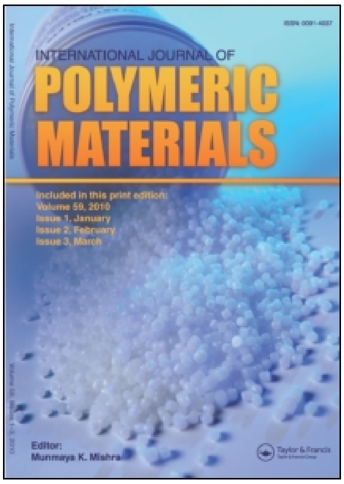


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Synthesis and Radical Copolymerization of Ethyl Acrylate and Butyl Acrylate with N-[4-N'-(Phenylamino-carbonyl) phenyl] maleimide

Shantilal Oswal[a]; Chetan B. Patel[a]; Naved I. Malek[a]
[a] Department of Chemistry, Veer Narmad South Gujarat University, Surat, India

To cite this Article Oswal, Shantilal , Patel, Chetan B. and Malek, Naved I.(2007) 'Synthesis and Radical Copolymerization of Ethyl Acrylate and Butyl Acrylate with N-[4-N'-(Phenylamino-carbonyl) phenyl] maleimide', International Journal of Polymeric Materials, 56: 1, 27 — 41

To link to this Article: DOI: 10.1080/00914030600701918

URL: http://dx.doi.org/10.1080/00914030600701918

International Journal of Polymeric Materials, 56:27–41, 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 0091-4037 print/1563-5333 online
DOI: 10.1080/00914030600701918

Synthesis and Radical Copolymerization of Ethyl Acrylate and Butyl Acrylate with N-[4-N′-(Phenylamino-carbonyl) phenyl] maleimide

Shantilal Oswal
Chetan B. Patel
Naved I. Malek
Department of Chemistry, Veer Narmad South Gujarat University,
Surat, India

Radical copolymerization of ethyl acrylate (EA) and butyl acrylate (BA) with 4-maleimidobenzanilide (MB), that is N-[4-N′-(phenylaminocarbonyl)phenyl] maleimide, initiated by AIBN was performed in THF solvent at 65°C. Nine copolymer samples of each type were prepared using different feed ratios of comonomers. All the polymer samples have been characterized by solubility test, 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 are 1.13 and 0.48 in MB/EA system and 0.45 and 0.52 MB/BA system. Alfrey-Price Q-e values for MB were $Q = 1.31$ and $e = 1.33$ in MB/EA and $Q = 2.04$ and $e = 2.06$ in MB/BA systems. The initial decomposition temperature of copolymer samples were in the range 310 to 365°C.

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

INTRODUCTION

There is a considerable interest not only in the synthesis of new types of plastic materials but also in the modification of exiting polymers in order to vary their properties to meet requirements for new

Received 27 January 2006; in final form 20 March 2006.

The authors acknowledge the Director, Department of Chemical Sciences, North Maharastra University, Jalagaon, for C, H, N analysis; Manager, Atul Industries Ltd., Atul, for scanning FT-IR spectra, and Heads, RSIC, CDRI Lucknow, and I.I.T. Powai, Mumbai, for scanning ^{1}H-NMR spectra.

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

applications under unusual working conditions. There are several classical vinyl polymers but they can not be used at high 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, Tg, has been widely used to improve the heat distortion temperature (HDT) [1–3].

During the past several years many publications appeared describing the chemical modification of various vinyl polymers such as methyl acrylate or methyl methacrylate by an addition of N-substituted maleimide [4–16]. It was observed that such copolymers have better thermal stability than the polymers of vinyl monomers. However, copolymerization of ethyl and butyl acrylates with N-substituted maleimide has not been investigated. The goal of this study is an assessment of ethyl and butyl acrylate monomers copolymerization with 4-maleimidobenzanilide (MB), whose incorporation into the backbone chain could present a considerable and promising interest. The MB monomer is a five member planer ring, which completely hinders the rotation of the imide residue around the backbone chain of the macromolecules and is expected to produce copolymers with a great structural stiffness as well as higher thermal stabilities. The physical, spectral, and thermal properties have been studied in order to characterize the copolymers. 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 and Kelen-Tudos methods.

EXPERIMENTAL

Materials

EA and BA (SISCO, AR) were 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-isobutyronitrile (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 [17]. DMF and methanol used in the present work were of Analytical Grade and were used as received.

Measurements

^{1}H-NMR spectra of polymer samples were taken in DMSO-d_6 on a Bruker DPX-200/DPX-300 Spectrometer at 200/300 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 ± 0.2°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°C/min.

Preparation of 4-maleimidobenzanilide (MB)

MB monomer was synthesized from maleic anhydride, p-aminobenzoic acid, and aniline, in four steps [18–20] as described in what follows and shown in Scheme 1.

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

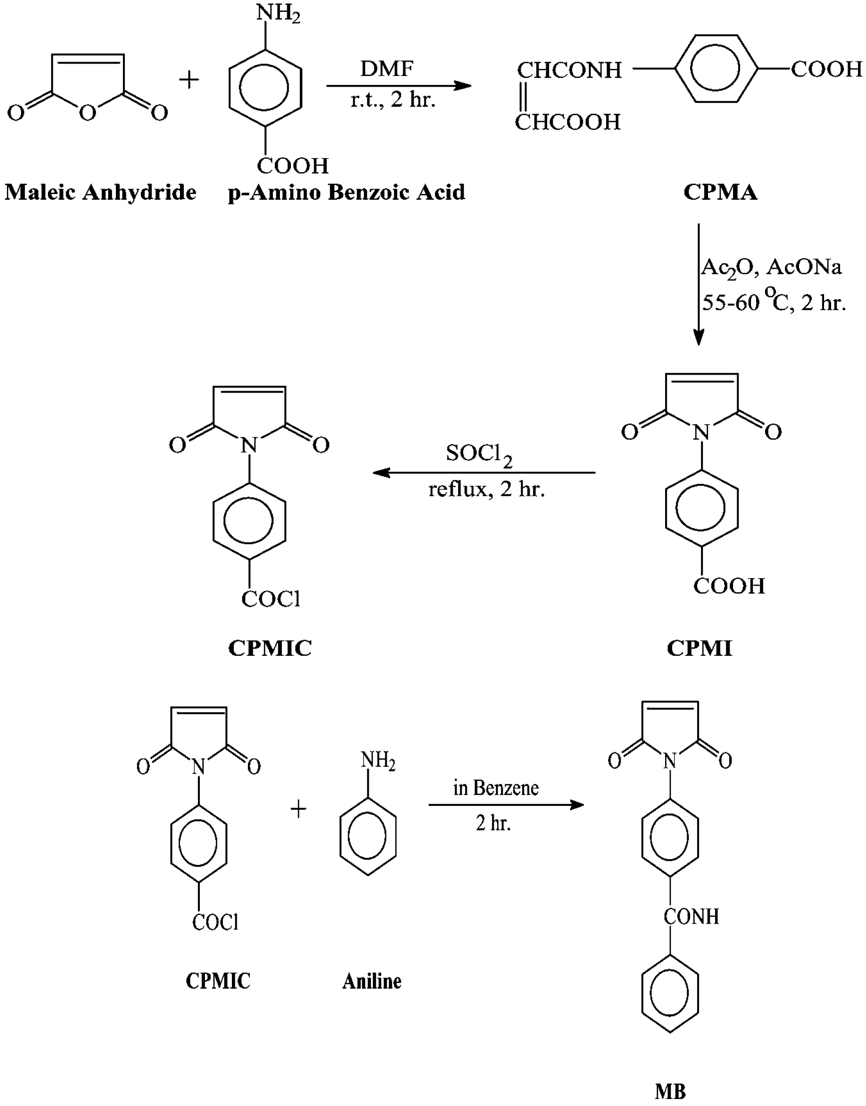
To a well-stirred solution of p-aminobenzoic acid (13.71 g, 0.1 mol) in DMF, a solution of maleic anhydride (9.81 g, 0.1 mol) in DMF was gradually added over a period of 15 min. The solution was stirred for 2 h at room temperature. The resulting solution was poured onto crushed ice to precipitate crude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



SCHEME 1 Monomer synthesis.

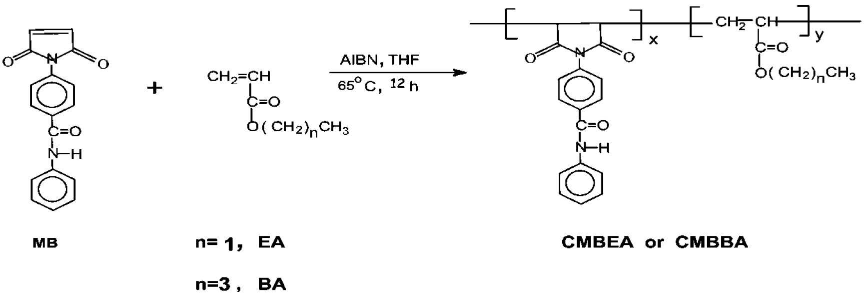
was distilled off. Light yellow crystals of acid chloride were obtained in 80% yield, mp 155–157°C (lit. mp 153–157°C [21] and 153°C [23]). The IR spectrum showed absorptions at 1776 (COCl), 1716 (–CONCO–), 1602 (C=C), 952, 825, 690 (CH=CH) cm^{-1}.

4-Maleimidobenzanilide (MB)

A benzene solution of aniline (5.7 ml, 0.063 mol) was added drop-wise 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 ^{1}H-NMR study. Anal. calcd. for $C_{17}H_{12}O_3N_2$, C, 69.86; H, 4.11; N, 9.59; Found C, 69.58; H, 4.15; N, 9.38. FT-IR: 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). ^{1}H-NMR (300 MHz, TMS, DMSO-d_6, δ, ppm): 7.23 (s, 2H, CH=CH); 8.06–8.03 (d, 2H in phenyl ring ortho- to maleimido); 7.80–7.77 (d, 2H in phenyl ring meta- 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, calculated amounts of comonomers EA or BA and MB in 35 ml THF were refluxed at 65°C for 12 h after adding 100 mg AIBN, with occasional shaking (Scheme 1). The copolymers samples were isolated by using an excess quantity of water containing 5% methanol. The 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.



SCHEME 2 Copolymerization of MB with EA and BA.

The nine-copolymer samples each of EA with MB (CMBEA1-CMBEA9) and of BA with MB (CMBBA1-CMBBA9), listed in Table 1, were prepared by the same procedure and identical reaction conditions as described in the preceding paragraph.

EA and BA were polymerized under identical conditions to that employed for the copolymerization of EA or BA and MB, except reducing the reaction to only 6 h. The PEA and PBA were isolated in water containing small amount of methanol. The homopolymers were precipitated and dried at 60°C under vacuum. The ^{1}H-NMR (200 MHz, DMSO-d_6, TMS) PEA:δ 1.28 ppm (3H, methyl), 1.58–1.75 ppm (2H, methylene), 2.07–2.23 ppm, (H, methine), 4.00 ppm (2H, $-OCH_2$); PBA : δ 1.24–1.31 ppm (2H, methylene) and 1.81–1.91 ppm (H, methine) in the polymer main chain, 0.95 ppm (3H, methyl), 1.37–1.54 ppm (4H, two methylene), 3.94 ppm (2H, $-OCH_2$).

TABLE 1 Radical Polymerization and Copolymerization of MB, EA and BA in THF at 65°C

Polymer code	Feed mol frac. of MB X_1	Polyn Time (h)	Yield (%)	Appearance*	$[\eta]$ dl/g	%N	Mol fract. of MB in copolymer F_1
Copolymer							
CMBEA1	0.1	12	78	LY-VL	0.231	3.90	0.190
CMBEA2	0.2	12	72	LY-S	0.219	5.47	0.312
CMBEA3	0.3	12	66	LY-S	0.206	6.04	0.368
CMBEA4	0.4	12	60	LY-S	0.194	6.92	0.470
CMBEA5	0.5	12	58	LY-S	0.188	7.63	0.571
CMBEA6	0.6	12	52	LY-S	0.179	8.22	0.673
CMBEA7	0.7	12	48	LY-S	0.166	8.70	0.770
CMBEA8	0.8	12	40	LY-S	0.151	9.02	0.844
CMBEA9	0.9	12	35	LY-S	0.128	9.28	0.912
CMBBA1	0.1	12	80	LY-S	0.240	2.85	0.156
CMBBA2	0.2	12	73	LY-S	0.227	3.72	0.218
CMBBA3	0.3	12	69	LY-S	0.211	4.98	0.321
CMBBA4	0.4	12	64	LY-S	0.201	5.49	0.370
CMBBA5	0.5	12	59	LY-S	0.191	6.45	0.474
CMBBA6	0.6	12	55	LY-S	0.184	7.37	0.593
CMBBA7	0.7	12	45	LY-S	0.170	7.73	0.646
CMBBA8	0.8	12	36	LY-S	0.154	8.25	0.730
CMBBA9	0.9	12	30	LY-S	0.133	8.72	0.815
Homopolymer							
PMP**	1.0	24	55	LY-S	0.141	9.38	
PEA	0.0	6	78	Wh-VL	0.316	0.0	
PBEA	0.0	6	85	Wh-VL	0.322	0.0	

*LY, Wh, S, and VL stand for light yellow, white, solid, and viscous liquid.

**From Reference [5].

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 of average [η] in DMF solution at 30°C are listed in Table 1. The values of [η] decrease from 0.316 to 0.128 dl/g and 0.322 to 0.133 dl/g for copolymers of MB with EA and BA, respectively, as the content of MB in the copolymer increased.

Solubility Behavior

Table 2 summarizes the relative solubilities of selected copolymer samples CMBEA1, CMBEA5, CMBEA9, CMBBA1, CMBBA5, and CMBBA9 in number of polar and nonpolar solvents at 30°C. The investigated copolymer samples are soluble in acetone, dioxane, THF, DMF, DMAc, DMSO, benzene, nitrobenzene, ethyl acetate, isobutyl acetate, and chloroform. They are partially soluble in carbon tetrachloride, o-xylene, and toluene. Solubility behavior in the latter solvents

TABLE 2 Solubility Behavior of Selected Copolymer Samples of CMBEA and CMBBA in Polar and Non-polar Solvents at 30°C

	CMBEA			CMBBA		
Solvent	1	5	9	1	5	9
Acetone	S	S	S	S	S	S
Dioxane	S	S	S	S	S	S
THF	S	S	S	S	S	S
DMF	S	S	S	S	S	S
DMAc	S	S	S	S	S	S
DMSO	S	S	S	S	S	S
Benzene	S	S	S	S	S	S
Nitrobenzene	S	S	S	S	S	S
Ethyl acetate	S	S	S	S	S	S
Isobutyl acetate	S	S	S	S	S	S
Chloroform	S	S	S	S	S	S
CCl_4	S	IS	IS	S	IS	IS
o-Xylene	PS	IS	IS	PS	IS	IS
Toluene	S	IS	IS	S	IS	IS
Hexane	IS	IS	IS	IS	IS	IS
Cyclohexane	IS	IS	IS	IS	IS	IS
Methanol	S	IS	IS	S	IS	IS
Ethanol	S	IS	IS	S	IS	IS

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

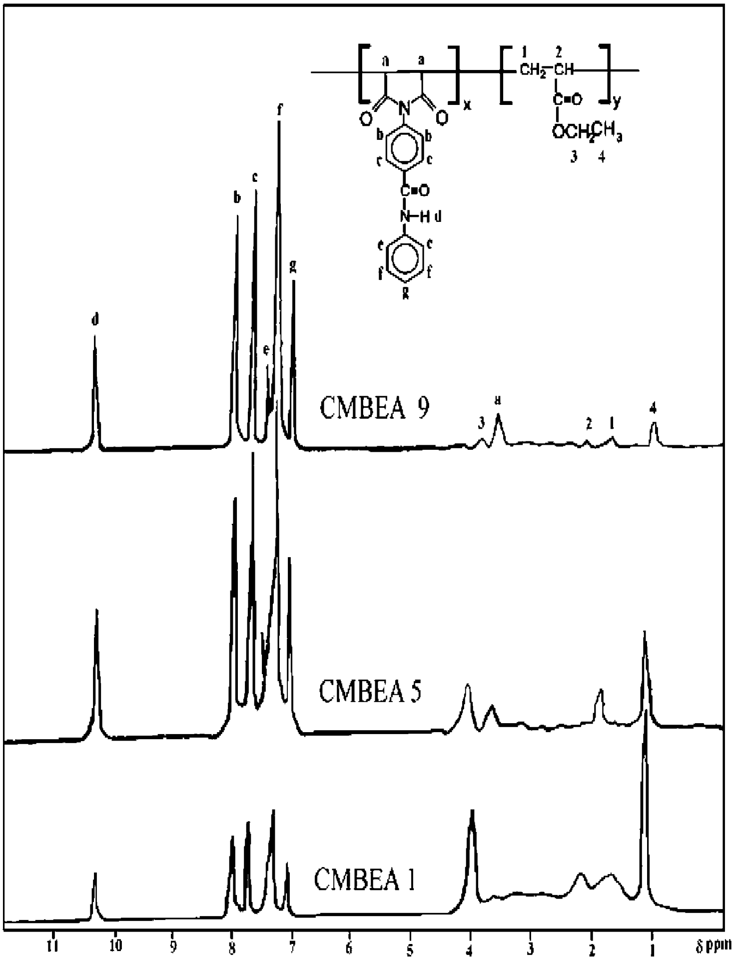


FIGURE 1 ^{1}H-NMR spectrum of copolymers (a) CMBEA1, (b) CMBEA5, and (c) CMBEA9 at 200 MHz in DMSO-d_6.

depends on the composition of copolymer. The solubility decreases with increase in the content of maleimide in copolymer.

Spectral Characterization

The major characteristic absorption bands at 3400–3300 (broad, –NH stretch), 3060 (aromatic C–H stretch), 1775, 1730–1710 (C=O symmetric and asymmetric stretch in a five-member imide ring [10] and C=O stretch of ester), 1660–1650, 1539 (CONH), 1600, 1508 (aromatic

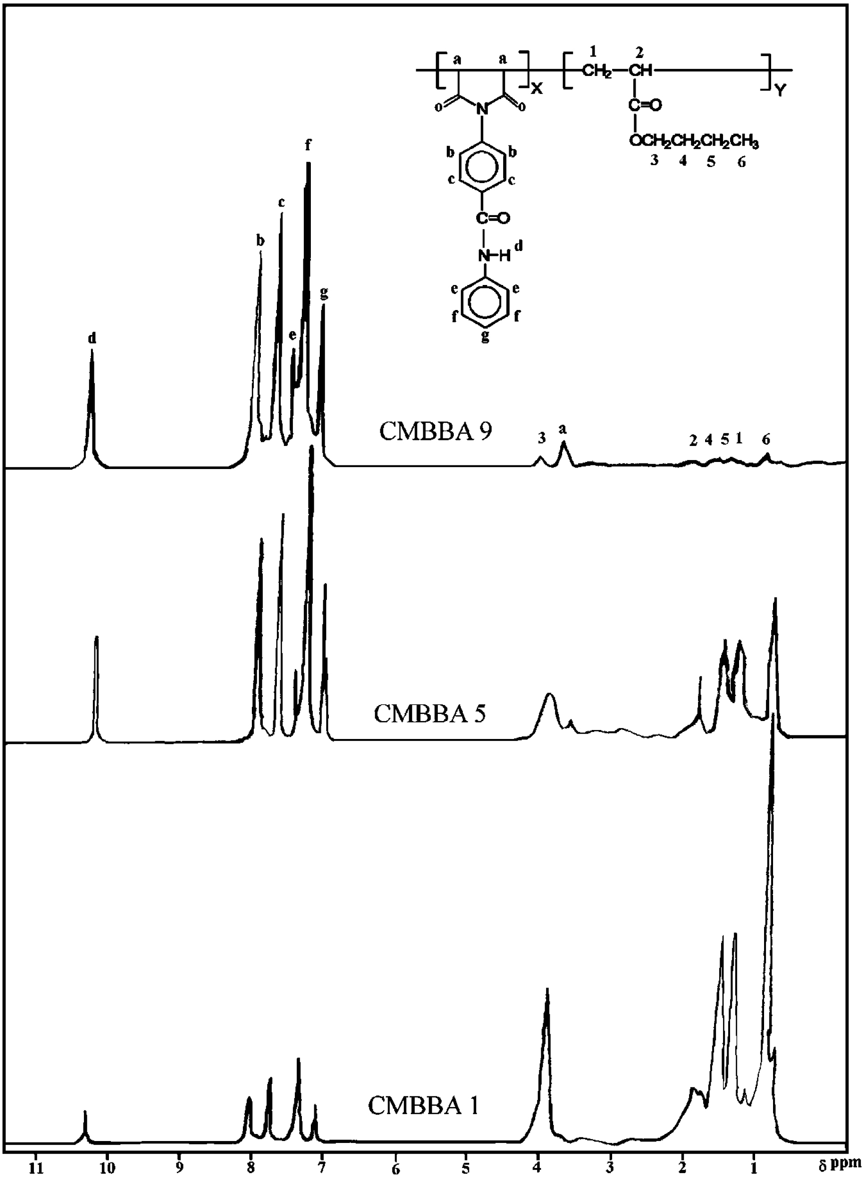


FIGURE 2 ^{1}H-NMR spectrum of copolymers (a) CMBBA1, (b) CMBBA5, and (c) CMBBA9 at 200 MHz in DMSO-d_6.

C=C stretch) in cm^{-1} confirm that units of both the monomers MB and EA/BA are present in the copolymer samples. The spectral pattern around frequencies 1780, 1708, and 1612–1514 has undergone a change as the copolymer composition was varied. The carbonyl absorption of MB at 1705 cm^{-1} merged with that of EA/BA to form single peak from 1730 to 1710 cm^{-1}. Its exact position depends on the relative contribution from MB and EA/BA. Further, with the increase of imide content in the copolymer the peak intensities at 1775 and 1612–1514 cm^{-1} have also gradually increased.

^{1}H-NMR for CMBEA1, CMBEA5, and CMBEA9 and CMBBA1, CMBBA5, and CMBBA9, shown in Figures 1 and 2, respectively, are consistent with the structure of the copolymer samples. The δ 7.23 observed for vinyl group (CH=CH) in the monomer MB[16] has been shifted to 3.6–3.8 ppm due to formation of $-[CH-CH]_n-$[20] in all copolymer samples. Further, it is observed that the intensity of Ar−H increases from CMBEA1 → CMBEA5 → CMBEA9 and from CMBBA1 → CMBBA5 → CMBBA9 whereas it decreases for methyl protons.

Monomer Reactivity Ratios

The composition for copolymer samples were determined from the N% analysis [10,20,24], which is shown in Figure 3. The monomer reactivity ratios were calculated using Fineman and Ross' [25] and Kelen and Tudos' [26] methods (Figures 4 and 5). The values of r_1 (MB) and

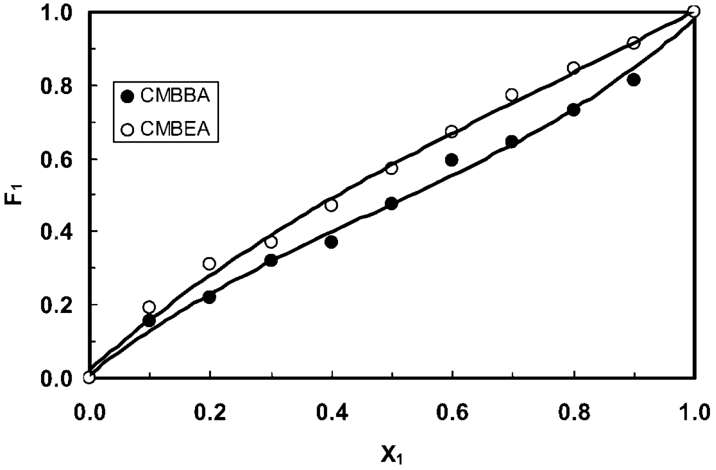


FIGURE 3 Variation of copolymer composition as a function of feed composition.

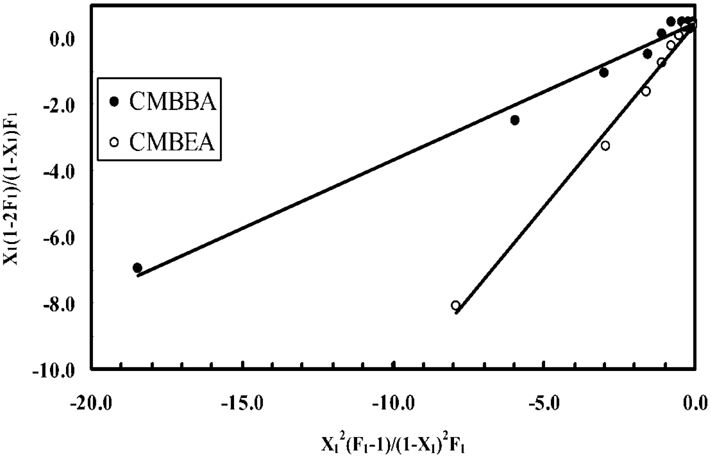


FIGURE 4 Finemann-Ross plots [25] for copolymers CMBEA and CMBBA.

r_2 (EA and BA) are given in Table 3. The average values of r_1 and r_2 are 1.13 and 0.48 in the MB/EA system and 0.45 and 0.52 in the MB/BA system. Alfrey and Price [27] Q-e values for MB were calculated as $Q = 1.31$ and $e = 1.33$ in the MB/EA system and $Q = 2.04$ and $e = 2.06$ in the MB/BA system. The large e value correlates with strong electron acceptor nature of the maleimide monomer.

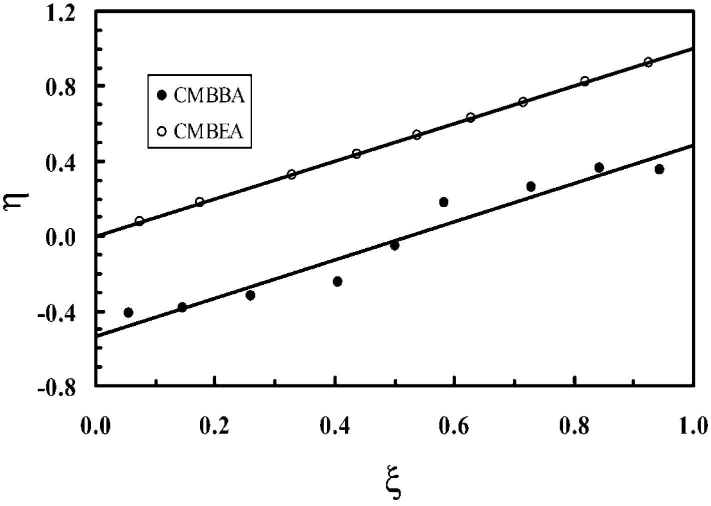


FIGURE 5 Kelen-Tudos plots [26] for copolymers CMBEA and CMBBA.

TABLE 3 Monomer Reactivity Ratios in Copolymers

	CMBEA		CMBBA	
Method	r_1	r_2	r_1	r_2
Finemann-Ross	1.11	0.44	0.41	0.44
Kelen-Tudos	1.15	0.51	0.48	0.59

Thermal Studies

The thermograms were obtained by heating copolymers samples in air at 10°C/min. The typical curves for CMBEA2, CMBEA5, CMBEA9, CMBBA2, CMBBA5, and CMBBA9 are presented in Figures 6 and 7. The temperatures for initial decomposition T_i, final decomposition T_f, and maximum rate of weight loss T_{max} determined from TGA are summarized in Table 4. The values of integral procedural decomposition temperatures (IPDT), an index of thermal stability as proposed by Doyle [28], were determined from a mass loss curve and are included in the Penultimate column of Table 4.

CMBEA. The copolymer samples CMBEA2, CMBEA5, and CMBEA9 decomposed through a two-step process. As the content of MB in the feed is increased, the copolymers began to decompose at

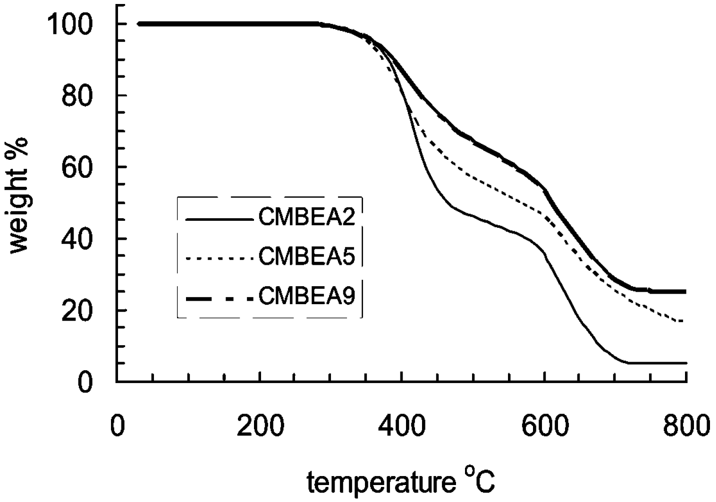


FIGURE 6 Thermograms of CMBEA2, CMBEA5, and CMBEA9 in air at heating rate of 10°C/min.

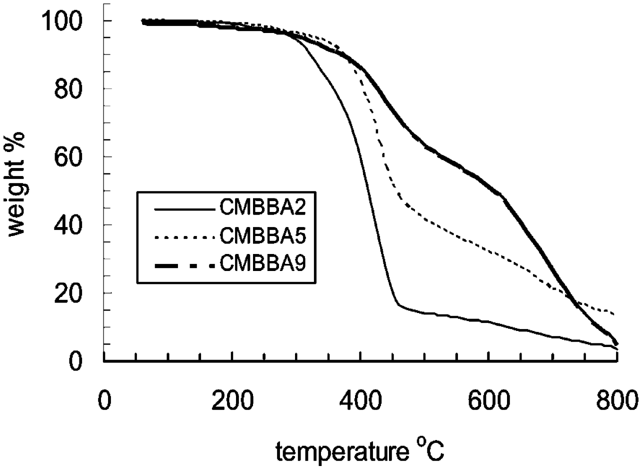


FIGURE 7 Thermograms of CMBBA2, CMBBA5, and CMBBA9 in air at heating rate of 10°C/min.

higher T_i and the weight loss for the first step became smaller. The first step weight loss ranged from 54.0 to 34.8%. The weight loss for the second-step became larger, increasing from 30.6 to 38.8% as the content of MB in copolymer is enhanced.

TABLE 4 Thermal Behavior of Copolymer Samples

Polymer	T_i°C	T_{max}°C	T_f°C	IPDT°C	Residue at 500°C, %
CMBEA2					
I	320	416	520	582	45.9
II	520	626	710		
CMBEA5					
I	319	405	530	591	56.6
II	530	633	720		
CMBEA9					
I	317	414	530	602	66.9
II	530	615	703		
CMBEA2					
I	310	428	470	409	20.7
CMBEA5					
I	363	430	530	608	44.6
II	635	667	760		
CMBEA9					
I	365	436	550	647	67.0
II	590	663	800		

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

Polymer	Step-I	Step-II
CMBEA2	35.7	44.3
CMBEA5	28.1	35.9
CMBEA9	26.6	39.3
CMBEA2	27.8	—
CMBEA5	38.8	48.9
CMBEA9	29.8	36.8

CMBBA. The copolymer sample CMBBA2 decomposed in a single-step, whereas CMBBA5 and CMBBA9 decomposed through a two-step process. As the content of MB in the feed is increased, the copolymers began to decompose at higher T_i and the weight loss for the first step became smaller. The first step weight loss ranged from 75.9 to 33.2%. The weight loss for the second step increased from 13.3 to 37.3% as the content of MB in copolymer was enhanced. The results in Table 4 clearly indicate that the thermal stability tends to increase as the MB content is increased in the copolymers.

The activation energy (E_a) of thermal degradation, given in Table 5, was estimated by employing the Broido method [29]. The values of E_a for the first step degradation for CMBEA2-CMBEA9 varies from 26.6 to 35.7 kcal mol^{-1}, whereas for the second step they are in the range of 35.9–44.3 kcal mol^{-1}. The values of E_a for the first step degradation for CMBBA2-CMBBA9 varies from 27.8 to 38.8 kcal mol^{-1}, whereas for the second step they are in the range of 36.8–48.9 kcal mol^{-1}.

CONCLUSIONS

The investigated copolymaleimides CMBEA and CMBBA 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 1.13 and 0.48 in the MB/EA system and 0.45 and 0.52 in the MB/BA system. Alfrey-Price Q-e values for MB were calculated as $Q = 1.31$ and $e = 1.33$ in the MB/EA system and $Q = 2.04$ and $e = 2.06$ in the MB/BA system. The copolymers show good thermal stability, which tends to increase as the MB content is increased.

REFERENCES

[1] Nield, E. and Rose J. B., U.S. Patent. 3, 652, 726 (1972).
[2] Sato, H., *Jpn. Kokai.* **87**, 156115 (1987).

[3] Masuko, S., Takahara, H., and Yamamoto, A., *Jpn. Kokai.* **88**, 245413 (1988).
[4] Coleman Jr., L. E. and Conrady, J. A., *J. Polym. Sci.* **38**, 241 (1959).
[5] Takase, I., Fukushima, N., Aida, H., and Yamada, M., *Kobunshi Kagaku* **30** (10), 632 (1973).
[6] Barrales-Rienda, J. M., Gonzalez de la, Campa, J. I., and Gonzalez Ramos, J., *J. Macromol. Sci. Chem.* **A11**, 267 (1977).
[7] Oishi, T., *Polym. J.* **13**, 65 (1981).
[8] Patel, J. D. and Patel, M. R., *J. Macromol. Sci. Chem.* **A19**, 801 (1983).
[9] Patel, J. D. and Patel, M. R., *J. Polym. Sci. Polym. Chem. Ed.* **21**, 3027 (1983).
[10] Nair, C. P. R., *Macromolecules* **26**, 47 (1993).
[11] Choudhary, L., Varma, D. S., Varma, I. K., and Wang, F. W., *J. Therm. Anal.* **39**, 633 (1993).
[12] Bharel, R., Choudhary, V., and Varma, I. K., *J. Appl. Polym. Sci.* **54**, 2165 (1994).
[13] Choudhary, V. and Mishra, A., *J. Appl. Polym. Sci.* **62**, 707 (1996).
[14] Salman, I. A., Al-Sagheer, F. A., and Elsabee, M. Z., *J. Macromol. Sci. Pure & Appl. Chem.* A., **34** (7), 1207 (1997).
[15] Ryttle, A., *Angew. Makromol. Chem.* **267**, 67 (1999).
[16] Patel, C. B., Malek, N. I., and Oswal, S. L., *J. Macromol. Sci. Part A Pure & Appl. Chem.* **43**, 289 (2006).
[17] Riddick, J. A., Bunger, W. B., and Sakano, T. K. (1986). *Organic Solvents Physical Properties and Methods of Purification*, Wiley Interscience, New York. p. 582ff.
[18] Searle, N. E., Synthesis of N-Arylmaleimides. U.S. Patent 2, 444, 536 (1948).
[19] Hoyt, A. E. and Benicewicz, B. C., *J. Polym. Sci. Part A Polym. Chem.* **28**, 3403 (1990).
[20] Oishi, T. and Fujimoto, M., *J. Polym. Sci. Part A Polym. Chem.* **30**, 1821 (1992).
[21] Park, J. O. and Jang, S. H., *J. Polym. Sci. Part A Polym. Chem.* **30**, 723 (1992).
[22] Liu, F. J., Munukuila, S., Livon, K., and Lisoko, G., *J. Polym. Sci. Part A Polym. Chem.* **30**, 157 (1992).
[23] Sadhir, R. K. and Smith, J. D. B., *J. Polym. Sci. Polym. Chem. Ed.* **30**, 589 (1992).
[24] Matsumoto, A., Kubota, T., and Otsu, T., *Macromolecules* **23**, 4508 (1990).
[25] Fineman, M. and Ross, S. D., *J. Polym. Sci.* **5**, 259 (1950).
[26] Kelen, T. and Tudos, F., *J. Macromol. Sci. Chem.* **A9** (1), 1 (1975).
[27] Alfrey Jr., T. and Price, C. C., *J. Polym. Sci.* **2**, 101 (1947).
[28] Doyle, C. D., *Anal. Chem.* **33** (1), 77 (1961).
[29] Broido, A., *J. Polym. Sci.* **A2** (7), 1761 (1968).