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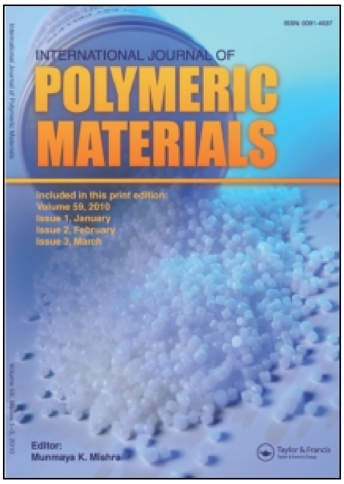

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The free radical copolymerization of methyl methacrylate (MMA) or styrene (St) with N-(4-carboxyphenyl)maleimide (CPMI) was carried with AIBN as an initiator in THF solvent at 80°C. A series of copolymers of MMA and St with CPMI were prepared using different feed ratios of comonomers. The values of monomer reactivity ratios (r_1, r_2) determined by Fineman-Ross and Kelen-Tudos methods are 0.26 and 2.51 in the CPMI/MMA system and 0.08 and 0.22 in the CPMI/St system. Alfrey–Price Q-e values for CPMI were calculated as $Q = 1.05$ and $e = 0.41$ in the CPMI/MMA system and $Q = 1.21$ and $e = 0.91$ in the CPMI/St system. The polymer samples have been characterized by solubility tests, intrinsic viscosity measurements, FT-IR and ^{1}H-NMR spectral analysis, and thermo-gravimetric analysis. It was found that the initial and final decomposition temperatures increased with increasing the amount of CPMI in the copolymer. The integral procedural decomposition temperature and energy of activation of thermal degradation have also been reported.

Keywords: maleimide copolymers, N-(4-carboxyphenyl)maleimide, reactivity ratios, thermogravimetric analysis

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INTRODUCTION

Polymers are widely used in many technological applications. The high demand for new materials requires the preparation of new polymers with enhanced properties and the copolymerization technique has been widely used to achieve this target. Copolymerization greatly increases the ability of polymer scientists to tailor-make polymer products with specifically designed properties by variations in the nature and relative amounts of the monomer units in the copolymer product. Thermal and relaxation behaviors of polymers are important parameters required to fully understand the behavior of polymers under various conditions. We have several classical vinyl polymers but they cannot be used at higher temperatures. Their properties can be improved by preparing copolymers of different compositions. Therefore, a reliable knowledge of copolymerization process and parameters is both theoretically and practically of great importance. The copolymerization with N-substituted maleimide to elevate the glass transition temperature T_g has been widely used to improve the heat distortion temperature (HDT) [1–4].

During the past several years many publications appeared describing the chemical modification of various vinyl polymers such as polymers of styrene, alkyl acrylates or methacrylates, vinyl acetate, vinyl chloride, acrylonitrile, and cyclohexene [5–15] through free radical copolymerization with N-substituted maleimides. Moreover, the maleimides-based copolymers have been found to have versatile applications in industries ranging from aerospace to the medical and microelectronics fields [16–17]. Other applications of N-substituted maleimide (MI) polymers include photo-resist with high T_g [18–19], flexibilizer for thermosetting polymers [20–21], nonlinear polymer with high T_g and flame retardant [22], and so on.

In previous articles [23–24], the authors have reported the polymerization of N-[4-N′-(phenylamino-carbonyl)phenyl]maleimide and its copolymerization with methyl methacrylate (MMA), ethyl acrylate and butyl acrylate, initiated by AIBN in THF. This article investigates the copolymerization of MMA and styrene (St) with p-maleimidobenzoic acid, that is, N-(4-carboxyphenyl)maleimide (CPMI). Functional maleimides have been studied as versatile vinyl monomers with merits of facilitating functional polymer synthesis with various functionalities [22].

The polymaleimides with pedant carboxylic acid groups, that is, multifunctional monomer, are very much desired in several applications wherein the special features of the carboxylic acid functions can be taken advantage of. Such prepolymers can be conveniently converted to other desired functional polymers through appropriate modification of the carboxylic acid group by esterification, amidification, and so on. The carboxyl groups were envisaged as being transformed to the required photosensitive groups by suitable chemical modification. Such polymers are used as electrochemically active and photoconductive materials [8,25] through copolymerization with acrylate monomers. The copolymer of CPMI with acrylamide is used as a potential flocculant [26]. The physical, spectral, and thermal properties have been studied in order to characterize the polymer samples. The effect of different feed ratios of monomers on the properties of copolymers has been examined. The reactivity ratios have been calculated by Fineman–Ross [27] and Kelen–Tudos [28] methods.

EXPERIMENTAL

Materials

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Maleic anhydride (SRL, extra pure) was first recrystallized from chloroform and then was further purified by sublimation at 54 ± 2°C. p-Aminobenzoic acid (SRL, pure) was used as received. MMA (BDH, AR) and styrene (Hindustan Inks and Resin Limited, AR) were shaken two to three times with 5% NaOH to eliminate hydroquinone inhibitor, dried over anhydrous $CaCl_2$ for 6 h and then distilled under reduced pressure. The head and tail fractions were discarded. AIBN (2,2′-azobis-isobutironitrile, Wilson Lab.) was recrystallized twice from methanol prior to use. THF was purified by distillation after being refluxed for 2 h in the presence of sodium. Anhydrous sodium acetate, acetic anhydride, DMF, acetone, methanol, and so on were of Analytical Grade and were used as received.

Measurements

The ^{1}H-NMR spectra were recorded at 60 or 300 MHz in DMSO-d_6 solvent on a Perkin Elmer Model-32 Spectrometer with a sweep time of 10 min at room temperature. The internal reference used was TMS. FT-IR spectra of the 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°C, using an Ubbelohde viscometer. The intrinsic viscosities were calculated by means of Huggins' equation [29] and Kraemer equation [30]. The densities of polymer samples were determined at 30°C by the displacement method using a single stem pycnometer and water as a non-solvent. Elemental analysis was made on a Carlo Erba Elemental Analyzer, Model 1106. The thermograms in air were obtained on a Mettler

TA-3000 system, Switzerland, at a heating rate of 10°C/min in the temperature range from ambient temperature to 800°C.

Preparation of N-(4-Carboxyphenyl)maleimide

CPMI monomer was synthesized by the condensation reaction of maleic anhydride and p-aminobenzoic acid followed by cyclodehydration using acetic anhydride and sodium acetate according to the modified method of Searle [31] and Hoyt and Benicewicz [32] as shown in Scheme 1.

To a well-stirred solution of p-aminobenzoic acid (13.71 g, 0.1 mol) in DMF, a solution of maleic anhydride (9.81 g, 0.1 mol) in acetone was slowly added using a dropping funnel. The reaction mixture was continuously stirred at room temperature over a period of 30 min; it turned highly viscous and yellow in color. The resulting solution was poured into crushed ice to precipitate an intermediate crude N-(4-carboxyphenyl)maleiamic acid (CPMA). The yellow precipitate was purified by recrystallization from 50% DMF/50% ethanol. Yield 92%, mp 215–217°C (lit. mp 215–219°C [26], 214–217°C [33]), FT-IR (in cm^{-1}) 3500–2500 (carboxylic acid O–H), 3321, 1537, 1504 (amide N–H), 1693 (carboxylic acid and amide), 1626 (C=C alkene), 1294 (carboxylic acid C–O), 848 (CH=CH), 675 (C–H bending).

Cyclodehydration of the CPMA was carried out by treating it with fused sodium acetate (2.0 g) and acetic anhydride (50 ml) in DMF for 2 hr at 55°C. A light yellow mass of CPMI, obtained by adding the solution to crushed-ice, was washed several times with water and then dried in an air oven at 60–70°C. The crude product was purified by

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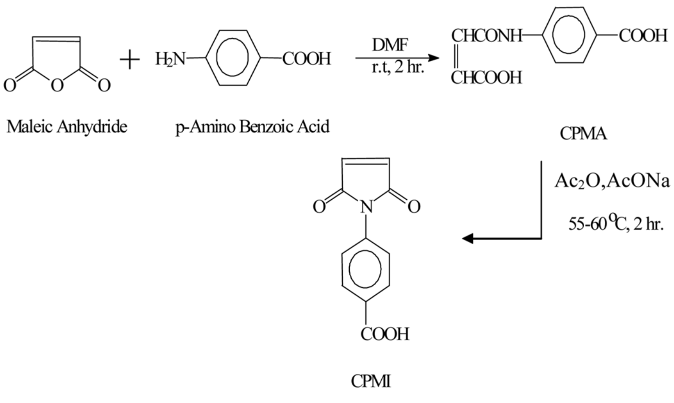

SCHEME 1 Synthesis of N-(4-carboxyphenyl)maleimide with methyl methacrylate and styrene.

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recrystallization from ethyl acetate/hexane. Yield 85%, mp 225–228°C (lit. mp 225–228°C [34] and 231°C [35]). Elemental Anal. calc. (C 60.83; H 3.23; N 6.45%); found (C 60.72; H 3.14; N 6.43%). FT-IR (in cm^{-1}) 3300–2300 (carboxylic acid O−H), 1774, 1715 (C=O symmetric and asymmetric stretch in a five-member imide ring [32,34,36], 1674 (aromatic acid stretching vibration of C=O group), 1641 (C=C, alkene), 1609 and 1511 (aromatic C=C), 1301 (C−N stretching [37], 1217 (carboxylic acid C−O), 950 (C−H bending, −CH=CH−), 704 (cis−CH=CH). ^{1}H-NMR (TMS, DMSO-d_6, δ, ppm): 7.04 (s, 2H, CH=CH); 8.00–8.13 (d, 2Ar-H, ortho- to −COOH); 7.37–7.50 (d, 2Ar-H, meta- to −COOH); 13.12 (broad s, 1H, −COOH). The present ^{1}H-NMR of CPMI is in agreement with the one reported by Oishi and Fujimoto [36] and Rao [38].

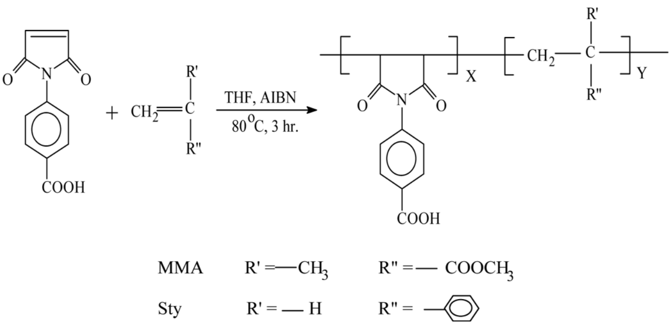
Polymerization Procedure

In a round bottom flask, fitted with a reflux condenser, calculated amounts of comonomers MMA/St and CPMI in 35 ml THF were refluxed, after adding 100 mg AIBN, at 80°C for 3 to 4 h, with occasional shaking (Table 1). The copolymers samples were isolated by using an excess quantity of methanol containing 5% water. The

TABLE 1 Poly- and Copolymerization of CPMI, MMA, and St in THF at 80°C

Polymer code	Feed (X_1)	Poly N Time (h)	Yield (%)	Density (g/ml)	[η] (dl/g)	%N	Copolymer (F_1)
PMMA	0.0	4	46	1.182	0.331	—	
CPMIMA1	0.1	4	33	1.180	0.268	0.59	0.044
CPMIMA2	0.2	4	35	1.178	0.258	1.06	0.083
CPMIMA3	0.3	4	34	1.176	0.252	1.75	0.146
CPMIMA4	0.4	4	31	1.173	0.236	2.52	0.228
CPMIMA5	0.5	4	30	1.172	0.231	2.67	0.246
CPMIMA6	0.6	4	28	1.168	0.220	3.33	0.330
CPMIMA7	0.7	4	24	1.165	0.209	3.91	0.415
CPMIMA8	0.8	4	20	1.159	0.198	4.72	0.557
CPMIMA9	0.9	4	15	1.152	0.182	5.55	0.740
PSt	0.0	4	58	1.045	0.456	—	0.000
CPMISt2	0.2	4	20	1.072	0.317	3.36	0.334
CPMISt3	0.3	4	34	1.077	0.284	3.90	0.413
CPMISt4	0.4	4	44	1.081	0.278	4.08	0.442
CPMISt5	0.5	4	52	1.083	0.265	4.20	0.463
CPMISt6	0.6	4	41	1.087	0.253	4.42	0.501
CPMISt7	0.7	4	25	1.089	0.246	4.54	0.523
CPMISt8	0.8	4	12	1.092	0.222	4.70	0.553
PCPMI	1.0	16	7	1.141	0.138	6.45	1.000

X_1 mole fraction of CPMI in Feed; F_1 mole fraction of CPMI in copolymer.



SCHEME 2 Copolymerization of N-(4-carboxyphenyl)maleimide with methyl methacrylate and styrene.

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crude copolymer was purified by dissolving in THF and reprecipitating from a methanol–water mixture. The process was repeated three times to purify the copolymer samples. The precipitated copolymers were washed with methanol several times and dried at 60°C under vacuum.

Two series of copolymer samples, one of MMA with CPMI (CPMIMA1 to CPMIMA9) and another of styrene with CPMI (CPMISt2 to CPMISt8) listed in Table 1 were prepared by the same procedure and identical reaction conditions as described in the preceding paragraph. The overall polymerization procedure is shown in Scheme 2.

Polymaleimide PCPMI was synthesized by refluxing CPMI (2.92 g, 0.01 mol) in 35 ml THF with 100 mg AIBN at 80°C for 16 h, with occasional shaking. The polymer PCPMI was isolated by using an excess quantity of methanol–water. The crude PCPMI was purified by dissolving in THF and reprecipitating from a methanol–water mixture. It was dried under vacuum at 60°C, obtaining PCPMI in 7% yield.

RESULTS AND DISCUSSION

The copolymers of MMA and St with CPMI were synthesized by radical polymerization 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.

Density of copolymer samples decreases with increase in CPMI content in copolymer. This is due to bulkiness of the maleimide molecule. However, the variation is much larger in case of copolymer involving MMA than St. Intrinsic viscosity $[\eta]$ is a measure of hydrodynamic volume and depends on molecular weight as well as on the size of

TABLE 2 Relative Solubility of the Polymer Samples at 30°C

Polymer code	PCPMI	CPMIMA1	CPMIMA5	CPMIMA9	CPMISt5
Acetone	S	S	S	S	S
Dioxane	S	S	S	S	S
THF	S	S	S	S	S
DMF	S	S	S	S	S
DMSO	S	S	S	S	S
Cyclohexanone	S	S	S	S	S
Aniline	S	S	S	S	S
Aq. NAOH	S	S	S	S	S
Ethyl acetate	PS	S	S	S	PS
Isobutyl acetate	PS	S	S	S	PS
Benzene	IS	PS	PS	PS	PS
Toluene	IS	PS	IS	IS	PS
Chloroform	IS	PS	IS	IS	IS
Methanol	IS	IS	IS	IS	IS
Petroleum ether	IS	IS	IS	IS	IS

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the polymer coil in a given solution. The values of average $[\eta]$ in DMF solution at 30°C (Table 1) decrease from 0.268 dl/g to 0.182 dl/g for CPMIMA and from 0.317 dl/g to 0.222 dl/g for CPMISt as the content of CPMI in the copolymer is increased.

Solubilities of the various polymer samples PCPMI, CPMIMA1, CPMIMA5, CPMIMA9, and CPMISt5 were examined in a number of polar and non-polar solvents at 30°C (Table 2). Like PMMA [23] and PSt [39], the PCPMI is completely soluble in acetone, dioxane, THF, DMF, DMSO, cyclohexanone, aniline, and aq. NaOH. Although PMMA is soluble in ethyl acetate and isobutyl acetate, benzene, toluene, and chloroform, the PCPMI is only partially soluble in ethyl acetate and isobutyl acetate and insoluble in benzene, toluene, and chloroform. The copolymer samples CPMIMA1, CPMIMA5, CPMIMA9, and CPMISt5 are soluble in acetone, dioxane, THF, DMF, DMSO, cyclohexanone, aniline, and aq. NaOH. The solubility behavior in ethyl acetate, isobutyl acetate, benzene, and toluene depends on the composition of the copolymers, that is, on the content of CPMI.

Spectral Characterization

PCPMI: FT-IR 3200–2500 (−COOH), 1778 and 1716 (C=O in imide ring), 1437 (Ar−N stretch), 1385 (C−N stretch), 1194 (C−N−C). The presence of IR absorption bands at 1778 and 1716 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. ^{1}H-NMR (300 MHz in DMSO-d_6, δ ppm) 4.1–4.3 (2H, $-$[CH$-$CH]$-$), 7.9–8.1 (2Ar$-$H, ortho- to $-$COOH); 7.3–7.7 (2Ar$-$H, meta- to $-$COOH); 13.2 (s, 1H, $-$COOH). The δ observed at 7.04 ppm due to $-$CH=CH$-$ in the monomer has shifted to 4.1–4.3 ppm in the polymer, as a result of the formation of a semi flexible poly(substituted methine) $-[CH-CH]_n-$ group [40]. Due to the terminal methyl protons of the AIBN moiety $-(CN)-C-(CH_3)_2$ a peak is observed at δ 1.4–2.0 ppm. The absence of a strong band at 1641 and 950/704 cm^{-1} and chemical shift δ at 7.04 ppm due to $-$CH=CH$-$ in a monomer having a vinyl group, indicate the formation of polymer via vinyl group polymerisation [41].

CPMIMA: The major characteristic absorption bands at 3200–2500 ($-$COOH stretching), 3060 (aromatic C$-$H stretch), 1775, 1732–1715(s) (C=O symmetric and asymmetric stretch in a five-member imide ring and due to overlapping of C=O stretch of imide, ester and carboxylic acid groups), 1609, 1512 (aromatic C=C stretch) in cm^{-1} confirm that CPMI monomer copolymerized with MMA. The spectral pattern around the frequencies of 1774, 1715, and 1609–1511 has undergone a change as the copolymer composition was varied. The carbonyl absorption of CPMI at 1715 cm^{-1} merged with that of MMA at 1732 cm^{-1} to form a single peak from 1732 to 1715 cm^{-1}. Its exact position depends on the relative contribution from CPMI and MMA. Further, with the increase of imide content in the copolymer the peak intensities at 1775 and 1612–1514 cm^{-1} have also gradually increased. The ^{1}H-NMR for CPMIMA5 is shown in Figure 1. The δ at 8.0–8.1 ppm is of 2Ar$-$H, ortho- to $-$COOH group while at 7.3–7.4 ppm for 2Ar$-$H, meta- to $-$COOH. A δ at 13.2 (broad) ppm appeared for 1H in $-$COOH group of CPMI segment. The δ observed at δ 3.5–3.8 ppm corresponds to 3H ($-OCH_3$) of MMA segment. The δ in the range 0.7–1.4 ppm is of 3H of $-CH_3$ group whereas at 1.6–2.2 ppm for 2H of methylene group. The small hump at 3.9 ppm corresponds to 2 imide protons.

CPMISt: The major characteristic absorption bands at 3200–2500 ($-$COOH stretching), 1775, 1713–1715 (C=O symmetric and asymmetric stretch in a five-member imide ring and due to overlapping of C=O stretch of imide, ester and carboxylic acid groups), 1608, 1511 (aromatic C=C stretch), 1383 and 1180 (imide), 1272 (the carboxylic C$-$O), 771 and 706 (out of plane C$-$H bending monosubstituted benzene) confirm that units of both the monomers CPMI and St are present in the copolymer samples. The spectral patterns around frequencies 1774, 1715, and 1609–1511 show only small changes as the feed composition is varied. This indicates that the composition of the

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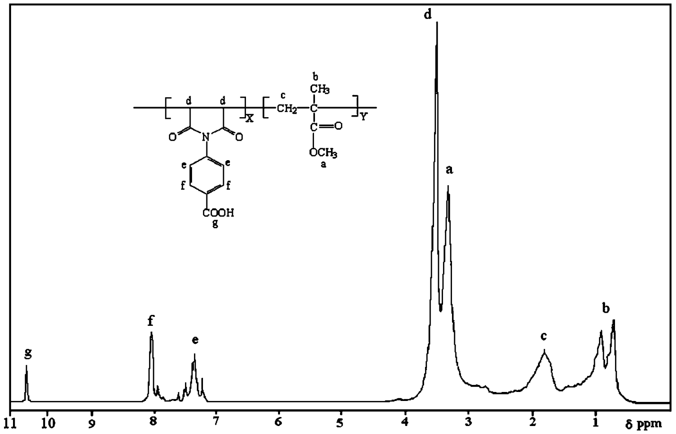

FIGURE 1 ^{1}H-NMR spectrum of copolymer CPMIMA5.

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polymer is not much different with change in feed composition under study; indicating a nearly alternating copolymerization behavior between St and CPMI. The ^{1}H-NMR for CPMISt5 is shown in Figure 2. δ at 7.0–8.1 ppm is of 9Ar–H, δ at 13.2 (broad) ppm appeared for H in –COOH group of CPMI segment. The δ observed at δ 2.9–3.6 ppm corresponds to 1H (–CH) and at 2.1–2.2 ppm for 2H of methylene group of St segment. Two imide protons seem to appear as a small hump in the vicinity of 3.8 ppm.

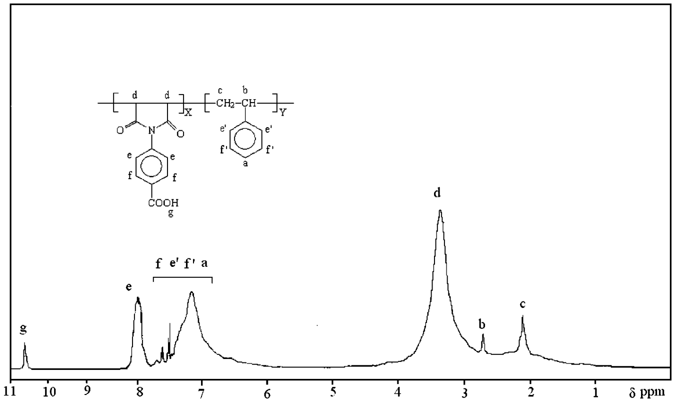

FIGURE 2 ^{1}H-NMR spectrum of copolymer CPMISt5.

Monomer Reactivity Ratios

The compositions of copolymer samples were determined from the N% analysis [10,34,38] which is shown in Figure 3. Two well defined types of copolymerization behavior have been found in the present work. In case of CPMIMA, the composition of CPMI in the chain of copolymer, gradually increased with increased CPMI feed content, such behavior was also observed in copolymerization of MMA with N-phenylmaleimide [5], N-cyclohexylmaleimide [15] and 4-[4-(N′-substituted aminocarbonyl)phenyl]maleimide [7,23]. In case of CPMISt, the curve in Figure 3 is typical curve for copolymerization of the CPMI/St system with a tendency toward alternation [5,22,34].

The monomer reactivity ratios were calculated using Fineman–Ross [27] and Kelen–Tudos [28] methods. The values of r_1 (CPMI) and r_2 (MMA) are given in Table 3. The Q and e values for the CPMI monomer, calculated by using the Alfrey and Price equation [42] are shown in Table 3. The average values of r_1 and r_2 are 0.26 and 2.51 in the CPMI/MMA system and 0.08 and 0.22 in the CPMI/St system. Alfrey–Price [42] Q-e values for CPMI were calculated as $Q = 1.05$ and $e = 0.41$ in the CPMI/MMA system and $Q = 1.21$ and $e = 0.91$ in the CPMI/St system.

In the copolymerization between CPMI and St, the value r_1 (CPMI) is only 0.08 and r_1r_2 is 0.018. These results corroborated the nearly

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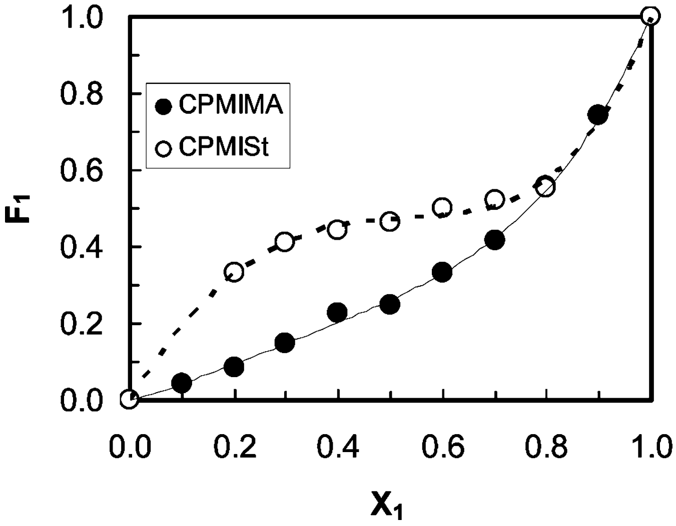

FIGURE 3 Variation of copolymer composition as a function of feed composition.

TABLE 3 Reactivity Ratios and Parameters of the Alfrey–Price Equation

	CPMI-co-MMA		CPMI-co-St	
Method	r_1 (M_1)	r_2 (M_2)	r_1 (M_1)	r_2 (M_2)
Fineman-Ross	0.29	2.62	0.08	0.22
Kelen-Tudos	0.24	2.40	0.09	0.23
Mean	0.26	2.51	0.08	0.22
Q	1.05	0.78 [43]	1.21	1.00 [43]
e	0.41	0.40 [43]	0.91	−0.80 [43]

alternating behavior observed in CPMISt [5,44,45]. This behavior is attributed to donor-acceptor complex formation between styrene and CPMI. In case of copolymerization between CPMI and MMA, both the monomers are electron acceptors and cannot form a charge transfer complex. The value r_1 (CPMI) is lower than r_2 (MMA) and the value of r_1 is less than unity. This is because that CPMI is less active than MMA. The copolymer is richer in the more reactive monomer (MMA) in the random placement. Table 1 shows that in the copolymer CPMIMA, the MMA composition is always grater than it was in the feed. Thus, copolymer CPMIMA is weakly ordered with predominantly random distribution of the monomer units in the copolymer chain [5,15].

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Thermal Studies

The thermograms (TG) were obtained by heating the polymer and copolymer samples in air at 10°C/min, and, for few selected polymer samples, are shown in Figures 4 and 5. The temperatures for initial decomposition T_i, temperature for 10% weight loss T_{10}, final decomposition T_f, and maximum rate of weight loss T_{max} and half volatilization temperature T_{50} determined from TGA for homopolymers and copolymers are summarized in Table 4. The values of integral procedural decomposition temperatures (IPDT), an index of thermal stability as proposed by Doyle [46], were determined from a mass loss curve are also included in the last column of Table 4. The values of activation energy (E_a) of thermal degradation by employing the Broido's method [47] are given in Table 5.

As expected the maleimide polymer PCPMI is a potential heat resistant material. PCPMI degraded in one step without forming stable intermediate. The degradation of PCPMI started at 385°C and degraded 50% at 586°C. The maximum rate of weight loss occurred at 531°C. Residue at 700°C was about 18%.

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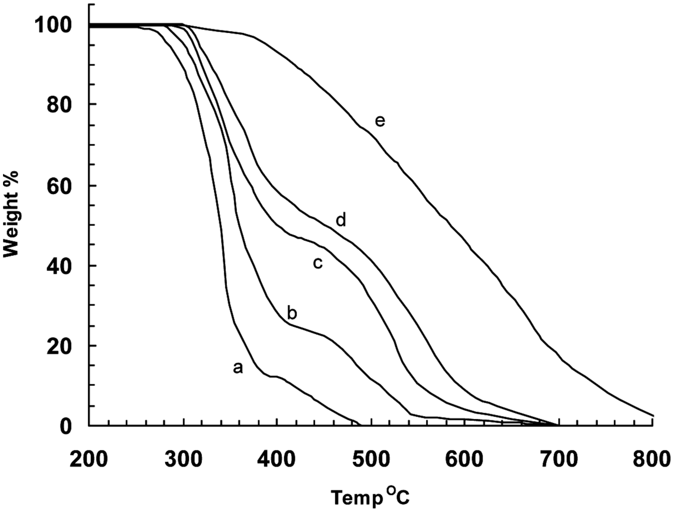

FIGURE 4 Thermograms of copolymers MMA with CPMI (a) CPMIMA1, (b) CPMIMA3, (c) CPMIMA5, (d) CPMIMA7, and (e) PCPMI.

The present copolymer samples show two-step degradation processes. The copolymers began to decompose at higher T_i and the weight loss for the first-step became smaller and the second-step became larger as the content of CPMI in copolymer was enhanced.

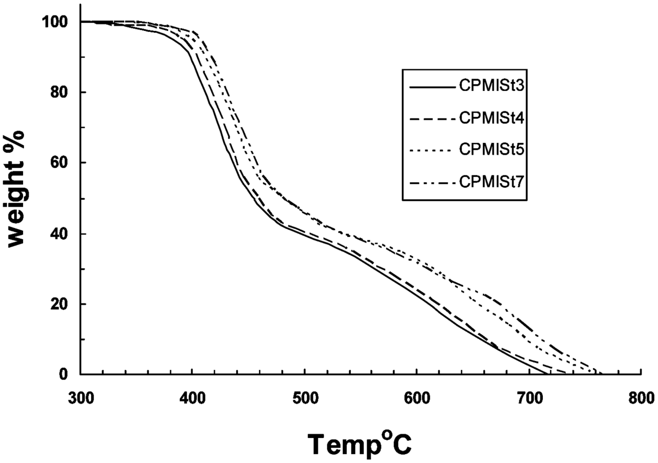

FIGURE 5 Thermograms of copolymers of Sty with CPMI (a) CPMISt3, (b) CPMISt4, (c) CPMISt5, and (d) CPMISt7.

TABLE 4 Thermal Behavior of Polymer Samples

Polymer	T_{i} (°C)	T_{10} (°C)	T_{max} (°C)	T_{50} (°C)	T_{f} (°C)	IPDT (°C)
PCPMI I	385	419	531	586	828	726
PMMA	212	263	310	312	496	400
PSt	282	304	412	423	508	435
CPMIMA1 I	293	295	345	340	400	403
II	405				490	
CPMIMA2 I	299	300	322	340	430	447
II	430		520		550	
CPMIMA3 I	299	315	353	360	430	448
II	430		510		540	
CPMIMA4 I	309	320	360	380	418	477
II	420		520		580	
CPMIMA5 I	315	320	349	400	419	500
II	420		540		600	
CPMIMA6 I	317	322	360	435	444	527
II	448		550		640	
CPMIMA7 I	320	329	375	445	420	537
II	465		530		650	
CPMIMA8 I	322	335	364	494	460	562
II	465		560		684	
CPMIMA9 I	325	338	380	485	475	570
II	480	520	625	670	690	
CPMISt3 I	375	398	428	455	455	537
II	484		616		717	
CPMISt4 I	380	404	437	459	465	556
II	492		643		735	
CPMISt5 I	400	413	440	481	481	593
II	517		684		760	
CPMISt7 I	408	416	438	481	484	634
II	519		710		766	

It is seen that incorporation of CPMI enhances the initial decomposition temperature of the copolymers by a factor of 81 to 113°C from poly(methylmethacrylate) and 93 to 126°C from poly(styrene). A similar trend was observed for IPDT of polymer samples. An improvement in thermal stability is also observed at high temperature, in the sense that the rate of decomposition has slowed down. This is because the incorporated five member plannar cyclic structure in the chain of copolymer enhances the thermal stability of copolymer [48].

CONCLUSIONS

Copolymers of MMA and St with CPMI were synthesized by radical polymerization using AIBN as an initiator in a THF solvent at 80°C.

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TABLE 5 Activation Energy E_a in kcal/mol of Thermal Degradation

Polymer	Step-I	Step-II
PCPMI	46.9	—
PMMA	13.0	
PSt	29.2	
CPMIMA1	15.5	
CPMIMA2	16.6	
CPMIMA3	25.2	33.1
CPMIMA4	30.8	15.9
CPMIMA5	22.4	14.9
CPMIMA6	18.1	24.8
CPMIMA7	13.2	27.0
CPMIMA8	14.2	28.7
CPMIMA9	10.9	29.8
CPMISt3	37.2	12.4
CPMISt4	39.1	12.6
CPMISt5	39.7	13.7
CPMISt7	41.4	14.2

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The copolymers CPMIMA and CPMISt show excellent solubility in acetone, dioxane, THF, DMF, DMSO, cyclohexanone, and aq. NaOH. The average values of r_1 and r_2 are 0.26 and 2.51 in the CPMI/MMA system and 0.08 and 0.22 in the CPMI/St system. Alfrey–Price Q-e values for CPMI were calculated as $Q = 1.05$ and $e = 0.41$ in the CPMI/MMA system and $Q = 1.21$ and $e = 0.91$ in the CPMI/St system. CPMIMA polymers are weakly ordered with predominantly random distribution of the monomer units in the copolymer chain whereas nearly alternating behavior was observed in case of CPMISt. The incorporation of CPMI in the PMMA or PSt enhances the initial and final decomposition temperatures of the copolymers.

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