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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Patel, C. B. , Malek, N. I. and Oswal, S. L.(2006) 'Synthesis and Radical Polymerization of N-[4-N'-(Phenylamino-carbonyl)phenyl]maleimide and its Copolymerization with Methyl Methacrylate', Journal of Macromolecular Science, Part A, 43: 2, 289 – 303

To link to this Article: DOI: 10.1080/10601320500437201

URL: <http://dx.doi.org/10.1080/10601320500437201>

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Synthesis and Radical Polymerization of N-[4-N'-(Phenylamino-carbonyl)phenyl]maleimide and its Copolymerization with Methyl Methacrylate

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A novel type of imide-amide monomer, 4-maleimidobenzanilide (MB) i.e., N-[4-N'-(phenylaminocarbonyl)phenyl]maleimide was synthesized from maleic anhydride, p-aminobenzoic acid and aniline. Radical polymerization of MB and its copolymerization with MMA (methyl methacrylate), initiated by AIBN, were performed in THF solvent at 65°C. Nine copolymer samples were prepared using different feed ratios of comonomers. All the polymer samples have been characterized by a solubility test, intrinsic viscosity measurements, FT-IR and ¹H-NMR spectral analysis, and thermo-gravimetric analysis. The values of monomer reactivity ratios of MB-MMA system (r_1 , r_2) and the Alfrey-Price parameters Q_1 and e_1 were determined.

Keywords maleimide copolymers, methyl methacrylate, 4-maleimidobenzanilide, reactivity ratios, thermogravimetric analysis

Introduction

Aromatic polyimides have been noted for excellent characteristics such as thermo-oxidative stabilities and electrical properties, as well as chemical resistance. These polymers have been widely used for a number of applications (1–4). However, most of the aromatic polyimides have one major drawback, their intractability in fully imidized form. Furthermore, there are several difficulties in processing due to insolubility and/or infusibility (5). Therefore, the preparation of soluble or thermoplastic polyimides has been of major interest in current research work. Earlier attempts to produce soluble and processable aromatic polyimides involved the introduction of flexible linkage (6) or molecular asymmetry (7) in to the backbone or the addition of bulky side group (8, 9). Alternative ways to overcome processing disadvantage in condensation polyimides is to develop addition polyimides and copolyimides (10–16). Furthermore, copolymerization is a method for improving the polymer properties to meet specific requirements. The knowledge of the copolymerization process is also of considerable interest to evaluate reactivity ratios of comonomers.

Received April 2005; Accepted June 2005.

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In this article, a novel imide-amide monomer, 4-maleimidobenzanilide (MB) i.e., N-[4-N'-(phenylaminocarbonyl)phenyl]maleimide, is prepared from maleic anhydride, p-aminobenzoic acid and aniline. MB is polymerized and copolymerized with methyl methacrylate (MMA) initiated by AIBN in THF at 65°C. The study of physical, spectral and thermal properties have been carried out in order to characterize the polymers. The effect of different feed ratios of monomers on the properties of copolymers has been examined.

Experimental

Materials

Maleic anhydride (SRL, extra pure) was first recrystallized from chloroform and then further purified by sublimation at $54 \pm 2^\circ\text{C}$. p-Aminobenzoic acid (SRL, pure) and aniline (Polypharm, AR) were used as received. MMA (BDH, AR) was shaken two to three times with 5% NaOH to eliminate hydroquinone inhibitor, dried over anhydrous CaCl_2 for 6 h and distilled (17). The head and tail fractions were discarded. AIBN (2,2'-azobis-isobutironitrile (Wilson Lab.)) was recrystallized twice from methanol prior to use. Anhydrous sodium acetate (SRL) was of good quality. DMF, THF, methanol, acetic anhydride, benzene, etc. used in the present work were of Analytical Grade and of purity better than 99 mol%, and were used as received. However, THF was purified by distillation after being refluxed for 2 h in the presence of sodium (17).

Measurements

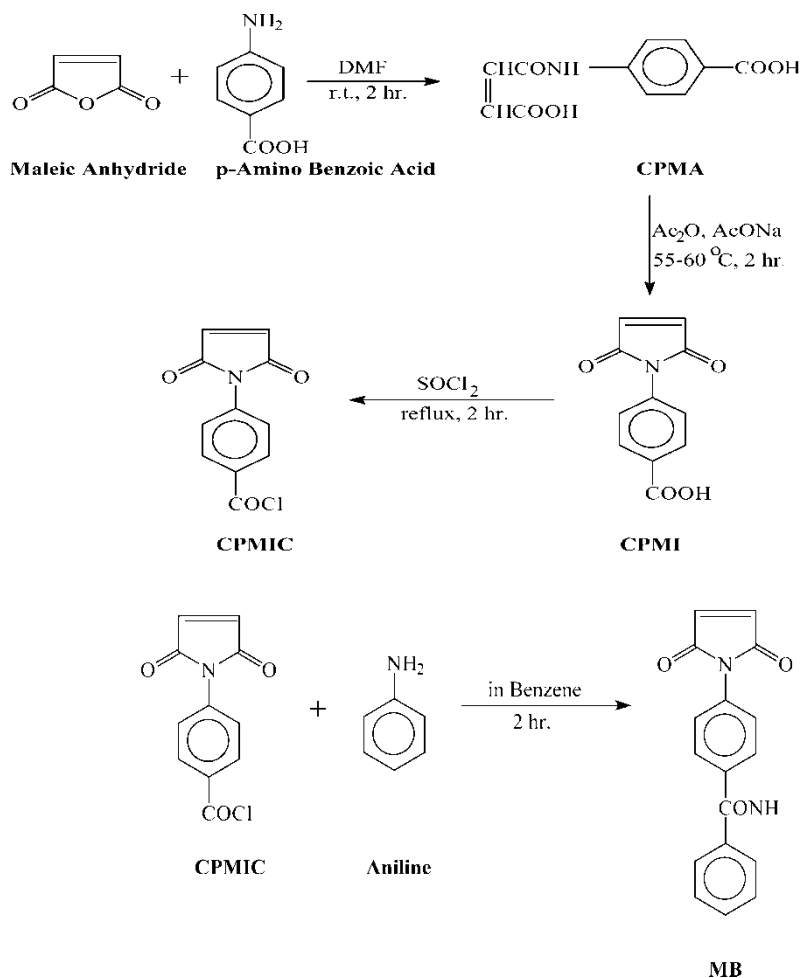
$^1\text{H-NMR}$ spectra of polymer samples were taken in DMSO-d_6 on a Bruker DPX-300 Spectrometer at 300 MHz. The internal reference used was TMS. FT-IR spectra of the polymer samples were recorded on a Perkin-Elmer IR Spectrometer, using a KBr pellet technique. The viscosities measurements were carried out in DMF at $30 \pm 0.2^\circ\text{C}$, using an Ubbelohde suspended level viscometer. Elemental analysis was made on a Carlo Erba Model NA 500 series analyzer. The thermograms in air were obtained on a Mettler TA-3000 system, at a heating rate of $10^\circ\text{C}/\text{min}$.

Preparation of 4-Maleimidobenzanilide (MB)

MB monomer was synthesized in four steps (18–20) from maleic anhydride, p-aminobenzoic acid and aniline (described below and shown in Scheme 1).

N-(4-Carboxyphenyl)maleamic acid (CPMA)

The solution of maleic anhydride (9.81 g, 0.1 mol) in DMF was gradually added over a period of 15 min to a well-stirred solution of p-aminobenzoic acid (13.71 g, 0.1 mol) in DMF. The solution was stirred for 2 h at room temperature. The resulting solution was poured into crushed ice to precipitate crude CPMA. The crude CPMA was filtered, dried and then recrystallized from methanol to obtain pure CPMA in a 97% yield, mp $225\text{--}226^\circ\text{C}$ (lit. mp $225\text{--}226^\circ\text{C}$ (20)). The IR spectrum showed absorptions at 3500–2500 (carboxylic acid O–H), 3321, 1537, 1504 (amide N–H),



Scheme 1.

1693 (carboxylic acid and amide), 1294 (carboxylic acid C–O), 848 (CH=CH), 675 (C–H bending) in cm^{-1} .

N-(4-Carboxyphenyl)maleimide (CPMI)

Cyclodehydration of the CPMA, an intermediate to maleimide was carried out by treating it with fused sodium acetate (2.0 g) and acetic anhydride (50 ml) in DMF for 2 h at 55–60°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, obtaining the product in a 82% yield with mp 228–230°C (lit. mp 225–228°C (21) and 231°C (22)). The IR spectrum showed absorptions at 3500–2500 (carboxylic acid O–H), 1774 (C=O stretch, 5-membered imide ring), 1712 (overlapping of imide and carboxylic acid C=O stretch), 1215 (carboxylic acid C–O), 1604, 1579, 1515 (aromatic C=C), and 952, 688 (CH=CH) cm^{-1} .

***N*-[4-(Chlorocarbonyl)phenyl]maleimide (CPMIC)**

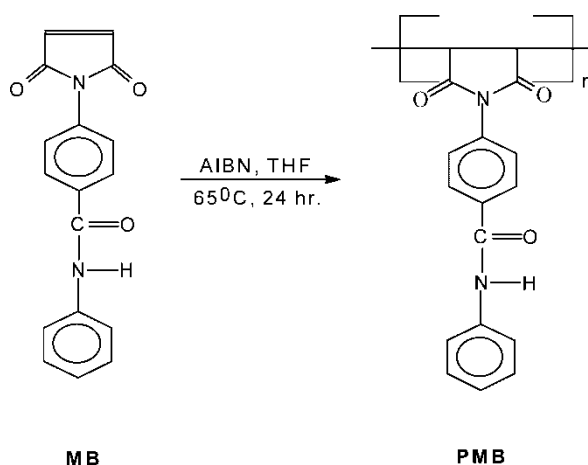
A mixture of CPMI (17.143 g, 0.079 mol) and thionyl chloride (143 ml, 1.98 mol) was refluxed at 80°C for 2 h. The unreacted thionyl chloride was distilled off. Light yellow crystals of acid chloride were obtained in 80% yield, mp 155–157°C (lit. mp 153–157°C (21) and 153°C (24)). The IR spectrum showed absorptions at 1776 (COCl), 1716 (–CONCO–), 1602 (C=C), 952, 825, 690 (CH=CH) cm⁻¹.

***4*-Maleimidobenzanilide (MB)**

A benzene solution of aniline (5.7 ml, 0.063 mol) was added dropwise to a CPMIC (18.396 g, 0.063 mol) solution in benzene at 0–5°C and the mixture was stirred at room temperature for 2 h. The precipitated product was filtered, washed with water, dried and then recrystallized twice from methanol/water to obtain pure MB in a 58% yield, mp 214–215°C. The purity and structure of the monomer was ascertained by elemental (C, H, N) analysis, IR and ¹H-NMR study. Anal. calcd. for C₁₇H₁₂O₃N₂, C, 69.86; H, 4.11; N, 9.59; Found C, 69.58; H, 4.15; N, 9.38. FT-IR (Figure 1): 3400–3300 (–NH), 1531, 1508, (CONH), 1774, 1705 (CONCO), 1440 (Ar–N), 1406 (C–N), 950, 692 (CH=CH) cm⁻¹. Other characteristic bands of imide were observed at 1155 cm⁻¹ (imide II), 1110 cm⁻¹ (imide III), 750 cm⁻¹ (imide IV). ¹H-NMR (300 MHz, TMS, DMSO-d₆, δ, ppm, Figure 2): 7.23 (s, 2H, CH=CH); 8.06–8.03 (d, 2H in phenyl ring meta- to maleimido); 7.80–7.77 (d, 2H in phenyl ring ortho- to maleimido); 10.31 (s, 1H, CONH); 7.54–7.51 (d, 2H in phenyl ring ortho- to amide); (f) 7.39–7.34 (t, 2H in phenyl ring meta- to amide); and 7.14–7.09 (t, 1H in phenyl ring para- to amide).

Polymerization

In a round bottom flask, fitted with a reflux condenser, MB (2.92 g, 0.01 mol) in 35 ml THF was refluxed after adding 100 mg AIBN at 65°C for 24 h, with occasional shaking. The polymer (PMB) was isolated by using an excess quantity of methanol-water. The crude PMB was purified by dissolving in THF and precipitating from a methanol-water mixture. It was dried under vacuum at 60°C, obtaining PMB in ca. A 55% yield. The yields were less for shorter duration reaction.



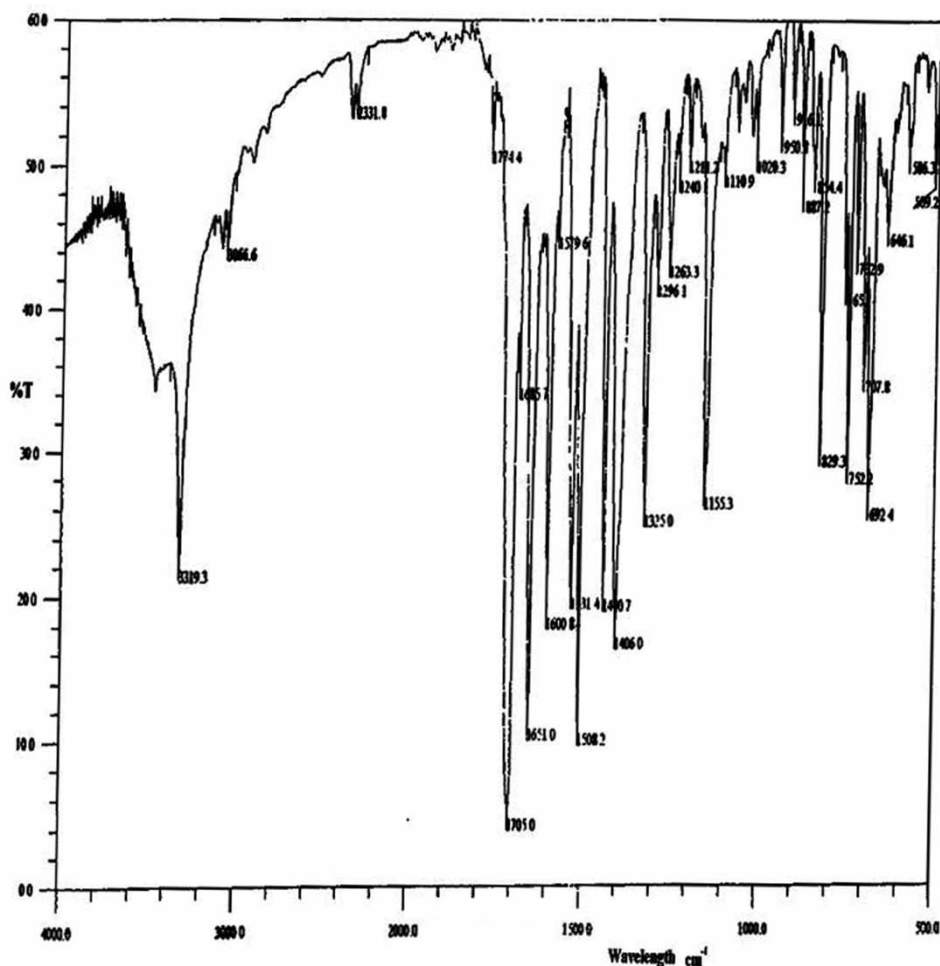


Figure 1. FT-IR spectrum of MB.

MMA was polymerized under identical conditions to that employed for the polymerization of MB, except reducing the reaction to only 6 h. The PMMA was isolated in water containing a small amount of methanol. The PMMA was precipitated and dried at 60°C under vacuum.

Copolymerization

The copolymerizations (Table 1) were carried out at 65°C for 12 h, employing calculated amounts of comonomers MMA and MB in 35 ml THF with 100 mg AIBN. The copolymer was isolated from an excess quantity of methanol containing 5% water. After dissolving the crude copolymer in THF, it was precipitated from an excess quantity of methanol-water mixture. The process was repeated three times to purify the copolymer sample. The precipitated copolymer was washed with methanol several times and dried at 60°C under vacuum. The nine-copolymer samples (CMM1 to CMM9), synthesized by using different feed ratios of monomer MB and MMA, are listed in Table 1.

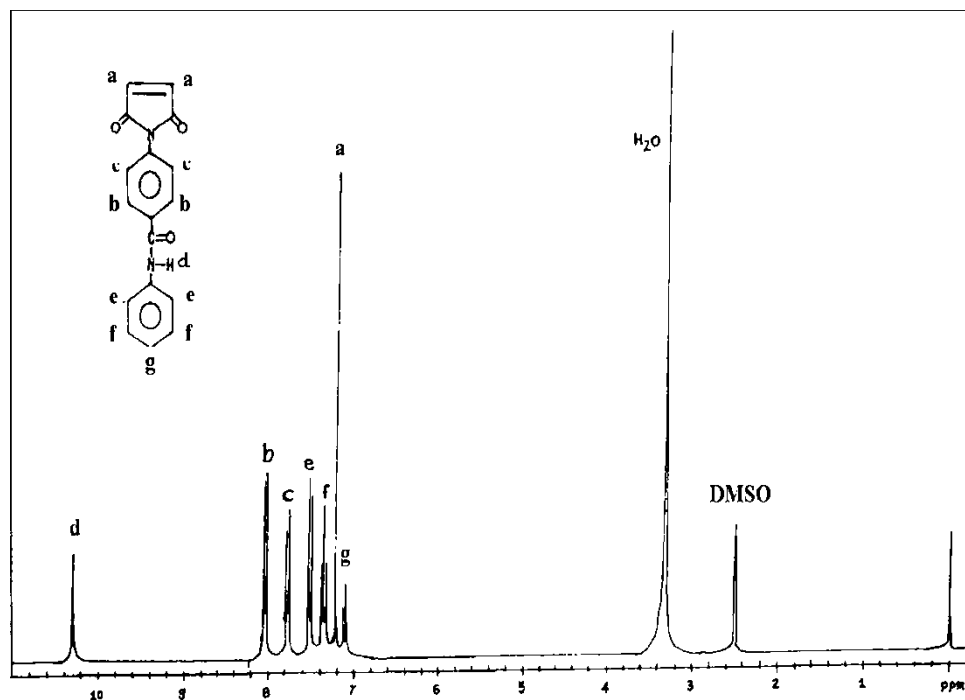
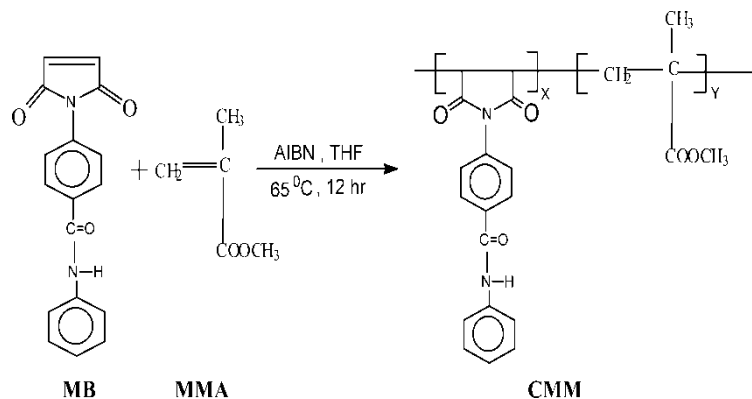


Figure 2. $^1\text{H-NMR}$ spectrum of MB.

Table 1

Radical polymerization and copolymerization of MB and MMA in THF at 65°C

Polymer Code	Feed mol fra. of MB X_1	Poly ⁿ Time (h)	Yield (%)	Appearance	$[\eta]$ dl/g	%N	Mol fra. of MB in Copolymer F_1
Copolymer							
CMM1	0.1	12	25	Light Yellow	0.216	1.90	0.078
CMM2	0.2	12	29	Light Yellow	0.209	3.87	0.214
CMM3	0.3	12	37	Light Yellow	0.201	5.21	0.289
CMM4	0.4	12	50	Light Yellow	0.189	5.76	0.340
CMM5	0.5	12	55	Light Yellow	0.186	6.80	0.455
CMM6	0.6	12	61	Light Yellow	0.179	7.22	0.511
CMM7	0.7	12	66	Light Yellow	0.163	7.35	0.529
CMM8	0.8	12	70	Light Yellow	0.148	7.81	0.600
CMM9	0.9	12	73	Light Yellow	0.127	8.46	0.719
Homopolymer							
PMB	1.0	24	55	Light Yellow	0.141	9.38	
PMMA	0.0	6	80	White	0.311	0.0	



Results and Discussion

Intrinsic Viscosity [η]

Intrinsic viscosity [η] 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 [η] in DMF solution at 30°C are listed in Table 1. The values of [η] decrease as the content of MB in the copolymer increased.

Solubility Behaviour

Solubility of the various polymer samples were examined in a number of polar and non-polar solvents. The PMB and PMMA are completely soluble in acetone, dioxane, THF, DMSO, DMF, DMAc, nitrobenzene, ethyl acetate, and isobutyl acetate and insoluble in hexane, cyclohexane, carbon tetrachloride, dichloromethane, petroleum ether, methanol, ethanol, and water. However, PMMA is soluble in benzene, toluene, o-xylene, CCl₄ and chloroform, while PMB is practically insoluble in these solvents.

The relative solubilities of three copolymer samples CMM1, CMM5, and CMM9 out of nine copolymer samples were determined at 30°C. The three investigated copolymers are soluble in acetone, dioxane, THF, DMF, DMAc, DMSO, nitrobenzene, ethyl acetate and isobutyl acetate. CMM1 and CMM5 are partially soluble in chloroform, carbon tetrachloride, o-xylene, toluene and benzene while CMM9 is completely insoluble in these solvents. All three copolymer samples are found to be totally insoluble in hexane, cyclohexane, methanol, ethanol, petroleum ether, and water.

Spectral Characterization

The FT-IR spectrum and ¹H-NMR spectrum (300 MHz in DMSO-d₆) of PMB are shown in Figures 3 and 4. The absence of a sharp band at 950 cm⁻¹ and chemical shift δ at 7.23 ppm due to CH=CH in a monomer having a vinyl group, such as monomer MB, indicates the formation of polymer via vinyl group polymerization (23, 24).

The presence of absorption bands at 1780 and 1710 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. The imide group is also confirmed from the

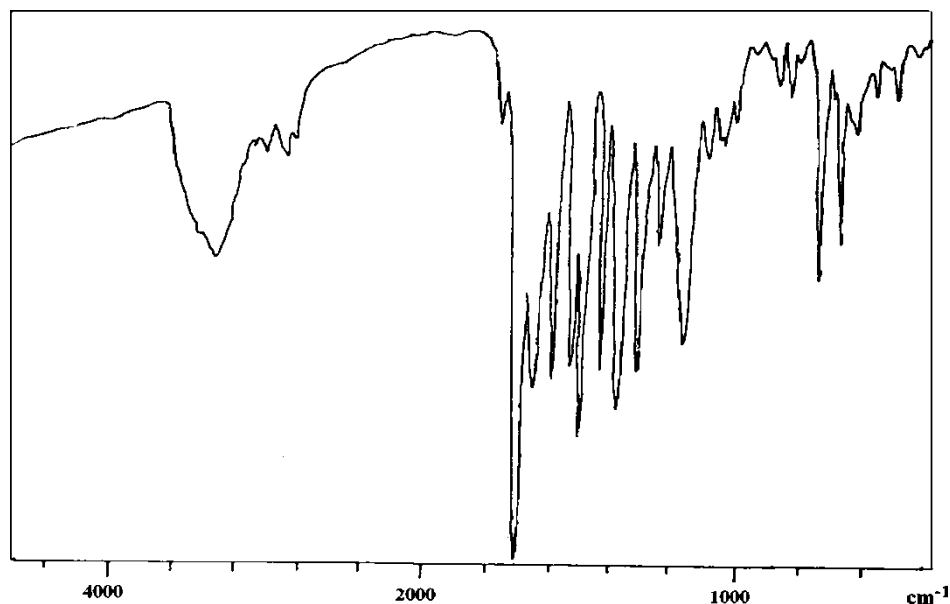


Figure 3. FT-IR spectrum of PMB.

bands observed at 1440 (Ar–N stretch), 1388 (C–N stretch), 1184 (C–N–C), 1109 cm^{-1} and 750 cm^{-1} . The broad medium intense band at 1660 cm^{-1} , strong intense band at 1508 cm^{-1} and a medium band at 1539 cm^{-1} correspond to the amide group. The broad stretching band at 3400–3300 cm^{-1} represent secondary amine (–NH).

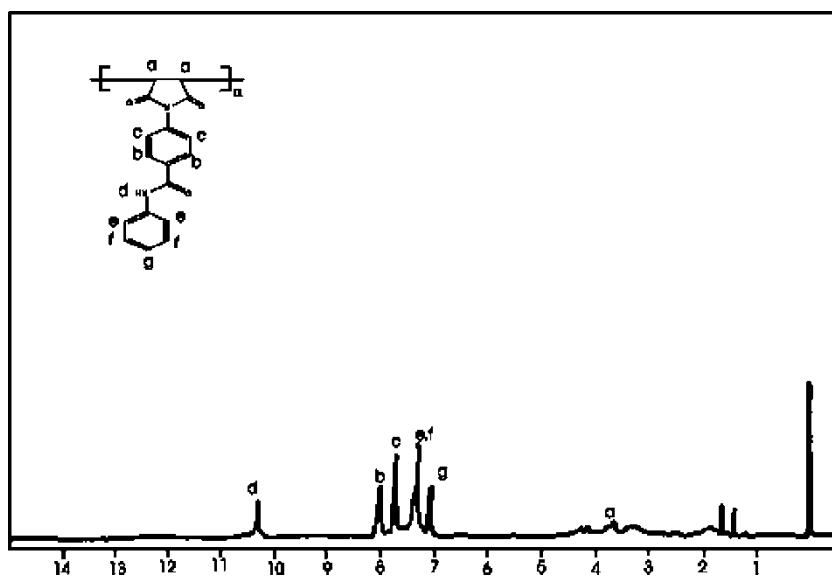


Figure 4. ^1H -NMR spectrum of PMB.

The δ observed at 7.23 ppm due to CH=CH in the monomer has shifted to 3.6–4.4 ppm in the polymer, as a result of the formation of a semi-flexible poly(substituted methine) – [CH–CH]_n– group (25). The δ for methine –(CH–CH)– protons has been reported in the range from 3.0–5.0 ppm depending upon the substitution in maleimide. The values of δ in the range 3.0–4.0 for poly[N-[4-N'-(α -methylbenzyl)aminocarbonyl phenyl]maleimide] (20), 3.5–4.5 for poly(N-alkyl substituted phenyl)maleimide (25) and poly[N-4-(cholesteroxycarbonyl phenyl)maleimide] (26) and 3.5–5.0 ppm for poly(N-phenylmaleimide) (27) have been reported. The broad peak at δ 7.0–8.1 ppm corresponds to 9 Ar-H. The δ at 1.4–2.0 ppm is due to terminal methyl protons of the AIBN moiety –(CN)–C–(CH₃)₂.

The major characteristic absorption bands (Figure 5 in cm⁻¹) are observed at 3400–3300 (broad, –NH stretch), 1780, 1730–1708 (C=O symmetric and asymmetric stretch in a five-member imide ring and C=O stretch of ester), 1612, 1514 (aromatic C=C and

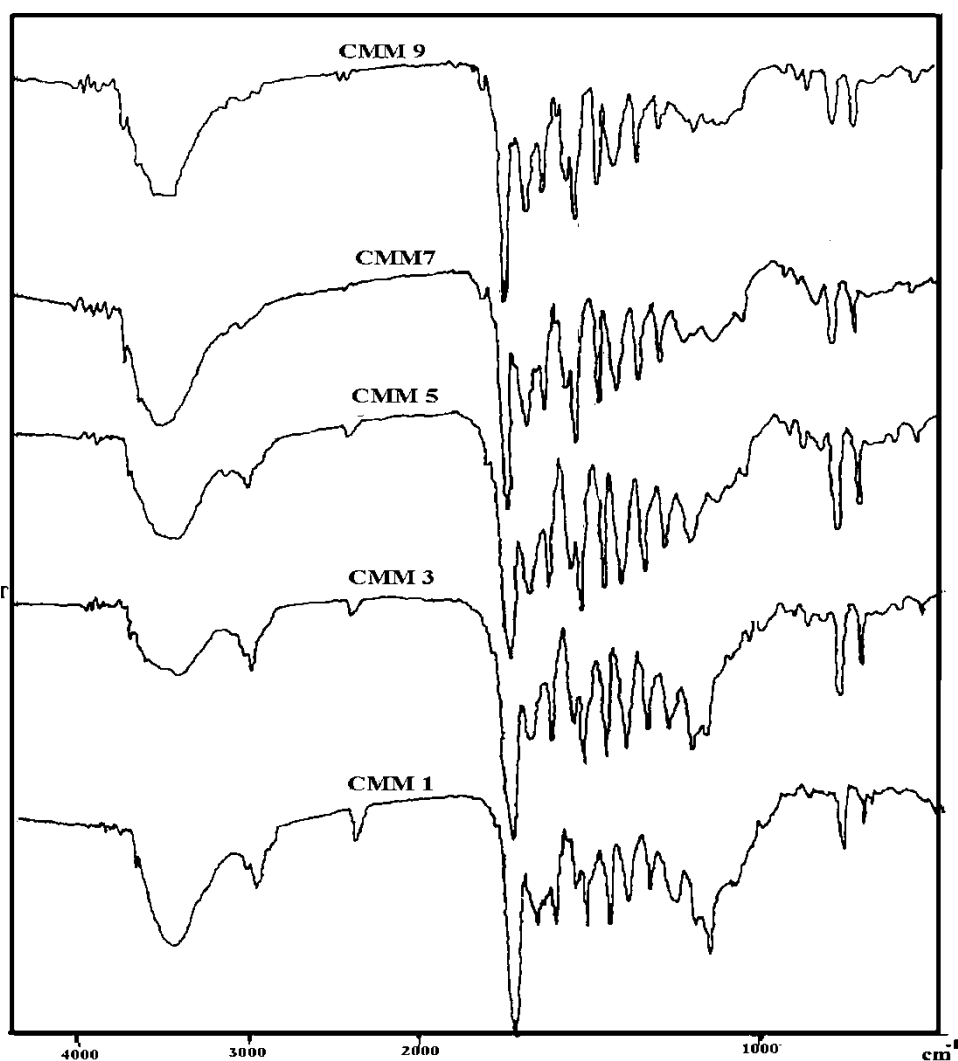


Figure 5. FT-IR spectrum of Copolymers CMM1, CMM3, CMM5, CMM7, and CMM9.

amide group). These characteristic bands confirm that units of both the monomers MB and MMA are present in the copolymer samples. The spectral pattern around frequencies 1780–1708 and 1612–1514 has undergone a change as the copolymer composition is varied. As the maleimide content was increased from 0.1 to 0.9 mole fractions in the feed, the band at 1732 due to ester group gradually drifts from 1732 to 1708 cm^{-1} , indicating the overlapping of C=O groups of maleimide and MMA. Furthermore, with the increase of imide content in the copolymer, the peak intensities at 1780 and 1614–1514 cm^{-1} have also gradually increased.

The $^1\text{H-NMR}$ in Figure 6 (a), (b), (c) for CMM1, CMM5, and CMM9 has the same absorption pattern with the variation in the peak intensities due to the variation in the contents in the copolymer. The δ at 8.00–8.15 ppm is of 2Ar–H, ortho- to N of imide group while at 7.70–7.85 ppm for 2Ar–H, meta- to N of imide group. The δ at 7.5–7.6 ppm is for 2Ar–H, ortho- to N of the amide group; at δ 7.3–7.5 ppm is for 2Ar–H, meta- to N of the amide group and at δ 7.0–7.2 (broad) is for 1Ar–H, para- to N of the amide group. A δ at 10.33 (broad) ppm appeared for 1H in –CONH– group of MB segment. The δ observed at δ 3.5–3.8 ppm corresponds to overlapping of 2H –(CH–CH)– in the polymer main chain and 3H (–OCH₃) of MMA segment. The δ in the range 0.7–1.4 ppm is of 3H of –CH₃ group while at 1.6–2.2 ppm for 2H of methylene group.

Monomer Reactivity Ratios

The copolymer composition for CMM samples were determined from the N% analysis (20, 25, 28). The monomer reactivity ratios were calculated using Finemann-Ross (29) and Kelen-Tudos (30) methods (Figure 7). The values of r_1 (MB) and r_2 (MMA) are given in Table 2. The Q_1 and e_1 values for the MB monomer, calculated by using the Alfrey and Price equation (31) are shown in Table 2.

The value r_1 (MB) is lower than r_2 (MMA) and the value of r_1 is less than unity. This indicates weakly ordered with predominantly random distribution of the monomer units in

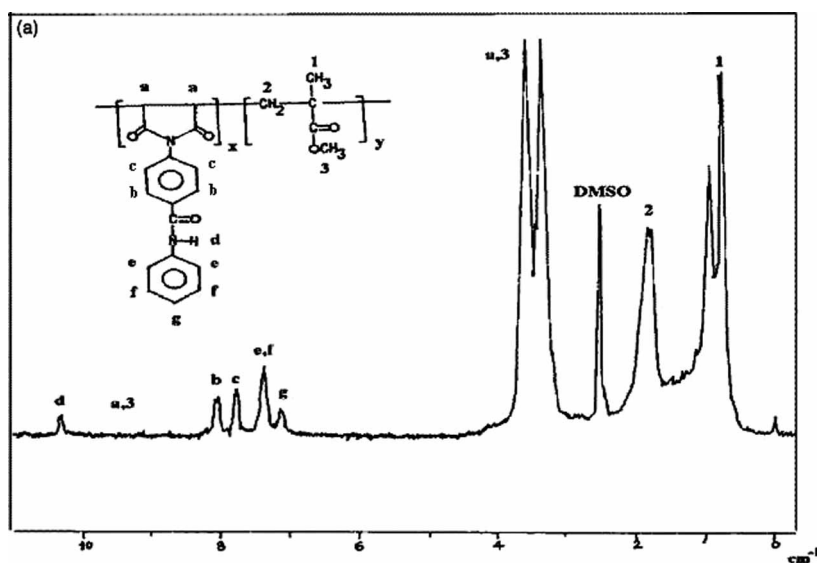


Figure 6. $^1\text{H-NMR}$ spectrum of copolymers (a) CMM1, (b) CMM5, and (c) CMM9.

(continued)

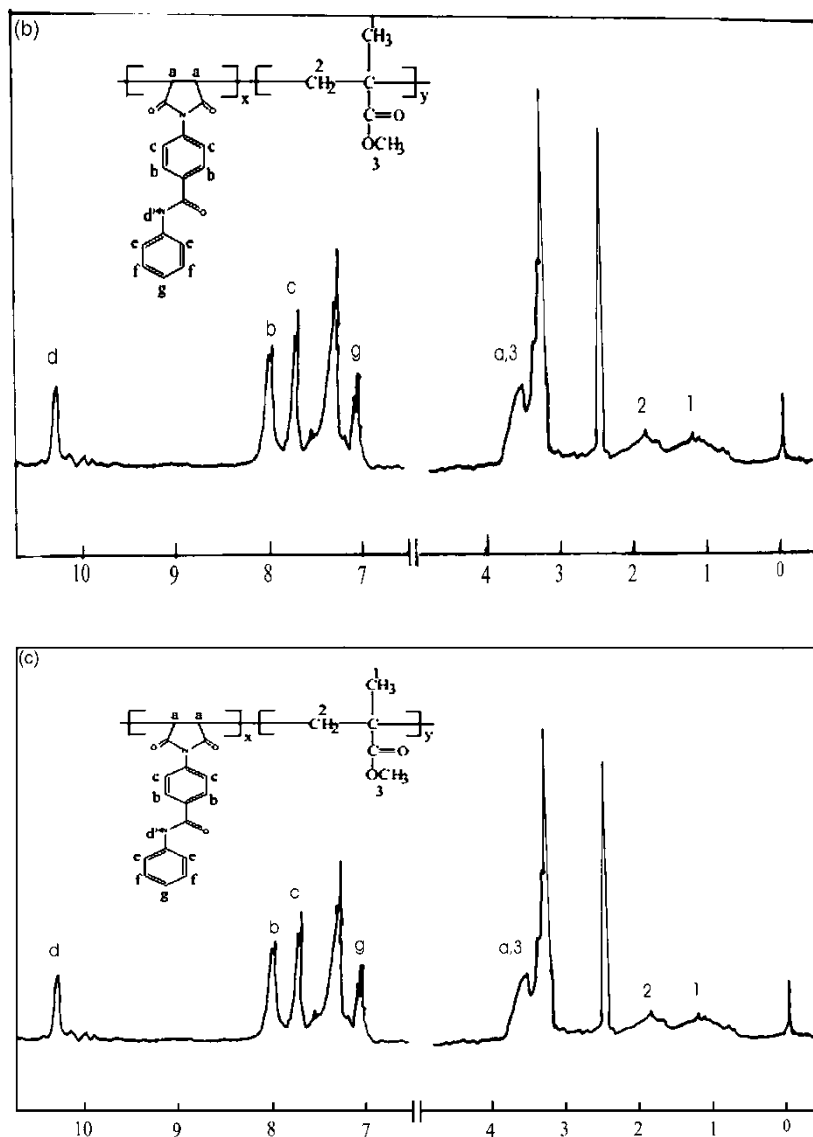


Figure 6. Continued.

the copolymer chain (32). The value of Q_1 and e_1 obtained are large. The large e_1 value correlates with strong electron acceptor nature of the maleimide monomer.

Thermal Studies

The thermograms (TG) were obtained by heating the polymer and copolymers samples in air at $10^\circ\text{C}/\text{min}$. Typical curves for PMMA, CMM1, CMM3, CMM5, CMM8 and PMB are presented in Figure 8. The temperatures for initial decomposition T_i , final decomposition T_f , and maximum rate of weight loss T_{max} determined from TGA for both homopolymers and nine copolymers are summarized in Table 3. The values of integral procedural

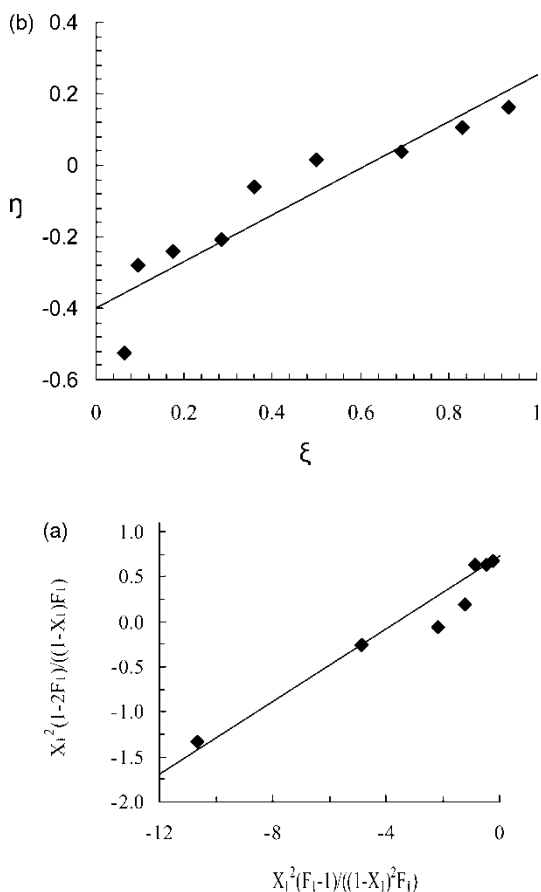


Figure 7. (a) Finemann-Ross plot (29) for copolymers CMM; (b) Kelen-Tudos plot (30) for copolymers CMM.

decomposition temperatures (IPDT) an index of thermal stability as proposed by Doyle (33) were determined from a mass loss curve are also included in the last column of Table 3.

As expected, the maleimide polymer PMB is a potential heat resistant material. Two-step degradation at temperature of over 300°C was observed for PMB. The T_f was about 718°C. The copolymer samples CMM1-CMM9 also decomposed through a two-step procedure. As the content of MB in the feed is increased, the copolymers began to

Table 2
Monomer reactivity ratios and parameter of the Alfrey-Price equation

System (M_1) (M_2)	Finemann-Ross method	Kelen-Tudos method	Q_1	e_1
MB-co-MMA				
r_1	0.20	0.20	1.68	1.77
r_2	0.73	0.79		

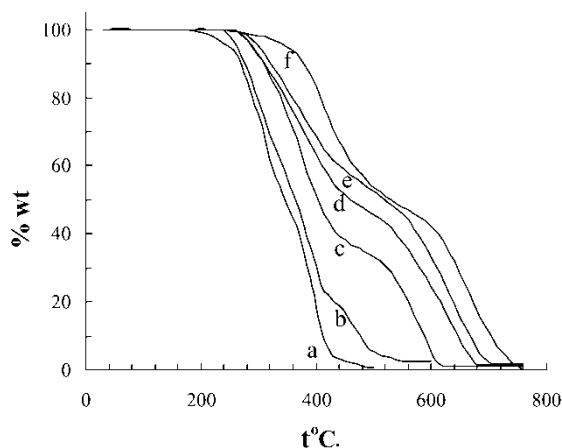


Figure 8. Thermograms of (a) PMMA, (b) CMM1, (c) CMM3, (d) CMM5, (e) CMM8, and (f) PMB.

decompose at higher T_i and the weight loss for the first-step became smaller. The first step weight loss ranged from 65.5 to 30.1%. The weight loss for the second-step became larger, increasing from 18.5 to 50.6% as the content of MB in copolymer is enhanced. The results in Table 3 clearly indicate that the thermal stability tends to increase as the MB content is

Table 3
Thermal behavior of polymer samples

Polymer	T_i (°C)	T_{max} (°C)	T_f (°C)	IPDT (°C)
PMB I	353	427	465	594
II	613	661	718	
PMMA I	212	310	496	400
CMM1 I	255	303	405	380
II	410	482	496	
CMM2 I	265	380	410	451
II	500	548	580	
CMM3 I	265	382	422	480
II	528	593	620	
CMM4 I	275	361	400	488
II	527	580	610	
CMM5 I	265	383	442	543
II	538	584	680	
CMM6 I	250	394	433	515
II	530	604	650	
CMM7 I	255	344	468	545
II	562	656	685	
CMM8 I	255	397	430	577
II	555	686	700	
CMM9 I	250	368	430	566
II	520	670	700	

Table 4
Activation energy E_a in kcal/mol of thermal degradation

Polymer	Step-I	Step-II
PMMA	13.00	—
PMB	28.86	57.22
CMM1	16.12	44.00
CMM2	15.88	63.52
CMM3	14.24	61.50
CMM4	17.20	65.52
CMM5	12.82	44.02
CMM6	11.68	52.52
CMM7	12.44	44.86
CMM8	13.08	46.24
CMM9	12.42	40.56

increased in the copolymers. The activation energy (E_a) of thermal degradation, given in Table 4, was estimated by employing the Broido method (34).

The values of E_a for the first step degradation for CMM1-CMM9 varies from 11.7 to 17.2 kcal mol⁻¹ while for the second step they are in the range of 40.6–65.5 kcal mol⁻¹. The value of E_a , 28.86 kcal mol⁻¹, for the first step degradation of PMB is considerably higher than 13.0 kcal mol⁻¹ for PMMA. The values of E_a of the first step degradation of copolymer samples is comparable with that of PMMA and one may infer that the first degradation-step may involve cleavage of MMA units while the second-step degradation involves cleavage of MB units.

Conclusions

A novel imide-amide monomer, 4-maleimidobenzanilide (MB) i.e., N-[4-N'-(phenylaminocarbonyl)phenyl]maleimide, is prepared from maleic anhydride, p-aminobenzoic acid and aniline. The investigated poly and copolymaleimide show excellent solubility in acetone, dioxane, THF, DMF, DMAc, DMSO, nitrobenzene, ethyl acetate and isobutyl acetate. The values of reactivity ratios indicate copolymers are weakly ordered with predominantly random distribution of the monomer units in the copolymer chain. The thermal stability tends to increase as the MB content is increased in the copolymers.

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