Copolymerization of *N*-Substituted Maleimide with Alkyl Acrylate and Its Industrial Applications

S. THAMIZHARASI, B. S. R. REDDY

Central Leather Research Institute, Adyar, Chennai 600 020, India

ABSTRACT: A series of new copolymers with desired thermal stability and mechanical properties for applications in leather industry were synthesized from various substituted maleimides and alkyl acrylates. Polymerization was carried out by a free-radical polymerization using benzoyl peroxide (BPO) as initiator. The monomers and polymers synthesized were characterized by elemental analysis, IR, and nuclear magnetic resonance (NMR). Interestingly, these polymers were soluble in common organic solvents. Copolymer composition and reactivity ratios were determined by ^{1}H-NMR spectra. The molecular weights of the polymers were determined by gel permeation chromatography. The homo- and copolymer of maleimide showed single-stage decomposition (ranging from 300–580°C). The initial decomposition temperatures of poly[*N*-(phenyl)-maleimide] [poly(PM)], poly[*N*-4-(methylphenyl)maleimide] [poly(MPM)] and poly[*N*-3-(chlorophenyl)maleimide] [poly(CPM)] were higher compared to those of the copolymers. Heat-resistant adhesives such as blends of epoxy resin with phenyl-substituted maleimide-*co*-glycidyl methacrylate copolymers with improved adhesion property were developed. Different adhesive formulations of these copolymaleimides were prepared by curing with diethanolamine at two different temperatures (30°C and 60°C). © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1870–1879, 2001

Key words: maleimides; acrylates; reactivity ratios; thermal studies; adhesive

INTRODUCTION

Tawney et al.[1] first polymerized maleimides by free-radical polymerization. Studies have been done of the adhesive properties of polystyrene with maleimide copolymers for reinforcement.[2] Tapolsky[3] has reported on bimaleimide-functionalized nonlinear optics (NLO) chromophore polymerized with amine to yield a thermally stable crosslinked matrix. Chang et al.[4] have reportedon their investigation of second-order NLO for *N*-phenyl maleimide polymers, which exhibited a high glass-transition temperature because of a rigid imide ring in the backbone.[5,6] The processibility of imide polymers can be enhanced by the incorporation of more flexible units such as arylene ether segments within the polymer backbone.[7] These imide-based materials have been found to have versatile applications in industries ranging from aerospace to the medical and microelectronics fields. Thus, the incorporation of oligomers and epoxy groups as components in adhesives and composites leads to high-strength joints[8] used in several industrial applications.

Information on adhesives based on epoxy and acrylic latex has been reported by Hisatumi et al.[9] The versatility of epoxy–amine modifiers was explained in detail by Pullian et al.[10] Buchner et
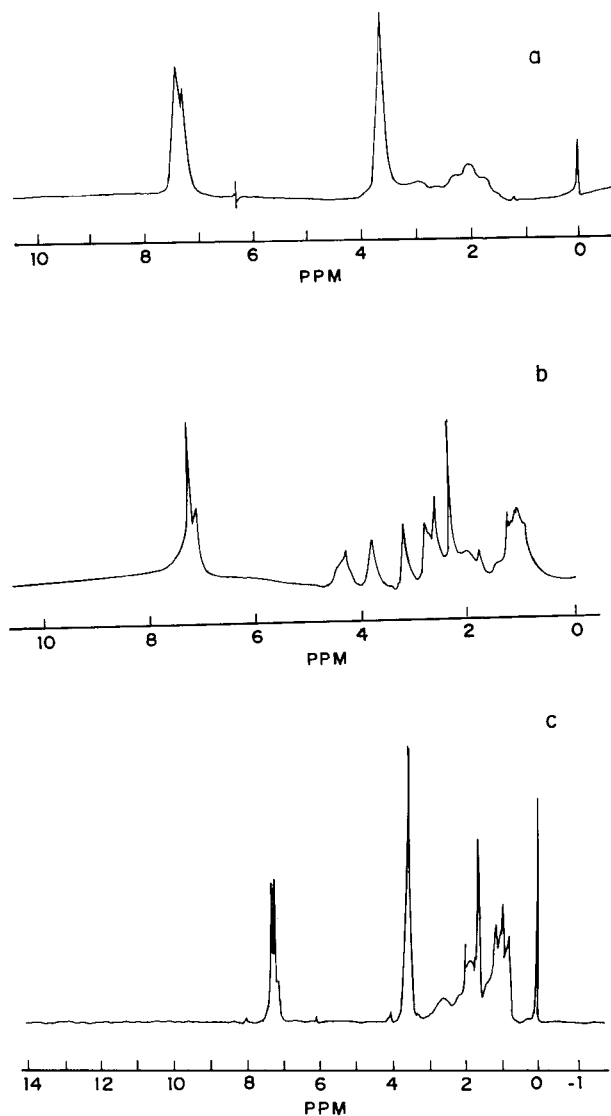
Figure 1   ^{1}H-NMR spectra of (a) poly(PM-*co*-MA), (b) poly(MPM-*co*-GMA), and (c) poly(CPM-*co*-BA).

al.[11] studied the dispersion of epoxy resins with the help of surfactants. Detailed studies on the network structure, characterization, and physico-chemical properties of crosslinked epoxy resins have also been reported.[12,13] This article deals with the synthesis, characterization, and reactivity ratios of three maleimide–acrylate copolymers. High-temperature-resistant adhesives as specialty chemicals for leather-to-leather bonding are in great demand for industrial applications. It is well known that epoxy resins are both brittle and very good adhesives. Perhaps when they are blended with rubber or acrylic compounds, they will likely to impart flexibility. With this in mind,

an attempt was made to develop adhesives for industrial applications.

EXPERIMENTAL

Purification of Solvents

Solvents used were purified according to standard procedures. The monomers used were washed with both a 10% NaOH solution and water, then dried in anhydrous Na_2CO_3 and distilled under reduced pressure.

Preparation of Monomers

Synthesis of N-(4-Methylphenyl)maleanilic Acid

To a three-necked flask provided with a paddle stirrer, maleic anhydride and 50 mL of diethyl
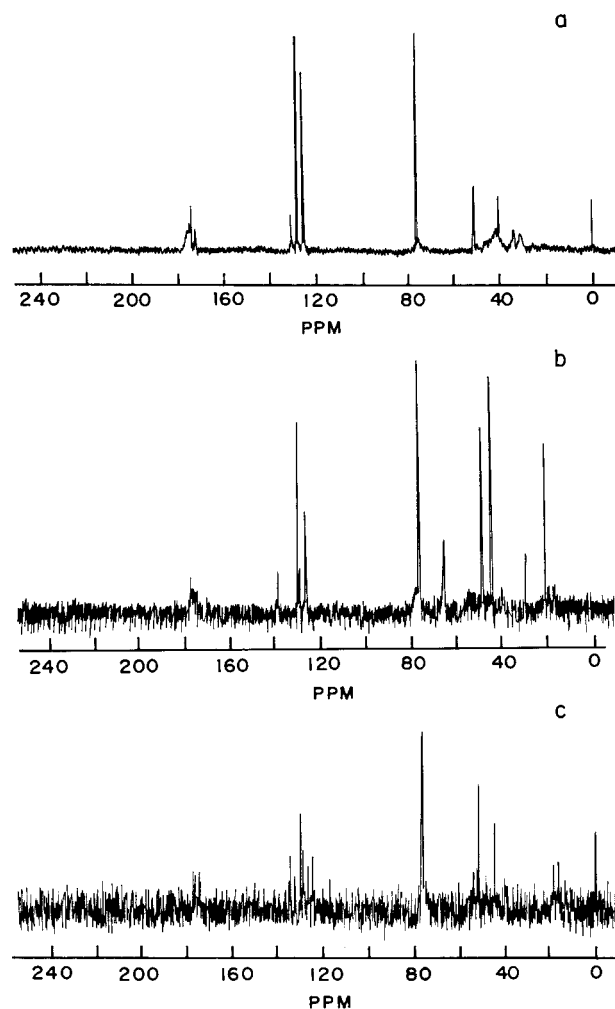
Figure 2   [13]-CMR spectra of (a) poly(PM-*co*-MA) (b) poly(MPM-*co*-GMA), and (c) poly(CPM-*co*-BA).

Table I   Copolymerization Data of Copolymers

|							
(I) Data for Copoly(PM–MA) System							
	Feed Composition in Mole Fraction			^{1}H-NMR Data		Copolymer Composition in Mole Fraction	
Sl. No.	M_1	M_2	Conversion	I_{Ar}	I_{ali}	m_1	m_2
1.	0.210	0.790	8.34	0.7	8.6	0.092	0.908
2.	0.348	0.652	11.21	1.4	8.5	0.175	0.825
3.	0.549	0.451	10.36	2.2	6.7	0.312	0.688
4.	0.651	0.349	9.84	2.4	4.9	0.422	0.578
5.	0.804	0.196	7.62	3.6	4.2	0.610	0.390
(II) Data for Copoly(MPM–GMA) System							
	Feed Composition in Mole Fraction			^{1}H-NMR Data		Copolymer Composition in Mole Fraction	
Sl. No.	M_1	M_2	Conversion	I_{Ar}	I_{ali}	m_1	m_2
1.	0.201	0.799	11.2	0.05	0.85	0.137	0.863
2.	0.362	0.638	8.4	0.20	1.62	0.267	0.733
3.	0.498	0.502	14.3	0.36	1.86	0.389	0.611
4.	0.648	0.352	11.7	0.28	1.02	0.511	0.489
5.	0.812	0.188	7.3	0.85	2.20	0.651	0.349
(III) Data for Copoly(CPM–BA) System							
	Feed Composition in Mole Fraction			^{1}H-NMR Data		Copolymer Composition in Mole Fraction	
Sl. No.	M_1	M_2	Conversion	I_{Ar}	I_{ali}	m_1	m_2
1.	0.186	0.814	8.84	0.3	8.2	0.101	0.899
2.	0.301	0.699	9.12	0.6	7.2	0.175	0.822
3.	0.512	0.488	10.34	1.4	6.4	0.424	0.576
4.	0.648	0.352	7.32	3.1	5.4	0.707	0.293
5.	0.810	0.190	11.14	3.0	3.3	0.833	0.167

ether were stirred until the maleic anhydride was dissolved completely. A solution of 4.28 g (0.02 mol) of toluidine in 4 mL of diethyl ether was run through a separating funnel. The resulting thick suspension was stirred at room temperature for 1 h and cooled in an ice bath. The product was filtered and dried; it had a yield of 86% and a 184°C mp.

Synthesis of N-(4-methylphenyl)maleimide

To synthesize MPM [N-(4-methylphenyl)maleimide] 13.4 mL (0.13 mol) of acetic anhydride and

1.3 g (0.015 mol) of anhydrous sodium acetate were put in a conical flask. Then 4.1 g (0.02 mol) of maleanilic acid was added, and the suspension was stirred for 1 h and then poured into cold water. It was washed thoroughly with water and petroleum ether and then recrystallized from cyclohexane. It had a yield of 78% and a 152–154°C mp.

^{1}H-NMR (CDCl$_3$): δ 7.04–7.34 (s, Ar, 5H), 6.78 (s, CH=, 2$\underline{H}$) and 2.24 (s, CH$_3$, 3H).
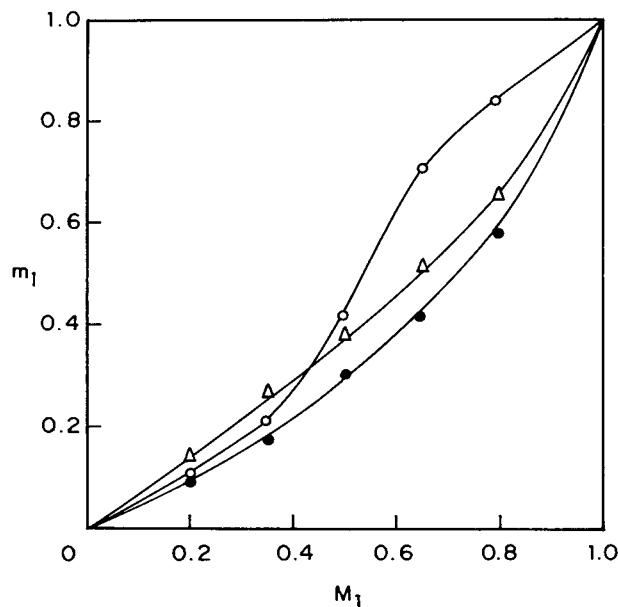
Figure 3 K–T plots of poly(MPM-*co*-GMA), poly-(CPM-*co*-BA), and poly(PM-*co*-MA).

^{13}C-NMR (CDCl$_3$): δ 165.05 (C=O), 134.2 (C=C), 129.2, 127.6, 126.3, 121.2 133.8 (Ar).

Microelemental ANAL. Calcd. for C$_{11}$H$_{12}$O$_3$N: C, 64.07%; H, 5.87%; N, 6.79%. Found: C, 64.08%; H, 5.89%; N, 6.80%.

The above-mentioned synthetic procedure was adopted for the synthesis of *N*-(phenyl)maleimide and *N*-(3-chlorophenyl)maleimide, in which maleanilic acid was prepared in the first stage and maleimide in the second stage.

N-(Phenyl)maleimide (2): Yield 82%; mp 90–92°C.
^{1}H-NMR (CDCl$_3$): δ 7.14–7.34 (s, Ar, 5H), 6.83 (s, CH=, 2$\underline{H}$).
^{13}C-NMR (CDCl$_3$): δ 165.05 (C=O), 134.2 (C=C), 129.2, 127.6, 126.3, 121.2, 133.8 (Ar).
Microelemental ANAL. Calcd. for C$_{17}$H$_{12}$O$_3$: C, 77.26%; H, 4.58%. Found: C, 77.34%; H, 4.54%.
N-(3-Chlorophenyl)maleimide (3): Yield 78%; mp 72–74°C;
^{1}H-NMR (CDCl$_3$): δ 7.14–7.36 (s, Ar, 5H), 6.83 (s, CH=, 2H).
^{13}C-NMR (CDCl$_3$): δ 165.05 (C=O), 134.2 (C=C), 129.2–133.8 (Ar).
Microelemental ANAL. Calcd. for C$_{10}$H$_6$O$_2$NCl: C, 57.88%; H, 2.91%; N, 6.75%; Cl, 17.09%. Found: C, 57.72%; H, 2.89%; N, 7.82%; Cl, 17.13%.

Polymerization

Copolymers were prepared by varying mole ratios of the N-substituted maleimide monomers with butyl acrylate (BA), methyl acrylate (MA), and glycidyl methacrylate (GMA) in chlorobenzene using BPO as initiator. Nitrogen gas was flushed for 20 min. The temperature was maintained at 70°C and after a suitable period, 1–3 h (when less than 15% conversion had taken place), the solution was precipitated by pouring into methanol. It was then redissolved in chloroform, reprecipitated in methanol, and then dried *in vacuo* at 40°C.

Preparation of High-Conversion Copolymers

After confirming the copolymer composition using ^{1}H-NMR spectroscopy, the copolymer in which both monomers were incorporated in near equal amounts—maleimide–GMA—was selected for making adhesives. After a maximum period (~12 h) of copolymerization, high-conversion polymers were precipitated in methanol. The copolymers were redissolved in chloroform and reprecipitated in methanol. Curing of the epoxy group of the resin and GMA was done by using 40% diethanolamine (based on the oxirane content of the blend) and 10 mL of chloroform as a solvent.

Estimation of Peel Strength

Cowhide leather strips measuring 15 × 2.5 cm were used for determining the peel strength of the prepared adhesive. The grains were removed by using emery paper (No. 80), and 1 g of the adhesive was applied on one side of the buffed surface of the leather piece to an area 7.5 × 2.5 cm in size. The coated surface of the two leather strips had to be aligned face to face without any air bubbles. The effect of temperature on curing was studied at 30°C and 60°C, and the peel strength of the leather to leather was determined by using an INSTRON instrument.

Measurements

The IR spectra of the samples were recorded on Nicolet FTIR spectrophotometer model 20 DXB. The samples were recorded as KBr pellets. The NMR spectra of the polymers were run on a Bruker 300 MHz spectrometer at room temperature using CDCl$_3$ as a solvent and tetramethylsilane as an internal reference. Proton-decoupled

Table II F–R and K–T Parameters for Copolymers

Sl. No.	$F = M_1/M_2$	$f = m_1/m_2$	$G = F(f - 1)/f$	$H = F^2/f$	$\eta = G/\alpha + H$	$\xi = H/\alpha + H$
			Copoly(PM–MA) System			
1.	0.2658	0.1013	−2.3581	0.6974	−0.6861	0.2029
2.	0.5337	0.2121	−1.9826	1.3429	−0.4857	0.3290
3.	1.2173	0.4535	−1.4669	3.2675	−0.2442	0.5440
4.	1.8653	0.7301	−0.6895	4.7655	−0.0919	0.6350
5.	4.1020	1.5641	1.4794	10.7579	0.1096	0.7971
	α	2.73908				
			Copoly(MPM–GMA) System			
1.	0.2516	0.1588	−1.3330	0.3986	−.05565	0.1664
2.	0.5674	0.3650	−0.9871	0.8820	−0.3429	0.3064
3.	0.9920	0.6367	−0.5660	1.5456	−0.1598	0.4363
4.	1.8410	1.0450	0.0793	3.2433	0.0151	0.6190
5.	4.3192	1.8652	2.0035	10.0019	0.1670	0.8336
	α	1.99669				
			Copoly(CPM–BA) System			
1.	0.2285	0.1124	−1.8044	0.4645	−1.0221	0.2631
2.	0.4306	0.2129	−1.5919	0.8709	−0.7330	0.4100
3.	1.0492	0.7361	−0.3761	1.4955	−0.1345	0.5348
4.	1.8409	2.4130	1.0780	1.4044	0.3985	0.5191
5.	4.2632	4.9880	3.4085	3.6437	0.6894	0.7369
	α	1.30096				

$\alpha = \sqrt{H_{min} \times H_{max}}$

^{13}C-NMR spectra were run on the same machine. Thermogravimetric analysis was performed on a DuPont 2000 microthermobalance. The heating rate for TGA was kept at 10°C and 20°C/min in a nitrogen atmosphere. Elemental analysis was done on a Coleman C—H—N analyzer. The number-average and weight-average molecular weights of the polymers were determined by gel permeation chromatography using polystyrene as standards. DMF was used as an eluent. The peel strength of the prepared adhesive was tested on an Instron 4501 mechanical testing machine.

RESULTS AND DISCUSSION

Substituted maleanilic acids were synthesized by reacting maleic anhydride and the corresponding substituted anilines at room temperature. These maleanilic acids undergo cyclization by the removal of water molecules to form N-substituted maleimides. The polymers were soluble in polar aprotic solvents such chloroform, THF, DMSO, and DMF.

Characterization of Polymers

The IR spectra of the polymers show a broad band around 3100–3150 cm^{-1} because of the imide ring. The intense peak at 3050 cm^{-1} is due to the aromatic ring stretching vibration. Absorption around 1740 cm^{-1} is a result of the C=O vibration of the imide. The peak around 1600 cm^{-1} due to the C=C of the maleimide monomers is absent with the polymers. The out-of-plane vibration of the aromatic ring appears at 810 cm^{-1}.
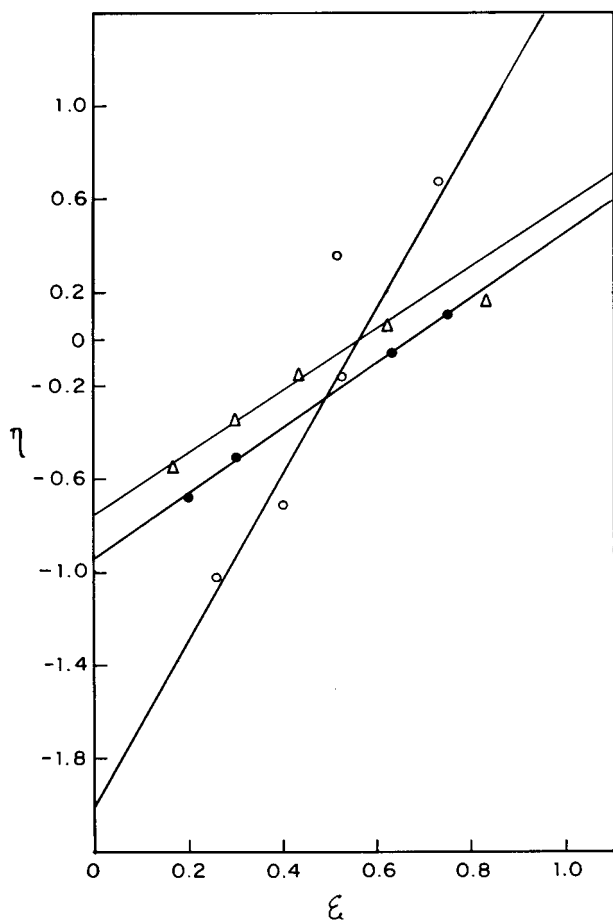
Figure 4 Copolymer composition curves of poly-(CPM-*co*-BA), poly(MPM-GMA), and poly(PM-*co*-MA) system.

The ¹H-NMR spectra of all the polymers show a strong peak between 7.6–7.03 ppm because of the aromatic protons. The upfield shift at 6.68–6.83 ppm (C=C of the monomers) to 2.28–2.31 ppm (C—C in the polymers) confirms the polymerization of the maleimide. The methyl protons of MPM appear at 1.2 ppm.

The proton-decoupled ¹³C-NMR spectra of the polymers show signals in the 136.6–120.3 ppm range due to aromatic carbons. The methyl carbon of MPM appears at 19.3 ppm, the backbone carbons (C—C) of the maleimide at around 48.95–49.21 ppm, and the carbonyl carbons at 175.4–176.2 ppm.

COPOLYMERIZATION

Five copolymers of different compositions were synthesized in ethyl acetate using BPO as initia-

tor. The formation of copolymer was confirmed by IR and NMR spectroscopies (Figs. 1 and 2).

The NMR spectra [Fig. 1(a)] of poly(PM-*co*-MA) show signals at 7.23–7.1 ppm because of the aromatic protons of the PM and a peak at 3.26 ppm as a result of the methoxy protons of the MA unit, while the peaks at 2.3 and 1.45 ppm are due to the backbone protons. The NMR spectra [Fig. 1(b)] of poly(MPM-*co*-GMA) show signals around 7.23–7.01 ppm due to the aromatic protons of the MPM unit and signals at 4.0 and 3.2 ppm because of the (—OCH₂) methylene and methine protons of the epoxy ring of GMA unit. The other peaks are the result of the backbone protons. The NMR spectra [Fig. 1(c)] of poly(CPM-*co*-BA) show signals at 7.5–7.04 ppm of the CPM unit, and the methoxy protons of the BA appear at 3.6 ppm. The other signals are due to the methyl, methylene, and methine protons of the comonomeric units.

The ¹³C-NMR spectra of all the copolymers show signals around 176.2–175.3 ppm, which are a result of the carbonyl carbon of the maleimide. The backbone carbons of the maleimide methine carbon appear at 48.92 ppm. For PM–MA copolymer [Fig. 2(a)], the aromatic carbons appear at 133.4, 129.6, and 120.2 ppm and the methyl carbon of the MA unit at 20.3 ppm. In the case of MPM–GMA [Fig. 2(b)] copolymer, the aromatic carbons appear at 134.6, 128.8, and 120.6 ppm. The well-resolved peaks at 65.48, 48.5, and 44.19 are due to O–CH₂, epoxy carbons, and methyl carbons, respectively. The butyl carbons of the
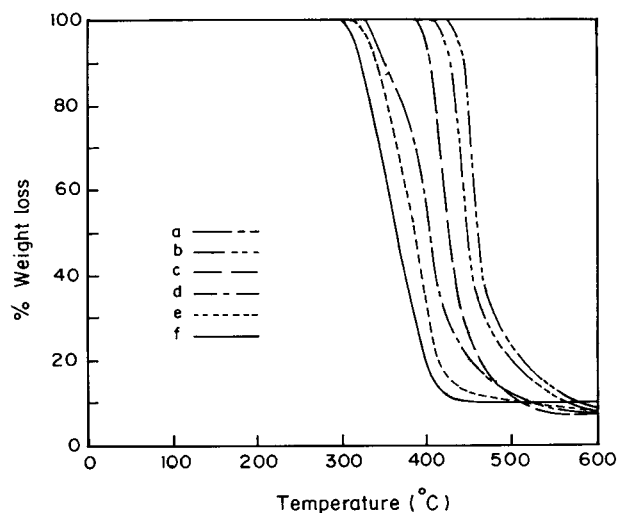
Figure 5 TGA curves of (a) poly(CPM), (b) poly(MPM), (c) poly(PM), (d) poly(CPM-*co*-BA), (e) poly(MPM-*co*-GMA), and (f) poly(PM-*co*-MA).

Table III Comparison of Reactivity Ratios for Different Copolymer Systems by F–R and K–T Methods

		(i) PM–MA Copolymer System			
Methods	r_1 (PM)	r_2 (MA)	$1/r_1$	$1/r_2$	$r_1 r_2$
F–R	0.45	2.70	2.22	0.37	1.22
K–T	0.47	2.52	2.15	0.40	1.17

		(ii) CPM–BA Copolymer System			
Methods	r_1 (CPM)	r_2 (BA)	$1/r_1$	$1/r_2$	$r_1 r_2$
F–R	1.63	2.75	0.61	0.36	4.48
K–T	1.58	2.55	0.63	0.39	4.03

		(iii) MPM–GMA Copolymer System			
Methods	r_1 (MPM)	r_2 (GMA)	$1/r_1$	$1/r_2$	$r_1 r_2$
F–R	0.70	1.75	1.43	0.57	1.23
K–T	0.58	1.48	1.72	0.68	0.86

CPM–BA copolymer [Fig. 2(c)] appear at 52.5, 48.3, 31.36, and 13.91 ppm, while those of the aromatic carbons of CPM appear at 134.8, 136.1, 128.4, and 11.8 ppm. The NMR data confirmed the formation of copolymer in all systems.

Copolymer Composition

^{1}H-NMR spectra were taken of polymers having different copolymer compositions. The mole fraction of MPM in the MPM–GMA copolymer chain was calculated by adopting a method[15] similar to that which we previously employed:

$$C = \frac{\text{Integral intensities of aromatic protons}}{\text{Integral intensities of aliphatic protons}}$$

$$= \frac{4m_1}{5m_1 + 10m_2}$$

where MPM and GMA are m_1 and $m_2 = (1 - m_1)$.

The mole fraction of CPM in poly(CPM-co-BA) was calculated using the ratio of integral values of aromatic to that of aliphatic protons. In the CPM–BA system, m_1 represents CPM and m_2 that of BA; $m_1 = 12$ C/(4 + 10 C). Similarly, the mole fraction of PM in poly(PM-co-MA) was found

Table IV Molecular Weight Data of Polymers

		Molecular Weight by GPC		
Sl. No.	Polymer	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	M_w/M_n
1	Poly(PM)	1.67	0.82	2.04
2	Poly(MPM)	2.15	0.96	2.24
3	Poly(CPM)	1.52	0.79	1.92
4	Poly(PM-co-MA)	2.65	1.36	1.95
5	Poly(MPM-co-GMA)	3.06	1.42	2.16
6	Poly(CPM-co-BA)	2.86	1.52	1.88

GPC: Gel permeation chromatography
Copolymers having almost equimolar copolymer compositions were used for GPC.

Table V   TGA Data of Homo- and Copoly(malemide-acrylate)

Polymer	IDT (°C)	Stage I (°C)	% Weight Loss at Different Temperatures (°C)				
			10	25	50	75	90
Poly(PM)	388	388–517	405	413	424	450	517
Poly(PM-*co*-MA)	302	302–450	320	337	364	392	450
Poly(MPM)	415	415–570	427	432	446	482	570
Poly(MPM-*co*-GMA)	332	332–503	341	360	386	407	503
Poly(CPM)	420	420–582	443	450	461	497	582
Poly(CPM-*co*-BA)	303	303–508	352	380	405	435	508

IDT—Initial decomposition temperature

by the ratio of the methoxy protons to that of the total aliphatic protons. In the PM–MA system, m_1 represents PM and m_2 is MA. The mole fraction of PM present in the copolymer was calculated by using $m_1 = 6 \, C/(5 + 4 \, C)$. Table I provides a list of the ratios and formulas used.

Reactivity Ratios Determined by Various Methods

The copolymer and feed composition curves of these copolymerizations are shown in Figure 3.

The methods of Fineman-Ross[16] and Kelen-Tüdos[17] were employed for calculating reactivity ratios for the copolymer. The F–R parameters for the poly(MPM-*co*-GMA), poly(PM-*co*-MA), and poly(CPM-*co*-BA) systems are given in Table II. K–T plots of η versus ζ for these systems are given in Figure 4. The K–T parameters for all the copolymers are shown in Table II. The reactivity ratio values for poly(PM-*co*-MA) system obtained by the F–R and K–T methods for PM (r_1) are 0.45 and 0.47 and for MA (r_2) 2.70 and 2.52, respec-

Table VI   Adhesive Property: Peel Strength of Cured Copolymer–Epoxy Blends

Temp	System	Blend Ratios (g)		Peel Strength (N/mm)
		Copolymer	Epoxy	
30°C	PM–GMA/Epoxy	1.00	1	0.398
	PM–GMA/Epoxy	0.75	1	0.277
	PM–GMA/Epoxy	0.50	1	0.220
	MPM–GMA/Epoxy	1.00	1	0.728
	MPM–GMA/Epoxy	0.75	1	0.451
	MPM–GMA/Epoxy	0.50	1	0.301
	CPM–GMA/Epoxy	1.00	1	1.175
	CPM–GMA/Epoxy	0.75	1	0.661
	CPM–GMA/Epoxy	0.50	1	0.701
60°C	PM–GMA/Epoxy	1.00	1	0.575
	PM–GMA/Epoxy	0.75	1	1.690
	PM–GMA/Epoxy	0.50	1	1.217
	MPM–GMA/Epoxy	1.00	1	2.456
	MPM–GMA/Epoxy	0.75	1	2.066
	MPM–GMA/Epoxy	0.50	1	1.601
	CPM–GMA/Epoxy	1.00	1	2.175
	CPM–GMA/Epoxy	0.75	1	2.066
	CPM–GMA/Epoxy	0.50	1	1.601

Copolymer: PM–GMA; MPM–GMA; CPM–GMA.

tively. The reactivity ratios obtained by the F–R and the K–T methods are given in Table III.

Comparison of Reactivity Ratios and Copolymerization Behavior

The reactivity ratios were found to be PM < MA and MPM < GMA, that is, $r_1 < r_2$. The tendency of two monomers to copolymerize is noted by r values between 0 and 1. An r_1 value less than unity means that M_1^* preferentially adds M_2, while if r_2 is greater than unity, then M_1^* preferentially adds M_1 instead of M_2. The product (Table III) was almost equal to 1, and therefore the entering of monomer into the copolymer is random in nature. The feed-versus-copolymer composition curves show concave shape. The feed–copolymer composition curves indicate azeotropic composition of CPM and BA in a ratio of 0.56:0.44. In general, reactivity ratios of the maleimide monomers were less reactive as compared to those of the acrylate monomers.

Molecular Weights

The number-average and weight-average molecular weights (M_n and M_w) of poly(PM), poly(MPM), poly(CPM), and their copolymers are shown in Table IV. The polydispersity index of the polymer is closer to 2, suggesting a strong tendency for chain termination by disproportionation.[18]

Thermal Studies

The thermal data of the polymers are shown in Table V. The thermal curve of poly(PM) and its copolymer show initial decomposition temperatures (IDT) at 390°C and 302°C. The high value of IDT indicates greater thermal stability and shows single-stage decomposition. Nearly 90% decomposition occurred between 302°C–450°C. Poly(MPM) has a higher IDT (415°C) than does poly(MPM-co-GMA) (332°C). Nearly 90% weight loss occurred for the MPM polymer at 570° C and 503°C for copoly(MPM–GMA). The thermal curve of poly(CPM-co-BA) shows single-stage degradation. The IDT for copoly(CPM–BA) is 310°C with 90% decomposition at 548°C. From this we concluded that in all the systems the homopolymer shows a higher initial decomposition temperature as compared to that of the copolymer.

Application

The copolymers of GMA with PM, CPM, and MPM, all of which have nearly 50:50 mole ratios in copolymer composition, were used for preparing adhesives. The epoxy resin was blended with various amounts of acrylic copolymers (1:1, 1:0.75, and 1:0.5 w/w), and the mixture was applied over the fresh surface of the standard leather pieces and left for 48 h at 30°C and 60°C. Testing was conducted according to the standard procedure, and the results are given in Table VI. Resin blends of copolymer and epoxy resin (1:1) showed a higher peel strength than did the other ratios. The adhesives cured at 60°C showed better results than did those cured at room temperature. The adhesives prepared from CPM–GMA with epoxy resin showed better adhesion property, with a maximum of 2.28 N/mm at 60°C.

CONCLUSIONS

All the monomers and polymers were well characterized by spectroscopic methods. From the reactivity ratios of the monomers it seem that the acrylate comonomers are more reactive than the substituted maleimides. The polymers undergo termination by a disproportionation mechanism. These polymers showed an excellent thermal stability and were soluble in common organic solvents. The adhesive property of these copolymers with epoxy resins showed comparable results to those of commercially available ones.

REFERENCES

1. Tawney, P. O.; Snyder, R. H.; Conger, R. P.; Liebbrand, K. A.; Stiteler, C. H.; Williams, A. R. J Org Chem 1961, 26, 15.
2. Cho, K. ; Seok, H.; Ahn, T. O.; Kin, J.; Kim, K. U. Polymer 1997, 38, 4825.
3. Tapolsky, G.; Lecomte, J. P.; Meyrueix, R. Macromoleculs 1993, 26, 7383.
4. Chang, J. Y.; Kim, T. J.; Han, M. J.; Choi, D. H.; Kim, N. Polymer 1997, 38, 4651.
5. Otsu, T.; Matsumoto, A.; Kubota, T.; Mori, S. Polym Bull 1990, 23, 43.
6. Matsumoto, A.; Kubota, T.; Otsu, T. Macromolecules 1990, 23, 4508.

7. Smith Jr., J. G.; Hergenrother, P. M. Polym Prepr 1994, 35, 353.

8. Mittal, K. In Polyimides, Synthesis, Characterization and Applications; Mittal, K., Ed.; Plenum: New York, 1984; Vol. 1.

9. Hisatumi, T.; Masanoba, K. Hikaku Kagaku 1987, 31, 249.

10. Pullian, L.; Sieber, A.; Drake, R. Adhesive Age, 1989, 32, 18.

11. Buchner, R. W.; Atzinger, G. D. Adhesive Age 1989, 32, 41.

12. Vakil, U. M.; Martin, G. B. J Appl Polym Sci 1992, 46, 2089.

13. Maistros, G. M.; Block Bucknel, H. ; Patridge, G. Polymer 1992, 33, 5876.

14. Vijayaragavan, P. G.; Reddy, B. S. R. J Appl Polym Sci 1996, 61, 935.

15. Thamizharasi, S.; Gnanasundaram, P.; Reddy, B. S. R. J Appl Polym Sci 1997, 65, 1285; J Polym Mat 1998, 15, 229.

16. Fineman, M.; Ross, S. D. J Polym Sci 1950, 5, 259.

17. Kelen, T.; Tudos, F. J Macromol Chem 1975, A9, 1.

18. Kamijo, M.; Sawatari, N.; Konishi, L.; Yoshizaki, T.; Yamakawa, H. Macromolecules 1994, 27, 5698.