

Synthesis, Characterization and Thermal Properties of Copoly(maleimide-methylmethacrylate), Terpoly(maleimide-methylmethacrylate-acrylic Acid), and Terpoly(maleimide-methylmethacrylate-methylacrylic acid)

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ABSTRACT

N-*p*-Anisylmaleimide (NPAMI) was copolymerized with methylmethacrylate (MMA) to derive copolymaleimide-acrylate poly(NPAMI-MMA). The effect of different free radical initiators: azobisisobutyronitrile (AIBN), benzoyl peroxide and hydrogen peroxide; and of various solvents: *p*-dioxane (DOX), tetrahydrofuran (THF), cyclohexanone (CHN), dimethylformamide (DMF) and ethyl acetate (EA) has been investigated to find the most suitable initiator-solvent system. Further, employing the equimolar ratio of NPAMI, MMA and acrylic acid (AA) or methacrylic acid (MAA) and using AIBN/DOX system two terpolymers poly(NPAMI-MMA-MAA) and poly(NPAMI-MMA-AA) were synthesized. Density measurement, solubility test, elemental analysis, IR, ¹H NMR and ¹³C NMR spectral analyses were used to characterize these polymer samples. The thermal behaviour was studied by TGA and DSC techniques.

Key Words:

radical copolymerization;
co- and ter-polymaleimides;
N-*p*-anisylmaleimide;
characterization; thermal stability.

INTRODUCTION

Aromatic polyimides are one of the most important classes of high-performance polymers. Due to their thermal, electrical and high-temperature mechanical properties, aromatic polyimides have found many applications as high temperature insula-

tors, coatings, adhesives and matrices for high-performance composites [1-5]. Most aromatic polyimides produced by the thermal solid state phase imidization show insolubility and infusibility, which make processing difficult. These undesirable

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properties, which limit wider applications of the polyimides, are due to their chain rigidity as well as to poor defined molecular architectures. Addition type polyimides were developed mainly to overcome processing disadvantages [6-9].

N-Substituted maleimides are known to homopolymerize and copolymerize both free radically and anionically [10-27]. In order to investigate the possibility of obtaining better polymers from *N*-substituted maleimide, in this paper we report the synthesis of copolymer of *N*-*p*-anisylmaleimide (NPAMI, M₁) with methyl methacrylate (MMA, M₂), and two terpolymers of NPAMI (M₁) with MMA (M₂) and methacrylic acid (MAA, M₃) or acrylic acid (AA, M₃) using free radical initiator and organic solvent system. The polymer samples have been characterized by density, solubility, elemental, spectral and thermal analysis. Abbreviations CPMIA1, TPMIA1 and TPMIA2 have been used for poly(NPAMI-MMA), poly(NPAMI-MMA-MAA) and poly(NPAMI-MMA-AA), respectively in the text.

EXPERIMENTAL

Materials

Maleic anhydride and *p*-anisidine of good quality were recrystallized from chloroform. MMA (BDH, AR), MAA (SISCO, AR), AA (SISCO, AR) and acetic anhydride (AcA) were purified by standard procedures as recommended by Riddick et al. [28] and were used after fractional distillation. Azobisisobutyronitrile (AIBN, Wilson Laboratory) was recrystallized from methanol prior to use. Benzoyl peroxide (BPO, Robert Johnson, LR) and hydrogen peroxide (H₂O₂, Polypharm, 6% w/v) were used as received. *p*-Dioxane (DOX) and tetrahydrofuran (THF), *N,N'*-dimethylformamide (DMF), cyclohexanone (CHN) and ethyl acetate (EA) were used after appropriate distillation [28].

Measurements

The densities of solid polymer samples were determined at 30 C by the displacement method with a single stem pycnometer [29] using water as a non-solvent. The intrinsic viscosity [η] measurements were carried out in dioxane at 30 C using an Ubbelohde suspended level viscometer. The temperature was controlled to -0.02 C by employing the water thermostat. The

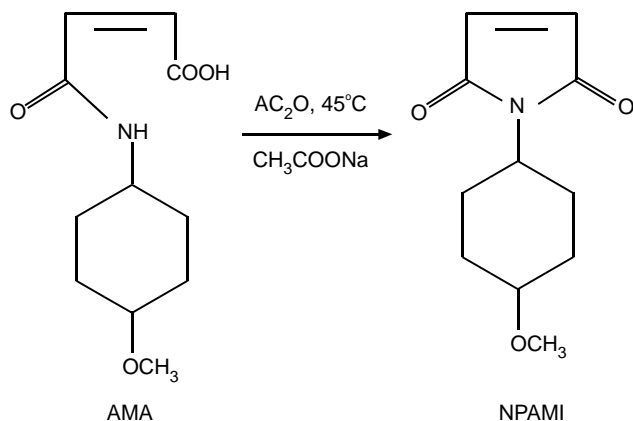
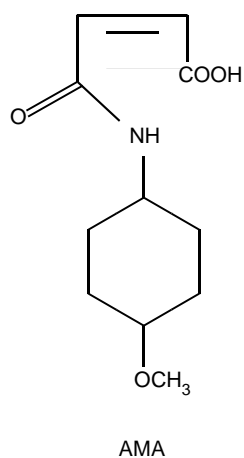
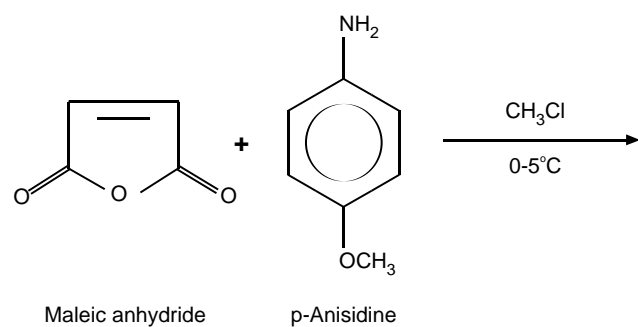
details of the procedure for the viscosity measurements have been described elsewhere [30]. Weight average molecular weight \bar{M}_w of the resulting polymers was determined by gel permeation chromatography technique using THF as a mobile phase and polystyrene as a standard [14,17].

The C, H, N elemental analysis was carried out on Carlo Erba Elemental Analyzer, model 1106. The IR spectra were scanned in KBr pellets on Perkin Elmer IR-spectrophotometer. ¹H NMR was taken at 300 MHz in DMSO-*d*₆ on a VXR-300 spectrometer with a sweep time of 10 min at 25 C. TMS was used as reference. ¹³C NMR spectra were recorded at 75.5 MHz in DMSO-*d*₆ on Bruker-300A spectrometer. HMDS was used as reference. Thermogravimetric analysis was carried out in air at a heating rate of 10 C/min by means of a Mettler TA-3000 system (Switzerland). The glass transition temperature (T_g) was determined by differential scanning calorimetry at a heating rate of 10 C/min with a Du Pont 9900.

Preparation of NPAMI

N-*p*-Anisylmaleimide (NPAMI) was synthesized by condensation of maleic anhydride with *p*-anisidine followed by cyclodehydration using AcA and sodium acetate [31,32] as shown in reaction presented Scheme I.

0.1 M Solution of *p*-anisidine in chloroform was added drop-wise with constant stirring into 0.1 M maleic anhydride solution in chloroform for a period of 30 min. The entire reaction mixture was cooled externally. The greenish yellow solid *N*-*p*-anisyl maleimic acid was filtered and dried at 55–5 C. It was recrystallized from methanol. 22.1 g (0.1 mol) maleimic acid, 16.4 g (0.2 mol) sodium acetate and 115 mL AcA in 200 mL DMF were reacted for 2 h at 45 C. Cooled reaction mixture was poured into crushed ice. Yellow needles of NPAMI was filtered, washed with 10% NaHCO₃ solution and dried at 55–5 C for several hours. It was further crystallized from chloroform. The yield was 60%. The purity and structure of NPAMI were ascertained by elemental analysis, mp, IR and ¹H NMR spectra. mp 145 C (lit. 148 C [33]), Anal. Calc. (C, 65.02; H, 4.43; N, 6.89%); found (C 65.01; H 4.36; N 6.81%). IR (cm⁻¹): 1778 and 1707 (C=O in a five-membered imide ring [34-36]), 1609, 1511 (C=C, aromatic [34-37]), 1395 (C-H bending [37]), 1301 (C-N stretching [37]), 1252 (C-OCH₃ [37]), 830 (CH=CH,



Scheme I

phenyl ring [36]), 690 (cis-CH=CH, [36,37]) and ^1H NMR (300 MHz, TMS, δ , ppm): $\delta = 7.16$ (s, 2H (-CH=CH-) [9]), 7.01-7.06 (d, 2Ar-H, o- to -OCH₃ in phenyl ring), 7.20-7.23 (d, 2Ar-H, m- to -OCH₃ in phenyl ring), 3.79 (s, 3H (-OCH₃) [11,12].

Preparation of Copolymer

Copolymerization of NPAMI (5 mmol) with MMA (5 mmol) was carried out in *p*-dioxane (50 mL) using

Table 1. Percentage yield and intrinsic viscosity of CPMIA1 in various initiator/solvent systems.

Initiator \ Solvent	AIBN		BPO		H ₂ O ₂	
	Y (%)	[η]	Y (%)	[η]	Y (%)	[η]
CHN	57	0.393	70	0.330	45	0.253
DMF	65	0.320	75	0.290	55	0.230
DOX	80	0.380	85	0.325	65	0.260
EA	68	0.310	75	0.275	60	0.245
THF	65	0.330	70	0.300	56	0.240

AIBN (25 mg) as free radical initiator at 65–5 C for 2h under nitrogen atmosphere. The copolymer CPMIA1 was isolated by precipitation to methanol. The precipitated copolymer was washed with methanol several times and dried in a vacuum oven. Similarly, the various samples of CPMIA1 were obtained using the other pairs of initiator (BPO and H₂O₂) and solvent (THF, DMF, CHN, and EA) combinations. The yield of polymers was determined gravimetrically. The polymers were purified by repeated reprecipitations. The percentage yield and [η] of CPMIA1 samples, using different initiator/solvent systems, are presented in Table 1.

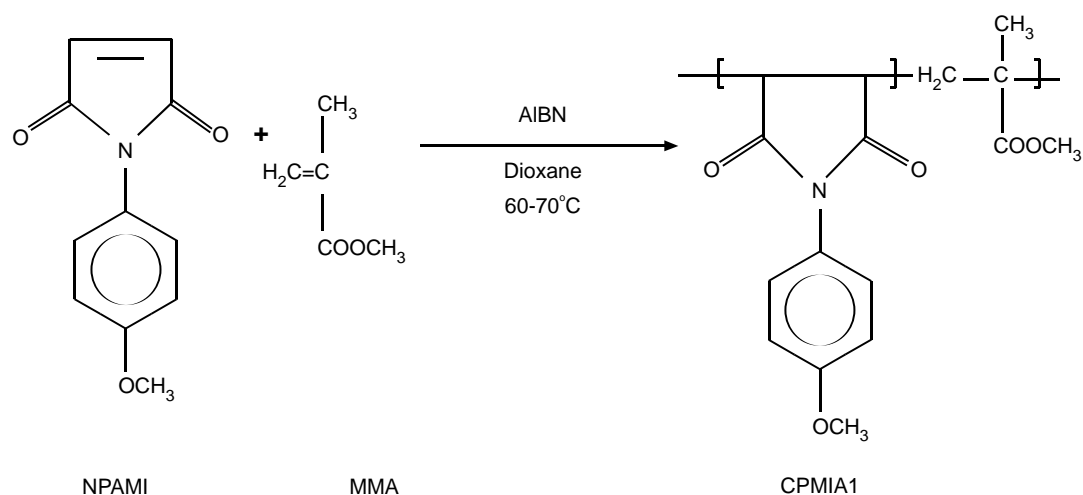
Preparation of Terpolymer

Terpolymers TPMIA1 and TPMIA2 were prepared by the similar procedure as adopted for the CPMIA1 using the AIBN as an initiator and DOX as a solvent. Equimolar ratios of all the three monomers NPAMI, MMA and MAA or AA were taken in the reaction mixture.

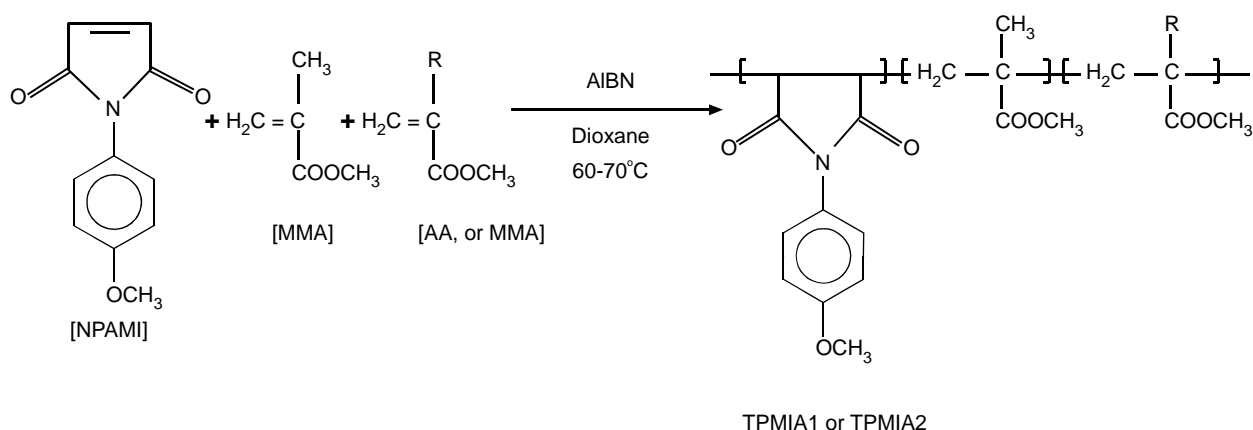
RESULTS AND DISCUSSION

Synthesis of Polymers and Selection of Initiator/Solvent System

Since free radical copolymerization of maleimide is known to be useful on the synthesis of general copoly-maleimide, this method was applied to their preparation from NPAMI and vinyl monomers. To find suitable conditions in which to prepare copolymaleimide and terpolymaleimide with relatively high \bar{M}_w , the effects of reaction solvent and initiators were investigated in detail. The effect of reaction solvents and initiators on [η] of CPMIA1, formed in different pairs of initiator/



Scheme II



Scheme III

organic solvent is outlined in Table 1. Table 1 reads that the values of $[\eta]$ of copolymer which are closely related with average \bar{M}_w of the macromolecules, decrease in the order of initiator $\text{AIBN} > \text{BPO} > \text{H}_2\text{O}_2$, in each of the solvent, while in case of percentage yield, the order changes a little to give rise to a new sequence: $\text{BPO} > \text{AIBN} > \text{H}_2\text{O}_2$. It is found that the copolymer CPMIA1 samples obtained using AIBN/ CHN and AIBN/DOX as initiator/solvent systems were found to have the high values of $[\eta]$ among all the systems investigated. However, the percentage yield of the CPMIA1 in the AIBN/CHN system was poor compared to that in AIBN/DOX system. The use of BPO/DOX system though gave slightly better yield of CPMIA1 over the AIBN/DOX but the value of $[\eta]$ using the latter system was much higher than that for the former

system. Examination of all the aspects, we considered system AIBN/DOX as most suitable for the present copolymerization process of NPAMI and MMA. We also employed the same AIBN/DOX system under the identical conditions for the synthesis of terpolymers TPMIA1 and TPMIA2.

The co- and terpolymerization reactions are represented as in Schemes II and III:

Physical and Spectral Properties

The yield %Y, density ρ , intrinsic viscosity $[\eta]$ and weight average molecular weight \bar{M}_w of the present polymer samples are listed in Table 2. The values of $[\eta]$ in dioxane at 30 C and the \bar{M}_w are decreasing in the order $\text{CPMIA1} > \text{TPMIA1} > \text{TPMIA2}$. Based on the experimentally observed C(%), H(%), and N(%) con-

Table 2. The percentage yield, density, intrinsic viscosity and molecular weight of polymaleimides.

Polymer code	Y (%)	Density ρ (g/cm ³)	$[\eta]^*$ dL/g	$10^{-4}\bar{M}_w^{**}$
CPMIA1	80	1.2737	0.380	5.11
TPMIA1	65	1.3066	0.360	4.83
TPMIA2	55	1.3133	0.326	4.37

(*) The viscosity measurement was carried out in *p*-dioxane at 30°C.

(**) Obtained by GPC method.

tents, the compositions of co- and terpolymers were determined which are given in Table 3. In CPMIA1, the mole ratio of two monomers NPAMI and MMA is 1:1.13. In case of both terpolymers TPMIA1 and TPMIA2, the acid monomer has comparatively higher mole ratio than that of imide monomer.

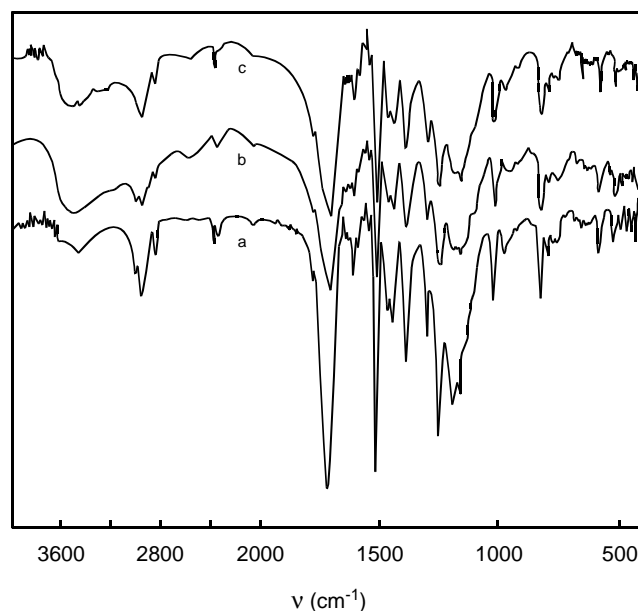
The relative solubilities were determined in variety of solvents at 30 C. All the three polymer samples are soluble in DOX, THF, DMF, CHN, 2-butanone, EA and dimethyl sulphoxide while completely insoluble in saturated hydrocarbons, alcohols and ethers. Furthermore, CPMIA1 is also soluble in haloalkanes such as chloroform, carbon tetrachloride, dichloromethane, dichloroethane, 1,1,2-trichloroethane and 1,1,2,2-tetrachloroethane while TPMIA1 and TPMIA2 are completely insoluble in these haloalkanes. The insolubility of TPMIA1 and TPMIA2 in haloalkanes may be attributed to presence of polar acidic group in them. According to Hildebrand's solubility parameter theory [38], the solubility of the polymer can be predicted from the knowledge of solubility parameters of solvent and polymer. In the present case, in general the solvents having in the range 18.2 to 24.8 J^{1/2}cm^{-3/2} are good solvents for the present polymers.

Table 3. The elemental analysis C, H and N contents and composition of polymaleimides.

Polymer code	Elemental analysis (%)			Composition (mole ratio) (%)		
	C	H	N	NPAMI (M ₁)	MMA (M ₂)	ACID (M ₃)
CPMIA1	63.07	5.49	4.43	1.00	1.13	
TPMIA1	60.42	5.46	3.61	1.00	1.11	1.13
TPMIA2	61.46	5.87	3.42	1.00	0.97	1.23

IR, ¹H NMR and ¹³C NMR confirm that imide monomer was copolymerized with vinyl monomers at 65 – 5 C without cleavage of the imide ring. The IR spectrums of CPMIA1, TPMIA1 and TPMIA2 (Figure 1 a,b,c) are very similar showing major absorption in cm⁻¹ at 3000, 2975, 2840 (aliphatic C-H stretching in the alkyl group in methylmethacrylate), 1780, 1715 (C=O stretching of imide and ester group), 1610, 1516 (C=C, aromatic), 1440 (C=O stretching and O-H bending), 1390 (CH bending -CH₃), 1305 (C-N stretching), 1253-1251 (C-O-C stretching vibration of the ether and ester groups), 830 (CH=CH, phenyl ring). The intensities of the peaks show variation in 1a, 1b and 1c. In the IR spectrum of terpolymers TPMIA1 and TPMIA2 peak at 1715 cm⁻¹ has broaden due to increase in C=O group as a result of incorporation of acrylic and methacrylic acid in polymer chain. Decrease in intensity of peak at 1620 cm⁻¹ corresponds to decrease in aromatic content in the terpolymers. It is important to note the inversion of peak intensities at 1200 and 1185 cm⁻¹ in terpolymer than that observed in copolymer CPMIA1. This change may be attributed to change in aromatic and aliphatic C-O groups in respective polymers.

In ¹H NMR of CPMIA1 (Figure 2) 4Ar-H and 2H (CH-CH) of maleimide unit appeared at δ 7.01-7.15 (m), and 3.76 (s) ppm, respectively [10,15]. The broad peak observed at δ 3.45-3.53 ppm is assigned to over-

**Figure 1.** IR Spectra of co- and terpolymers, (a) CPMIA1, (b) TPMIA1, and (c) TPMIA2.

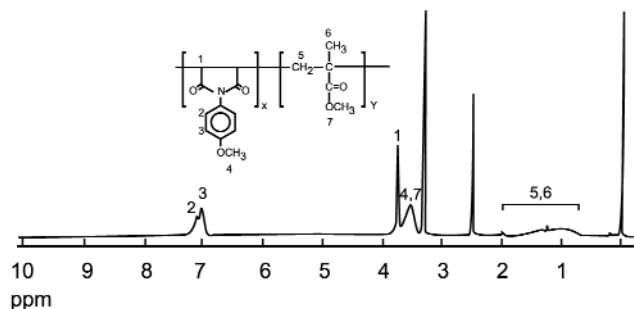


Figure 2. ¹H NMR Spectrum of CPMIA1 in DMSO-d₆ at 300 MHz.

lapping of two -OCH₃ groups, one in MMA and other in maleimide segments [15, 39]. The broad peak in the range 0.81 to 1.98 ppm is a result of protons in -CH₂ and -CH₃ in MMA unit [15]. In ¹H NMR of TPMIA1 (Figure 3) 4Ar-H and 2H (CH-CH) of maleimide unit appeared at δ 7.01-7.25(m), and 3.77-3.78(d) ppm, respectively. The δ at 3.53-3.65 ppm is assigned to overlapping of two -OCH₃ groups of MMA and maleimide segments. The 4H of two -CH₂ groups and 6H of two -CH₃ showed at 1.85-2.27(b) and 0.8-1.4(b) ppm. The H due to -COOH appeared at 12.4-12.8 ppm. In ¹H NMR of TPMIA2 (Figure 4): 4Ar-H and 2H (CH-CH), of maleimide unit appeared at δ 7.01-7.11(m), and 3.77(s) ppm, respectively. The δ observed at 3.54-3.56 ppm is assigned to overlapping of two -OCH₃ groups in MMA and maleimide segments. 4H of two -CH₂ groups and 3H of -CH₃ showed at 1.97-2.36(b) and 0.8-1.4(b) ppm. The H due to -CH and -COOH resonated at 4.19 and 12.45-12.90 ppm, respectively.

¹³C NMR for copolymer CPMIA1 and terpolymer TPMIA2 given in Figures 5 and 6 are similar, except additional peaks at 67.4 and 170.5 ppm in TPMIA2. The resonance (Figure 5) at 176.7 – 0.9 ppm resulted

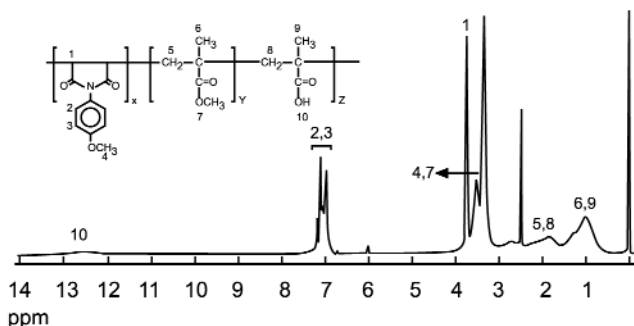


Figure 3. ¹H NMR Spectrum of TPMIA1 in DMSO-d₆ at 300 MHz.

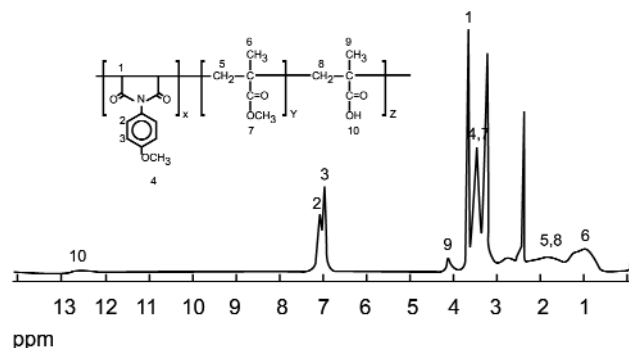


Figure 4. ¹H NMR Spectrum of TPMIA2 in DMSO-d₆ at 300 MHz.

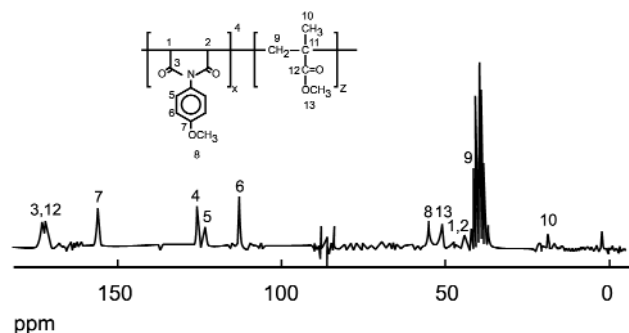


Figure 5. ¹³C NMR Spectrum of CPMIA1 in DMSO-d₆ at 75.5 MHz.

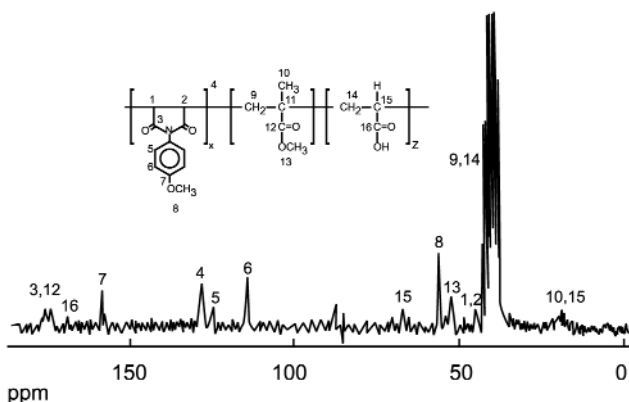


Figure 6. ¹³C NMR Spectrum of TPMIA1 in DMSO-d₆ at 75.5 MHz.

from the carbonyl carbons on both the imide and MMA units in copolymer [13,17, 40]. The resonance signals for aromatic carbons =CH, and =CN are found to appear in the range 115.2 to 129.0 and for =COCH₃ at 159.5 – 0.5 ppm [17,40]. The δ multiplets centered around 44.5 and in between 40.7 to 41.6 corresponded to the methine and methylene carbon of backbone chain [17,40,41]. The δ at 51.5 and 55.6 ppm corresponded to

ester and ether carbon in $-\text{OCH}_3$, respectively [37]. The additional peaks at 67.4 and 170.6 ppm in ^{13}C -NMR (Figure 6) are attributed to $-\text{CH}$ and $-\text{COOH}$ carbons of AA unit [42], confirming its participation in the terpolymer TPMIA2 formation. The absence of alkene peak in the range 131-137 ppm showed that the co- and terpolymers formation was via vinyl group and with no contamination of monomer units [39,41].

Thermal Analysis

TGAs are shown in Figure 7. A two-step thermal degradation was observed in all the cases. The results of percentage weight loss suffered from 200 to 700 C at 100 intervals are furnished in Table 4. Table 4 reveals that weight loss was below 2.4 to 8.6% upto 300 C. The maximum weight loss in the range 48.1 to 56.4% occurred between 300 to 400 C. The total weight loss upto 600 C is 90 to 97%. The initial decomposition temperature T_i , temperature for maximum rate of weight loss T_{max} , and final decomposition temperature T_f of first and second degradation steps of are given in Table 5. The results in Table 5 indicated that the relative thermal stability on the basis of T_i follows the order CPMIA1 > TPMIA1 > TPMIA2.

A comparison of TGA, of the present copolymer CPMIA1 with polymethylmethacrylate (PMMA), showed significant changes in thermal behaviour. In PMMA, a three-step decomposition was observed [43],

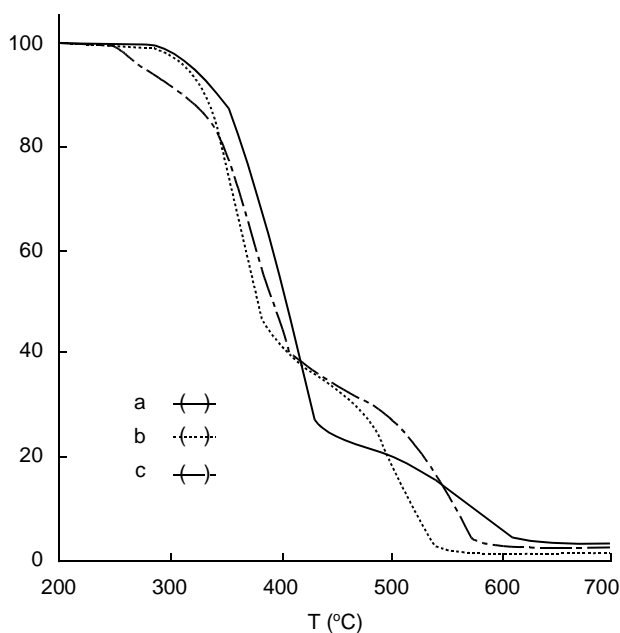


Figure 7. TGA of (a) CPMIA1, (b) TPMIA1, and (c) TPMIA2 in air at 10 C/min.

Table 4. Percentage weight loss of polymaleimides at various temperatures from the TGA.

Polymer	200	300	400	500	600	700
	(°C)					
	Weight loss (%)					
CPMIA1	0.1	2.4	50.5	80.0	95.0	97.0
TPMIA1	0.4	2.9	59.4	70.6	90.5	98.7
TPMIA2	0.3	8.6	57.8	82.5	97.0	97.6

Table 5. Thermal analysis data for polymaleimides*.

Polymer code	T_g	first step				second step			
		T_i	T_{max}	T_f	E_a	T_i	T_{max}	T_f	E_a
CPMIA1	155.4	290	402	440	29.3	440	573	620	31.5
TPMIA1	61.9	288	354	420	32.2	450	581	640	34.7
TPMIA2	93.5	266	376	430	28.3	500	554	580	54.9

(* Unit for T_g , T_i , T_{max} , and T_f is °C and for E_a is kcal mol $^{-1}$.)

whereas in copolymer CPMIA1, only a two-step was seen. Further, it was observed that incorporation of maleimide unit in the PMMA backbone has increased the T_i . This may be attributed to the stop of the H-H or chain end initiated degradation [43]. Once a random scission has been initiated (i.e., above 290 C) in copolymer CPMIA1, and in terpolymers TPMIA1 and TPMIA2, further degradation proceeded by a zipper mechanism.

The estimated values of energy of activation E_a for thermal degradation from thermograms employing the Broido's method [44] for CPMIA1, TPMIA1 and TPMIA2 are 29.3, 32.2 and 28.3 kcal mol $^{-1}$, respectively, for the first decomposition step, while they are 31.5, 34.7 and 54.9 kcal mol $^{-1}$, for the second decomposition step. The glass transition temperatures T_g determined from DSC for CPMIA1, TPMIA1 and TPMIA2 are 155.4, 61.9 and 93.5 C, respectively. A comparison of T_g indicates that the presence of carboxylic group in the terpolymers TPMIA1 and TPMIA2 reduces the T_g , without affecting the thermal stability significantly.

CONCLUSION

Synthesis through free radical copolymerization of copoly(maleimide-methylmethacrylate) and terpolymerization of terpoly(maleimide-methylmethacrylate-

acrylic acid), and terpoly(maleimide-methylmethacrylate-methylacrylic acid) have been investigated. The most suitable initiator/solvent pair for the copolymerization of NPAMI with vinyl monomers was found to be AIBN/DOX. The characterization of co- and terpolymers has been carried out through density measurement, solubility test, elemental analysis, IR, ^1H NMR and ^{13}C NMR spectral analysis. Copolymer poly(NPAMI-MMA) and terpolymers poly(NPAMI-MMA-MAA) and poly(NPAMI-MMA-AA) show good thermal stability and degrade in two steps.

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