	4.20	0.438	
CMIEA5	0.5	12	52	LY-S	0.186	4.80	0.536	0.530
CMIEA6	0.6	12	48	LY-S	0.178	5.16	0.601	
CMIEA7	0.7	12	45	LY-S	0.167	5.43	0.653	0.649
CMIEA8	0.8	12	36	LY-S	0.151	6.01	0.779	
CMIEA9	0.9	12	32	LY-S	0.129	6.40	0.875	
PBA	0.0	06	76	Cl-VL	0.316	0.00	0.0	
CMIBA1	0.1	12	71	LY-S	0.248	1.43	0.143	0.125
CMIBA2	0.2	12	65	LY-S	0.236	2.17	0.226	
CMIBA3	0.3	12	63	LY-S	0.220	3.07	0.339	0.305
CMIBA4	0.4	12	59	LY-S	0.202	3.63	0.416	
CMIBA5	0.5	12	53	LY-S	0.185	4.06	0.479	0.430
CMIBA6	0.6	12	50	LY-S	0.172	4.83	0.601	
CMIBA7	0.7	12	40	LY-S	0.161	5.24	0.672	0.650
CMIBA8	0.8	12	31	LY-S	0.151	5.79	0.775	
CMIBA9	0.9	12	25	LY-S	0.142	6.31	0.881	0.860

*LY-S, Wh-S, and Cl-VL stand for light yellow powder, white powder, and colorless viscous material.

decreases in all three series of copolymer samples CMIMA, CMIEA, and CMIBA, as the content of AMI in the copolymer is increased.

Solubility Behavior

Solubility of the various polymer samples were examined in a number of polar and nonpolar solvents (Table 2). The PAMI was completely



SCHEME 2

soluble in THF, dioxane, DMF, DMSO, DMAc, nitrobenzene, ethyl acetate, isobutyl acetate, chloroform, and acetone. A comparison of solubility of PAMI with PMMA, PEA, and PBA [26–27] indicated that the solubility pattern of PAMI in some of the solvents was quite different, especially in the case of CCl_4, benzene, toluene, and o-xylene. The

TABLE 2 Relative Solubility of Polymer Samples

	CMIMA			CMIEA			CMIBA			
Solvent	1	5	9	1	5	9	1	5	9	PAMI
Acetone	S	S	S	S	S	S	S	S	S	S
Dioxane	S	S	S	S	S	S	S	S	S	S
THF	S	S	S	S	S	S	S	S	S	S
DMF	S	S	S	S	S	S	S	S	S	S
DMAc	S	S	S	S	S	S	S	S	S	S
DMSO	S	S	S	S	S	S	S	S	S	S
Benzene	S	S	S	S	S	S	S	S	S	IS
Nitrobenzene	S	S	S	S	S	S	S	S	S	S
Ethyl acetate	S	S	S	S	S	S	S	S	S	S
Isobutyl acetate	S	S	S	S	S	S	S	S	S	S
Chloroform	S	S	S	S	S	S	S	S	S	S
CCl_4	S	IS	IS	S	IS	IS	S	IS	IS	IS
o-Xylene	PS	IS	IS	PS	IS	IS	PS	IS	IS	IS
Toluene	S	IS	IS	S	IS	IS	S	IS	IS	IS
Hexane	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS
Cyclohexane	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS
Methanol	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS
Ethanol	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS
Petroleum ether	IS	IS	IS	IS	IS	IS	IS	IS	IS	IS

S = Soluble, IS = Insoluble, PS = Partially soluble.

PAMI was insoluble in the later solvents whereas the PMMA, PEA, and PBA were soluble.

The relative solubilities of nine copolymer samples: CMIMA1, CMIMA5, CMIMA9, CMIEA1, CMIEA5, CMIEA9, CMIBA1, CMIBA5, and CMIBA9 out of twenty seven copolymer samples synthesized were determined at 30°C (Table 2). Of the nine investigated copolymers CMIMA, CMIEA, and CMIBA were soluble in THF, dioxane, DMF, DMSO, DMAc, ethyl acetate, isobutyl acetate, nitrobenzene, benzene, chloroform, and acetone. These copolymers were found to be partially soluble in CCl_4, toluene, and o-xylene. The solubility behaviour in CCl_4, toluene and o-xylene was interesting. PAMI was insoluble whereas its copolymers with MMA, EA, and BA were partially soluble. All the copolymer samples were found to be totally insoluble in hexane, cyclohexane, methanol, ethanol, and petroleum ether.

Spectral Characterization

The absence of a sharp band at 958 cm^{-1} (in FT-IR) and chemical shift δ at 7.154 ppm (in ^{1}H-NMR, 300 MHz in DMSO-d_6, Figure 2) in PAMI due to $-CH{=}CH-$ in AMI monomer, indicates the formation of polymer via vinyl group polymerization [34]. The δ observed at 7.154 ppm due to $-CH{=}CH-$ in monomer AMI (Figure 1) has shifted to 3.89–4.24 ppm in PAMI as a result of the formation of semi-flexible poly(substituted methine) $-[CH-CH]_n-$ group [35]. The presence of absorption bands at 1780 and 1715 cm^{-1} due to symmetric and asymmetric stretching of C=O in the five-member imide ring indicates that the imide ring remained intact in the polymerization. δ at 1.46–2.12 ppm are due to terminal methyl protons of AIBN moiety $[-(CN)-C-(CH_3)_2]$.

FT-IR spectra of copolymer samples CMIMA, CMIEA, and CMIBA in Figures 3(a–c) show major characteristic absorption bands at 1780, 1720 ± 5 (C=O symmetric and asymmetric stretch in a five-member imide ring and C=O stretch of ester), 1601, 1503 (C=C aromatic), and 756 (1,2-disubstituted benzene). These characteristic bands confirm that the monomer AMI copolymerized with MMA/EA/BA. The spectral pattern around frequencies 1780–1705, 1601–1503, and 665 cm^{-1} has undergone a change as the copolymer composition is varied. The carbonyl absorption of AMI at 1705 cm^{-1} merged with that of MMA/EA/BA at 1732 cm^{-1} to form single peak from 1732 to 1716 cm^{-1}. Its exact position depends on the relative contribution from AMI and vinyl acrylate. Further, with the increase of imide content in the copolymer the peak intensities at 1780 and 1601–1503 cm^{-1} have also gradually increased.

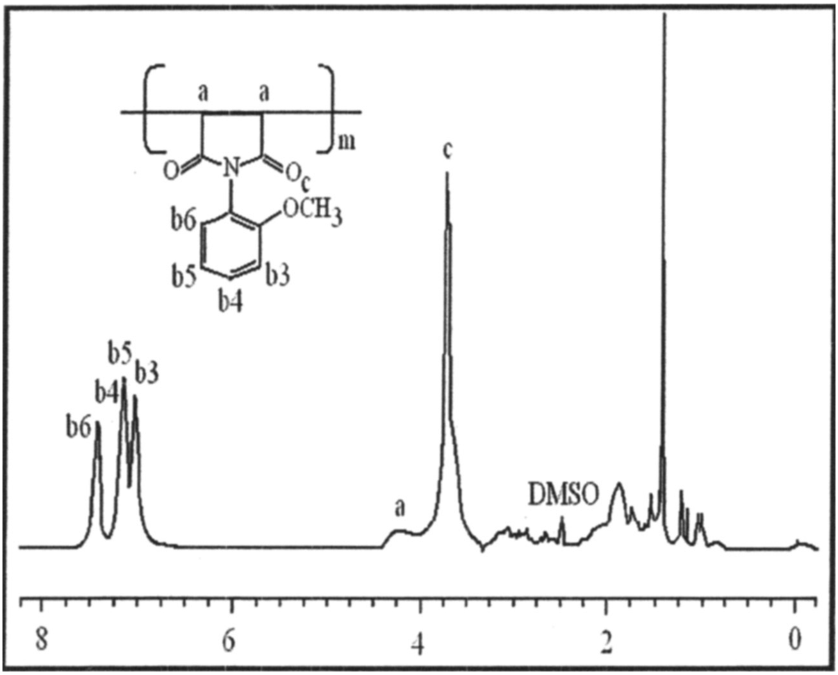
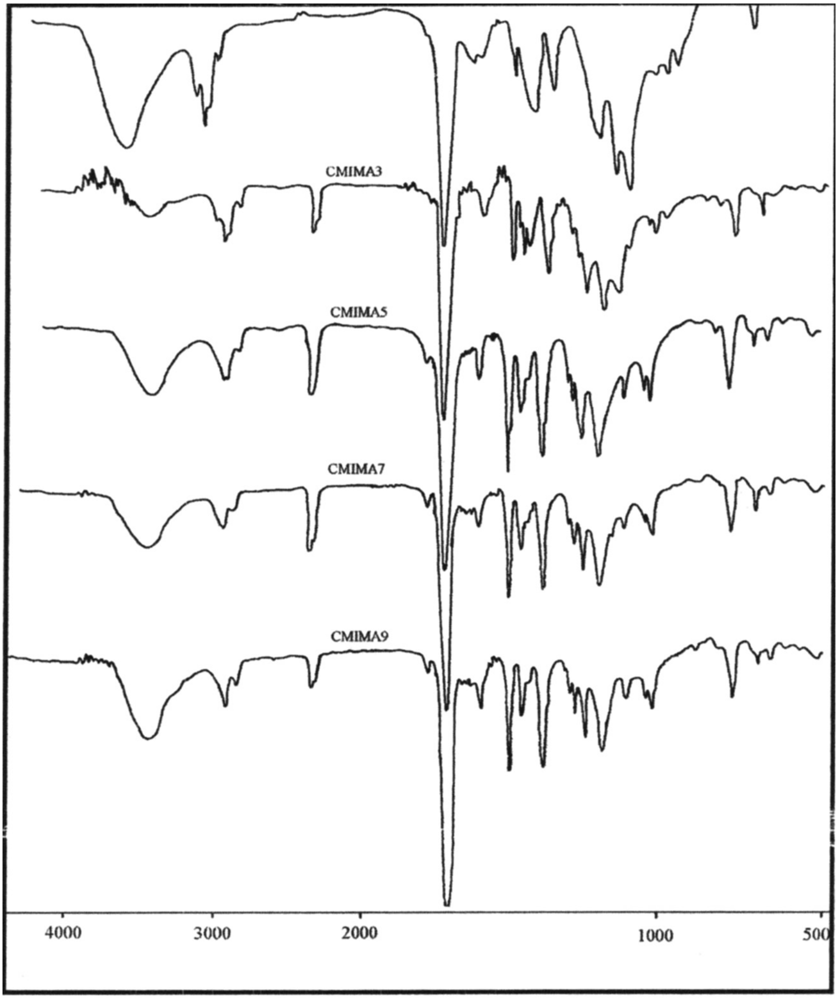


FIGURE 2 ^{1}H-NMR spectrum of PAMI at 300 MHz in DMSO-d_6.

The ^{1}H-NMR of CMIMA [200 MHz, TMS, DMSO-d_6, δ, ppm, Figure 4(a)] has the same absorption pattern with the variation in the peak intensities as a result of the variation in the contents of the copolymer. For the present copolymer CMIMA samples, δ for Ar-H, $-CH-CH-$ and $-OCH_3$ of imide unit is observed at 7.11–7.43, 3.85–4.35, and 3.71 ppm, respectively. Protons for $-OCH_3$, $-CH_2$, $-CH_3$ in MMA unit appear at 3.54, 1.87, 0.75–1.30 ppm, respectively. The peak intensity of imide protons is increased whereas that of MMA protons decreased in going from samples CMIMA1 to CMIMA9. For the present copolymer CMIEA samples [Figure 4(b)], δ for Ar-H, and $-OCH_3$ of imide unit is observed at 7.04–7.44 and 3.72 ppm, respectively. The EA protons for $-CH_2$ and $-CH_3$ appear at 1.42–1.86 and 0.84–1.29 ppm, respectively. The 2H of $-CH-CH-$ and 2H of $-OCH_2$ overlap at 3.95–4.36 ppm. For the copolymer CMIBA samples [Figure 4(c)], δ for Ar-H and $-OCH_3$ of imide unit is observed at 7.02–7.44 and 3.69–3.74 ppm, respectively. The protons in BA unit for one $-CH$, three $-CH_2$, and one $-CH_3$ appear at 1.95, 1.23–1.85, 0.84–1.06 ppm, respectively. The 2H of $-CH-CH-$ and 2H of $-OCH_2$ overlap and appear at 3.91–4.40 ppm.

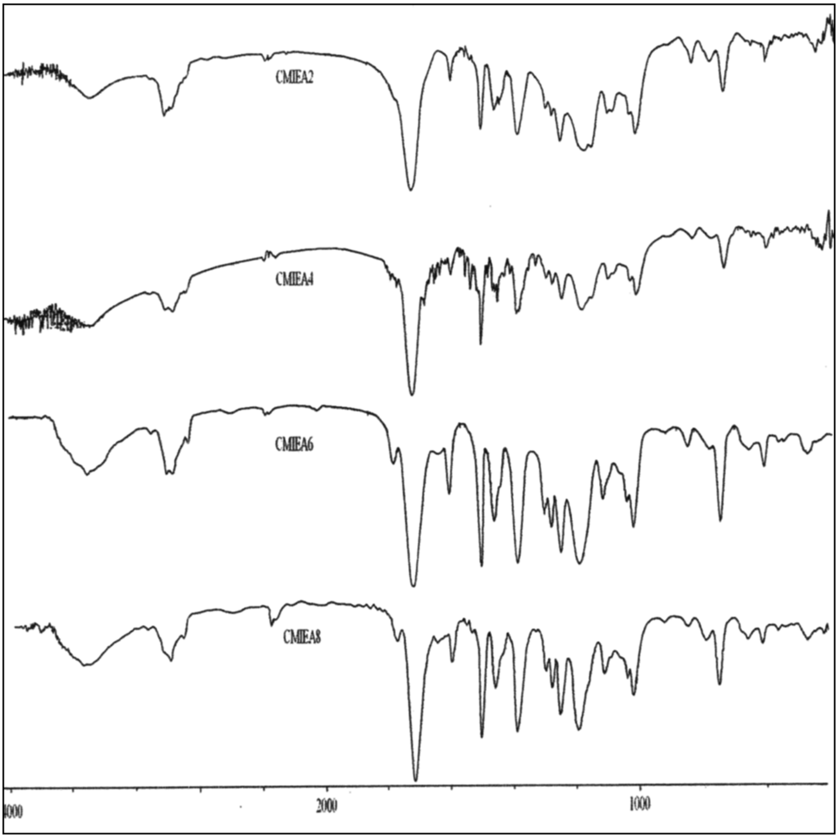


(a)

FIGURE 3 (a) FT-IR spectrum of copolymers of AMI and MMA; (b) FT-IR spectrum of copolymers of AMI and EA; (c) FT-IR spectrum of copolymers of AMI and BA.

Copolymer Composition

The copolymer compositions of CMIMA1-CMIMA9, CMIEA1-CMIEA9 and CMIBA1-CMIBA9 samples have been determined from the two techniques: (i) elemental analysis (N% analysis [34]) and (ii) ^{1}H-NMR spectral analysis [36]. The ratio of peak area of proton resonance



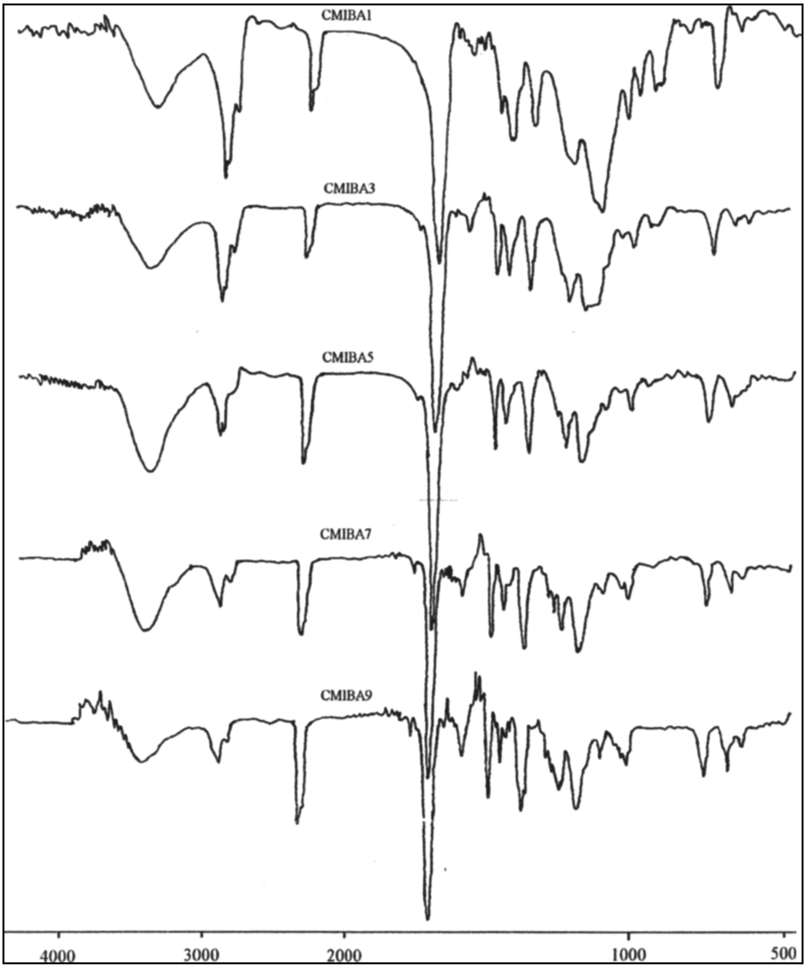
(b)

FIGURE 3 Continued.

signals due to methyl protons of MMA, EA and BA ($\delta = 0.75$–1.30 ppm) and the aromatic protons ($\delta = 7.02$–7.44 ppm) of AMI were used to estimate the copolymer composition by ^{1}H-NMR. As mole fraction of AMI in feed is increased the mole ratio of AMI in copolymer also increases (Table 1). This behavior indicates that the copolymers have random distribution of the monomer units in the polymer chain.

Monomer Reactivity Ratios

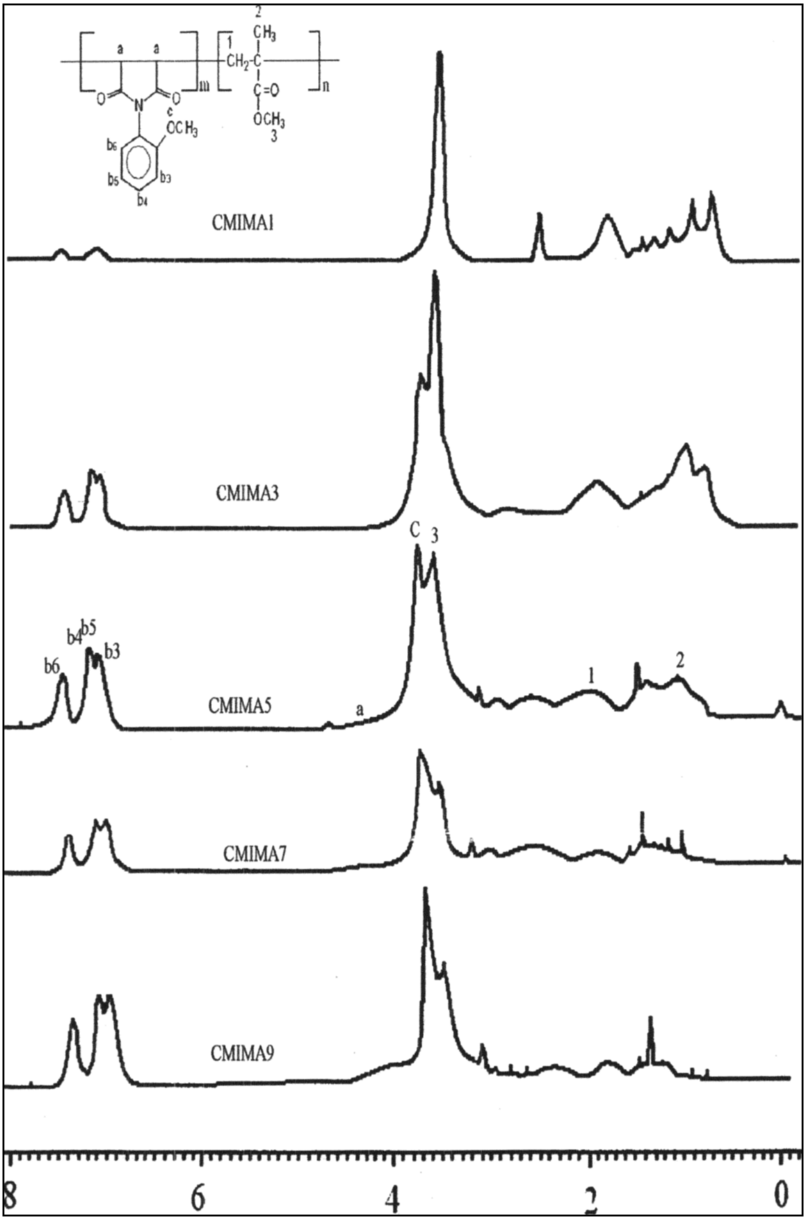
The monomer reactivity ratios were calculated from the knowledge of copolymer composition using Fineman–Ross [37] and Kelen–Tudos [38] methods. The values of r_1 (AMI) and r_2 (MMA/EA/BA) are given



(c)

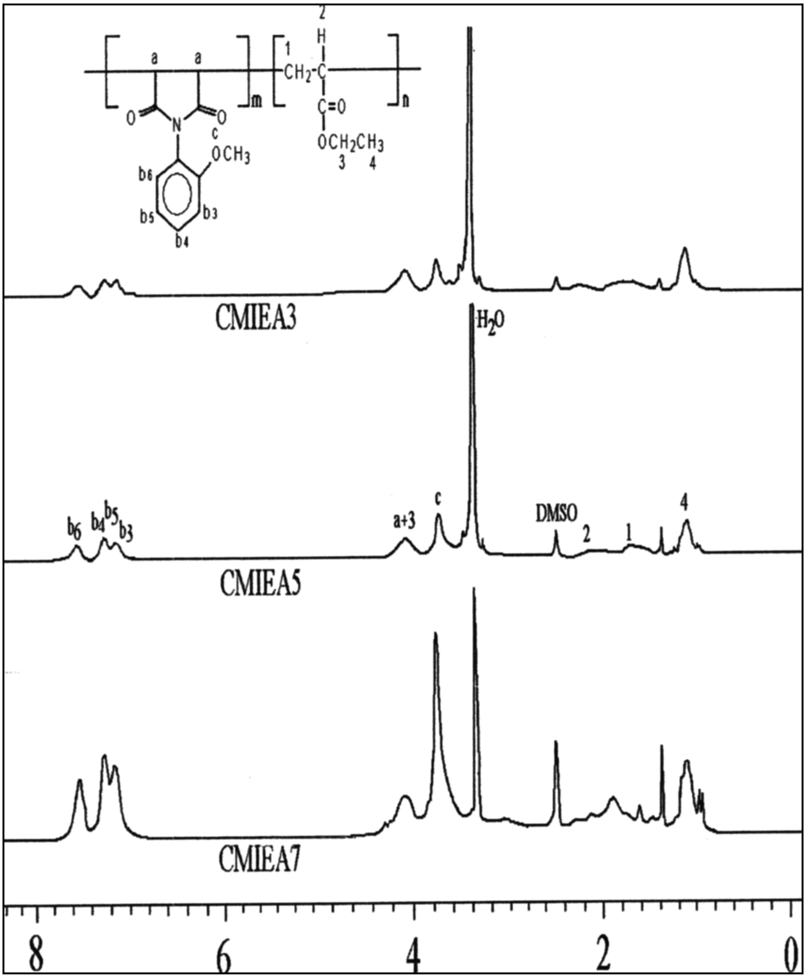
FIGURE 3 Continued.

in Table 3. The Q and e values for the AMI monomer, calculated by using the Alfrey and Price equation [39] are shown in Table 3. The average values of r_1 and r_2 are 0.43 and 0.42 in the AMI/MMA system, 0.72 and 0.62 in the AMI/EA system, and 0.76 and 0.72 in the AMI/BA system. Alfrey-Price Q-e values for APMI were calculated as $Q = 3.13$ and $e = 1.71$ in the AMI/MMA system, $Q = 1.10$ and $e = 1.46$ in the AMI/EA system, and $Q = 1.02$ and $e = 1.63$ in the AMI/BA system. The large e value correlates with strong electron



(a)

FIGURE 4 (a) ^{1}H-NMR spectrum of copolymers of AMI and MMA at 200 MHz in DMSO-d_6; (b) ^{1}H-NMR spectrum of copolymers of AMI and EA at 200 MHz in DMSO-d_6; (c) ^{1}H-NMR spectrum of copolymers of AMI and BA at 200 MHz in DMSO-d_6.



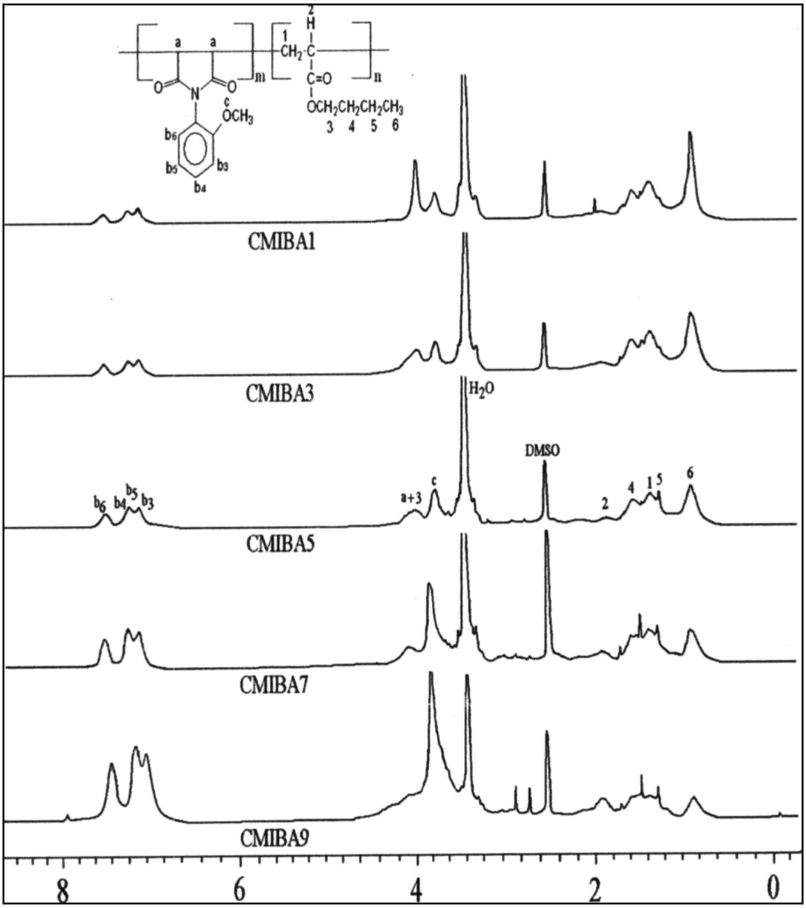
(b)

FIGURE 4 Continued.

acceptor nature of the maleimide monomer. The values of r_1 and r_2 for all three systems are less than unity and greater than zero, indicating that the copolymer involves predominantly random distribution of the monomer units in the polymer chain.

Thermal Studies

The thermograms (TG) were obtained by heating the polymer and copolymers samples in air at 10°C/min. Typical curves for few selected



(c)

FIGURE 4 Continued.

homo- and copolymer samples are presented in Figures 5–7. The TG of PAMI and CMIMA4 were also obtained by heating the polymer samples under nitrogen atmosphere at 10°C/min in order to see the effect of atmosphere in thermal degradation. The temperatures for initial decomposition T_i, final decomposition T_f, maximum rate of weight loss T_{max}, fifty percent decomposition T_{50}, and residue at 500°C determined from TGA for polymer samples are summarized in Table 4. The values of integral procedural decomposition temperatures (IPDT), an index of thermal stability as proposed by Doyle [40], were determined from a mass loss curve and are included in Table 4.

TABLE 3 Monomer Reactivity Ratios in Copolymers

System	Finman-Ross		Kelen-Tudos		Average		Q	e
	r_1	r_2	r_1	r_2	r_1	r_2		
AMI/MMA	0.43	0.42	0.43	0.42	0.43	0.42	3.13	1.71
AMI/EA	0.72	0.61	0.70	0.62	0.71	0.62	1.10	1.46
AMI/BA	0.78	0.75	0.74	0.69	0.76	0.72	1.02	1.63

The maleimide polymer PAMI is a potential heat-resistant material and has a significantly higher thermal stability than PMMA. Two-step degradation at temperature of over 306°C was observed for PAMI. The T_f was about 620°C. Thermal stability is slightly higher under N_2 atmosphere than that in air. The copolymer samples CMIMA2, CMIMA4, GMIMA5, and CMIMA7 also decomposed in a two-step procedure. As the content of AMI in the feed has increased, the copolymers began to decompose at higher T_i and the weight loss for

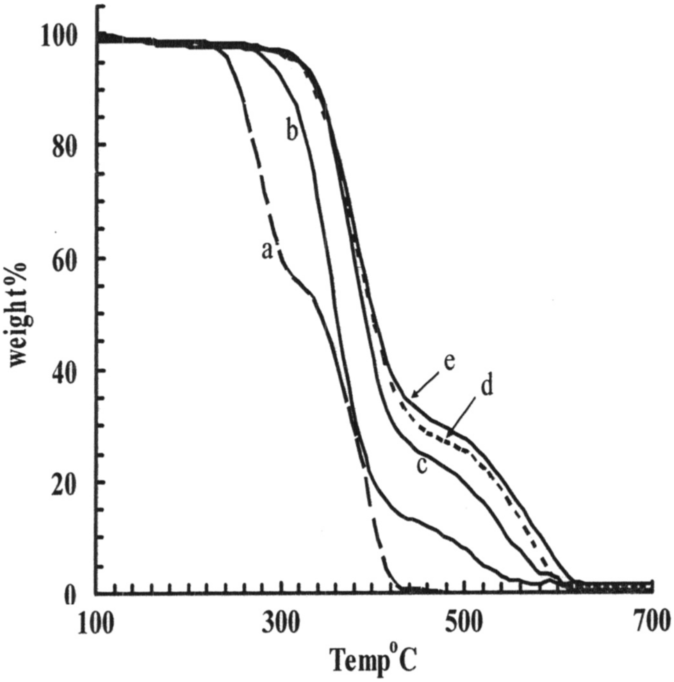


FIGURE 5 Thermograms of (a) PMMA, (b) CMIMA2, (c) CMIMA4, (d) CMIMA5, (e) CMIMA7, and (f) PAMI in air at heating rate of 10°C.

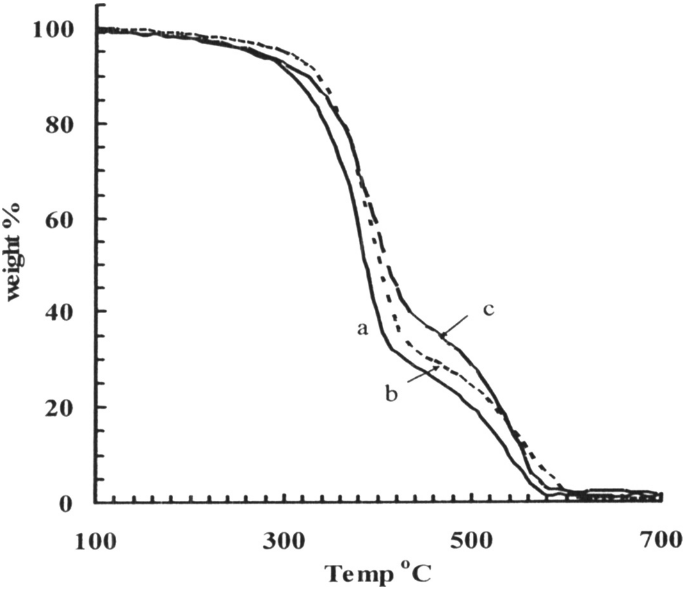


FIGURE 6 Thermograms of (a) CMIEA3, (b) CMIEA5, (c) CMIEA7 in air at heating rate of 10°C.

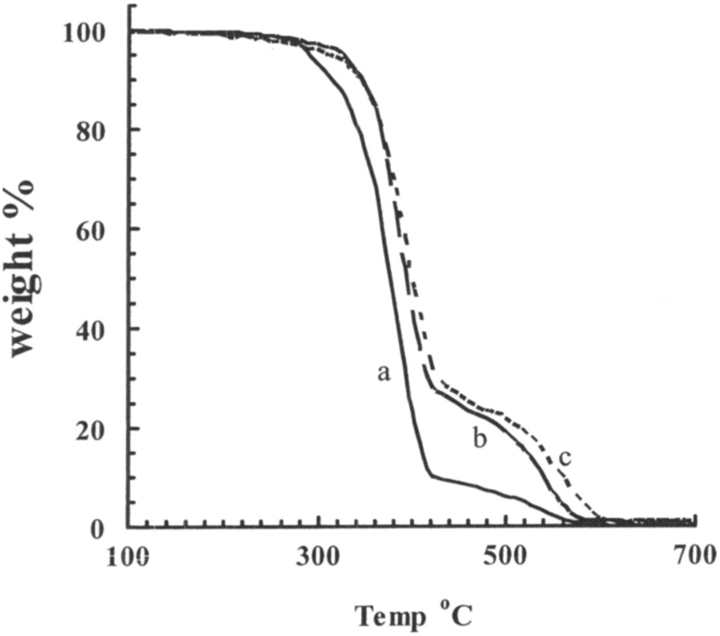


FIGURE 7 Thermograms of (a) CMIBA2, (b) CMIBA5, (c) CMIBA6 in air at heating rate of 10°C.

TABLE 4 Thermal Behavior of Polymer Samples in Air and Nitrogen Atmosphere

Polymer	Step	T_i (°C)	T_{max} (°C)	T_f (°C)	T_{50} (°C)	IPDT (°C)	%Residue at 500°C	Ea (kcal mol^{-1})
PAMI[a]	I	306	400	468	399	416	26.7	29.6
	II	473	582	620	—	—	—	38.2
PAMI[b]	I	310	401	477	401	416	21.7	29.9
	II	534	664	700	—	—	—	34.6
PMMA[b]	I	236	282	318	337	327	0.0	27.5
	II	318	401	439	—	—	—	35.3
CMIMA2[a]	I	289	357	453	360	356	7.1	21.4
	II	458	516	572	—	—	—	42.7
CMIMA4[a]	I	325	369	458	386	393	18.3	27.1
	II	487	547	582	—	—	—	36.2
CMIMA4[b]	I	330	383	460	390	394	19.6	27.1
	II	487	547	582	—	—	—	36.3
CMIMA5[a]	I	330	383	460	390	394	19.6	29.2
	II	490	545	590	—	—	—	47.8
CMIMA7[a]	I	335	382	468	398	399	24.3	25.3
	II	506	576	616	—	—	—	57.3
CMIEA3[a]	I	285	386	458	388	365	19.0	29.9
	II	477	532	575	—	—	—	43.6
CMIEA5[a]	I	297	398	464	403	375	23.3	32.3
	II	487	566	610	—	—	—	40.1
CMIEA7[a]	I	290	402	474	411	379	27.2	31.0
	II	481	553	588	—	—	—	51.4
CMIBA2[a]	I	287	383	449	376	377	5.9	30.4
	II	449	525	585	—	—	—	35.2
CMIBA5[a]	I	306	392	458	394	392	17.8	39.7
	II	458	541	601	—	—	—	45.9
CMIBA6[a]	I	316	395	468	399	395	20.9	36.8
	II	468	566	623	—	—	—	44.6

[a] Air.
[b] Nitrogen atmosphere.

the first-step became smaller. The first step weight loss ranged from 87.8 to 72.3%. The weight loss for the second-step increased from 10.6 to 26.8% as the content of AMI in copolymer is enhanced. An increase in residual char yield (%) at 500°C was also observed by increasing the AMI content in the copolymer samples. It is also observed that there is no significant change in thermal behavior of copolymer sample CMIMA4, whether it is degraded in air or under N_2 atmosphere. Similar thermal behavior was observed for thermal degradation of copolymers of EA and BA with AMI. The results in Table 4 clearly indicate that the thermal stability of vinyl polymers is greatly enhanced by copolymerizing them with AMI and it tends to increase as the AMI content is increased in the copolymers.

The activation energy E_a of thermal degradation, given in Table 4, was estimated by employing the Broido method [41]. The value of E_a, 29.6 kcal mol^{-1}, for the first step degradation of PAMI is higher than 27.5 kcal mol^{-1} for PMMA. The values of E_a for the first step degradation for CMIMA2-CMIMA7 varied from 21.4 to 29.2 kcal mol^{-1} while for the second step they were in the range of 36.3–57.3 kcal mol^{-1}. In case of CMIEA the values of E_a for the first step degradation vary from 29.9 to 32.3 kcal mol^{-1} and for the second step they are in the range of 40.1–51.4 kcal mol^{-1}. The E_a for the first step degradation in CMIEA are much higher than that observed for PMMA. This means that even small mole fraction of maleimide units in a copolymer stabilizes the copolymer to very great extent. In case of CMIBA the value of E_a for the first step degradation varies from 30.4–39.7 kcal/mol and for the second step it is in the range of 35.2–45.9 kcal mol^{-1}. On comparison of thermal stability of different copolymers with the same mole ratio, the following sequence is observed: CMIMA $>$ CMIBA $>$ CMIEA.

CONCLUSIONS

The investigated copoly(vinyl-maleimide)s show excellent solubility in acetone, dioxane, THF, DMF, DMAc, DMSO, nitrobenzene, ethyl acetate, and isobutyl acetate. The average values of r_1 and r_2 are 0.43 and 0.42 in the AMI/MMA system, 0.72 and 0.62 in the AMI/EA system, and 0.76 and 0.72 in the AMI/BA system. Alfrey-Price Q-e values for APMI were calculated as $Q = 3.13$ and $e = 1.71$ in the AMI/MMA system, $Q = 1.10$ and $e = 1.46$ in the AMI/EA system, and $Q = 1.02$ and $e = 1.63$ in the AMI/BA system. The thermal stability of vinyl polymer is greatly enhanced by copolymerizing them with AMI and it tends to increase as the AMI content is increased in the copolymer samples.

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