Copolymerization of 4-Methyl- and 4-Methoxyphenyl Acrylates with Glycidyl Methacrylate: Synthesis, Characterization, Reactivity Ratios, and Application as Adhesives for the Leather Industry

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SYNOPSIS

Copolymers of 4-methyl- and 4-methoxyphenyl acrylates with glycidyl methacrylate having different copolymer compositions were synthesized in 1,4-dioxan using benzoyl peroxide as a radical initiator at $70 \pm 0.5°C$. The composition of the monomers in the copolymers were calculated using ^{1}H-NMR spectroscopy by comparing the integral values of well-separated aromatic and alifatic proton peaks. The reactivity ratios were calculated by Fineman–Ross, Kelen–Tudos, and extended Kelen–Tudos methods. The copolymers were characterized by ^{1}H-NMR and proton decoupled ^{13}C-NMR spectroscopic techniques. Gel permeation chromatography was used for determining the M_w and M_n and polydispersity indexes of the copolymers. Thermal stability of the homo- and copolymers was calculated using thermogravimetric analysis, while differential scanning calorimetry was utilized in determining the glass transition temperature. Copolymers of suitable composition were chosen for curing reactions with diethanolamine in chloroform. The cured resins were tested as adhesives for leather–leather bonding at different temperatures (50, 90, 100, and 110°C). It was found that copoly(MOPA–GMA) at 50°C gave the best adhesive property over all other samples tested. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Epoxy adhesives are a class of thermosetting adhesives that have gained popularity over the years because of their superior performance in many applications.[1] One important feature of the epoxy adhesives is that elevated temperatures are often not required to produce an adhesive bond.[2] Paul Schlack[3] described the preparation of a resin from epichlorohydrin and bisphenol A which was cured with an equivalent amount of amines, diamines, or polyamines. This was the first reported epoxide adhesive. Pierre Casten[4] cured these resins with phthalic anhydride and reported excellent adhesion to glass,

porcelain, and metal. The development of epoxy resins as commercial adhesives was marketed by Ciba company under the trade name Araldite[5] based on Casten's work. It has already been established that considerable improvement in adhesion was obtained by incorporation of aluminium powder,[6] aluminium oxide,[7] reactive diluents,[8] and other ingredients[9] into epoxide–amine formulations. De Bruyne[10] has demonstrated that the hydroxyl content greatly influences the addition of epoxide resins and tested a series of epoxides having different hydroxyl values after curing them with pthalic anhydride. These findings were confirmed by May,[11] who varied the hydroxyl content of the epoxy system by replacing a part of the phthalic anhydride used as a curing agent by an equivalent amount of pthalic acid. The cure behavior and the relationship between structure and ultimate properties[12,13] of the epoxy resins have also been studied. The presence of the

epoxy group in GMA allows us experimentally to modify the copolymers further for various applications.[14-16] Paul and Ranby[17] synthesized MMA–GMA copolymers of low molecular weight and modified them by opening the oxirane ring of the GMA by reaction with diethanolamine (DEA). They also found that the addition of a hydrogen bond acceptor like nitrobenzene decreases, while the addition of a hydrogen bond donor like phenol increases, the rate of epoxy ring opening with DEA.

Speciality chemicals for high-temperature resistant adhesives for leather–leather bonding are in great demand for industrial applications. To develop heat-resistant adhesives, this article describes the synthesis, characterization, and reactivity ratios of copoly(MPA–GMA) and copoly(MOPA–GMA). The copoly(MOPA–GMA) system has been investigated for use as a high-temperature adhesive in the leather industry.

EXPERIMENTAL

Materials

Glycidyl methacrylate (Aldrich, USA) was distilled under vacuum before use. Benzoyl peroxide (Fluka) was recrystallized with chloroform. Petroleum ether (Sisco Chem), methanol (Fisher), 1,4-dioxan (S. D. Fine Chem), chloroform, and triethylamine (Merck) were distilled and stored before use. Acrylic acid (Sisco Chem), 4-methyl and 4-methoxyphenols (S. D. Fine Chem), and Diethanolamine (Indofil Chem) were used as received without further purification.

R : CH₃ / OCH₃
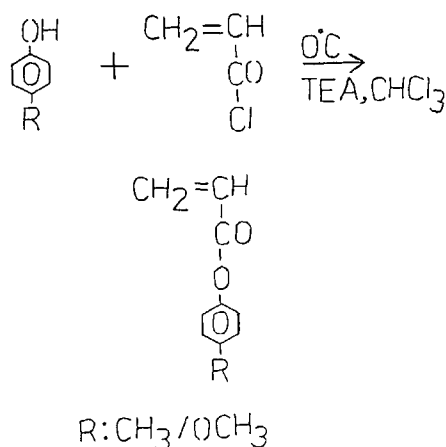
Scheme 1 Synthesis of MPA and MOPA.
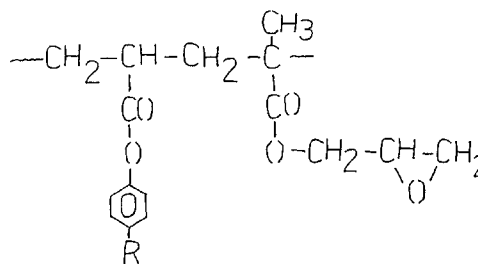
Scheme 2 Structure of copoly(MPA–GMA) and copoly(MOPA–GMA).

Synthesis of 4-Methyl (MPA) and 4-Methoxyphenyl (MOPA) Acrylates

Acryloyl chloride was prepared by reacting acrylic acid with benzoyl chloride by following the procedure of Stampel et al.[18] MPA and MOPA were synthesized (Scheme 1) by reacting 4-methylphenol or 4-methoxyphenol with acryloyl chloride in solution in the presence of triethylamine. In a typical experiment, the respective phenols (0.1 mol) with triethylamine (0.1 mol) in 100 mL chloroform were placed in a three-necked RB flask fitted with a stirrer, thermometer, and dropping funnel. Acryloyl chloride (0.12 mol) in 25 mL chloroform was added slowly through the dropping funnel while the temperature was maintained between 0 and 5°C. After the addition was completed, the reaction mixture was stirred for 1 h, and the contents were transferred to a separating funnel and washed with water and 10% sodium hydroxide solution to remove the unreacted reagents. The solvent was finally removed by evaporation to obtain pure monomers. MPA was pale yellow in color, while MOPA was reddish yellow. The monomers were characterized by ^{1}H- and ^{13}C-NMR data

^{1}H-NMR (δ, ppm) (MPA): 7.1–6.9 (4H), 6.5 (2H), 6.3–5.9 (1H) (MOPA): 7.0 (4H), 6.8 (2H), 6.5–5.9 (1H).

^{13}C-NMR (δ, ppm) (MPA): 132.13 (=CH₂), 127.75 (=CH), 164.45 (C=O), 148.12 ([1]C), 120.95 ([2]C & [6]C), 129.89 ([3]C & [5]C), 135.23 ([4]C).

(MOPA): 132.07 (CH₂), 127.72 (=CH), 164.61 (C=O), 143.02 ([1]C), 114.21 ([2]C & [6]C), 122.06 ([3]C & [5]C) 157.04 ([4]C).

Copolymerization

Calculated amounts of MPA or MOPA and GMA in 50 mL 1,4-dioxan and benzoyl peroxide as a free radical initiator (0.5% based on the weight of monomers and solvent) were placed in a reaction tube (100 mL), and the contents were flushed with a slow stream of nitrogen for 5 min. The tube after sealing was placed in a thermostated water bath maintained at 70 ± 0.5°C. Copolymerization was allowed to proceed to ca. 15% conversion. The copolymers were precipitated into excess methanol, filtered, redissolved in chloroform, and once again precipitated into excess methanol and dried in vacuum at 40°C for 15 h (Scheme 2).

Instruments

The ^{1}H- and ^{13}C-NMR spectra of the copolymers were run on a Bruker CXP 90 MHz Fourier transform nuclear magnetic resonance FT-NMR spectrometer at room temperature. CDCl$_3$ and TMS were used as solvent and internal standard, respectively. The proton decoupled ^{13}C-NMR spectra operated at 22.63 MHz. Thermal analysis was carried out using DuPont 2000 in nitrogen atmosphere with a heating rate of 10°C min for TGA and 5°C min^{-1} for differential scanning calorimetry (DSC), respectively. Gel permeation chromatography was carried out using a Shimadzu instrument. Tetrahydrofuran was the eluent at a flow rate of 1 mL min^{-1}, and polystyrene standards were employed for calibration. Satra AM 1 and 11 was used for estimating the peel strength of the adhesives.

Preparation of Copolymers to High Conversion

After confirming the copolymer composition using ^{1}H-NMR spectroscopy, the copolymer in which both monomers are incorporated near equal amounts was chosen and the copolymers were synthesized by using 1.5% benzoyl peroxide and 50 mL of 1,4-dioxan at 70 ± 0.5°C. The reaction was carried out for a period of 72 h to get the maximum yield ($\simeq$ 80%) for application in the leather industry as adhesives. Curing of the epoxy group of the GMA was done using 40% of diethanolamine (based on the GMA content of the copolymer) and 10 mL of chloroform as a solvent.

Estimation of Peel Strength

Cow side leather strips measuring 15 × 2.5 cm were used for determining the peel strength of the adhesives prepared. After removing the grain by using emery paper (No. 80), 0.75 g of the adhesive was applied for an area of 7.5 × 2.5 cm at one end of the

Table I Copolymer Composition and Molecular Weights Data*

Feed Composition in Mole Fraction		Conversion (%)	Copolymer Composition in Mole Fraction		Molecular Weights		
M_1	M_2		m_1	m_2	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
(a) 4-Methylphenyl Acrylate–GMA System							
0.11	0.89	9.8	0.03	0.97	47875	39420	1.2
0.29	0.71	9.6	0.12	0.88			
0.39	0.61	9.3	0.17	0.83			
0.49	0.51	7.6	0.31	0.69	41970	32680	1.3
0.86	0.14	7.0	0.86	0.14	35970	26170	1.3
(b) 4-Methoxyphenyl Acrylate–GMA System							
0.10	0.90	14.6	0.02	0.98	42530	31635	1.3
0.30	0.70	10.8	0.10	0.90			
0.39	0.61	14.4	0.16	0.84			
0.49	0.51	9.1	0.21	0.79	37060	27504	1.3
0.80	0.20	11.0	0.62	0.38			

* Temperature: 70 ± 0.5°C; benzoyl peroxide: 0.05 g; solvent: 1,4-dioxan; nonsolvent: methanol.
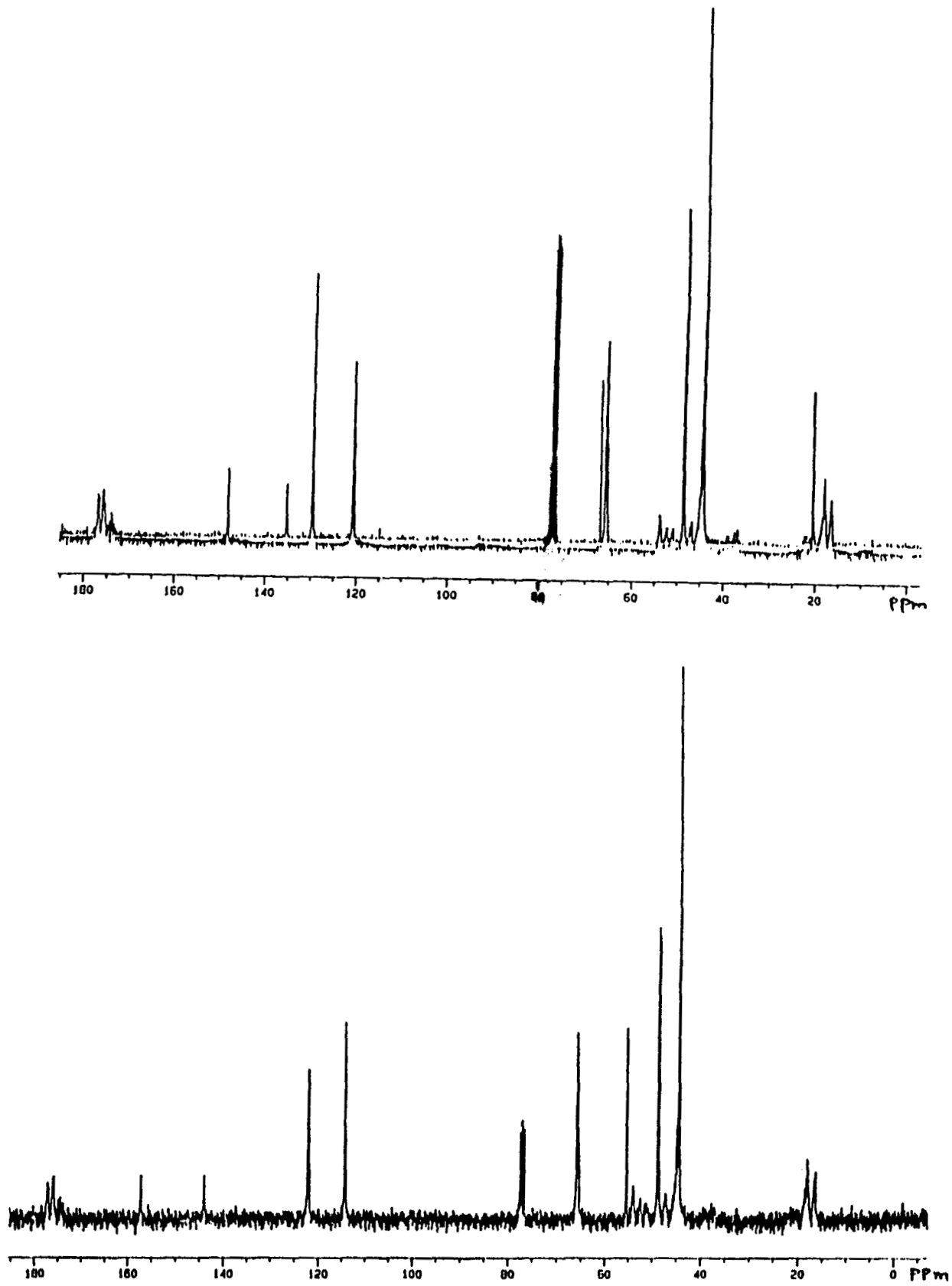
Figure 1 ^{13}C-NMR spectrum of (a) copoly(MPA–GMA) (49 : 51) and (b) copoly(MOPA–GMA) (49 : 51).

buffed surface of each strip so that pores, if any, were completely filled, forming a uniform layer of adhesive. After the adhesive film was dried to a condition in which there was still some tackiness, the coated surface of the two leather strips could be aligned face to face carefully without the formation of air bubbles in such a way that the free ends of the leather strips lie in the same direction. The effect of time and temperature on curing was studied in detail (96 h for 50°C and 24 h for 90, 100, and 110°C) and the peel strength on leather to leather was determined.

RESULTS AND DISCUSSION

Five copolymers each of MPA or MOPA and GMA having different copolymer compositions were synthesized by solution polymerization using benzoyl peroxide as a free radical initiator (Table I).

^{13}C-NMR Spectroscopy

The proton decoupled ^{13}C-NMR spectra of copoly(MPA–GMA) and copoly(MOPA–GMA) are shown in Figure 1. The ester carbonyls of MPA and MOPA gave a signal at 177.20 and 177.15 ppm, respectively. Due to the presence of the ester group adjacent to the phenyl ring, the ^{1}C of MPA appears at 148.21 ppm while that of MOPA appears at 143.92 ppm. This follows sharp signals at 129.77 and 121.98 ppm, which are due to the ^{3}C and ^{5}C of MPA and MOPA units, respectively. The ^{4}C of MPA and M0PA are seen at 135 and 157.12 ppm, respectively. The down-field chemical shift of ^{4}C in the case of MOPA was due to the electronegative oxygen present in the methoxygroup. The backbone methylene of the MPA and MOPA are seen at 44.52 and 44.51

ppm, respectively. The ester carbonyl of GMA and MPA or MOPA units gave signals at 174.55 and 176 ppm, respectively. Clear signals are obtained at 65.78 and 65.79 ppm which are due to the —OCH$_2$ of GMA. The backbone carbons (— C —) of the two units appear between 48.82 and 48.66 ppm. The group of lines appearing between 18.16–20.72 ppm and 18.18–18.57 ppm correspond to the α-methyl group of the GMA and confirm the tacticity of the copolymers.

Thermogravimetric Analysis

Thermogravimetric analysis (Table II) was employed in estimating the percent weight loss of the copolymer which undergoes decomposition. It was observed from Table II that incorporation of GMA into MPA and MOPA reduces the thermal stabilities of the respective copolymers.

Differential Scanning Calorimetry

From Table II, it was observed that poly(MOPA) has a T_g value of 58°C and made the composition ideal for the preparation of adhesives. The higher value of 74°C in the case of poly(MPA) also explains the absence of adhesion in copoly(MPA–GMA).

Copolymer Composition

The compositions of MPA and MOPA in the respective copolymers were estimated by ^{1}H-NMR spectroscopy (typical spectra shown as an example in Fig. 2). The mole fractions of MPA or MOPA were calculated by comparing the intensities of well-separated aromatic and alifatic protons of both units by the following equation:

Table II   TGA and DSC Data of Homo- and Copolymers

Polymer	Temperature (°C)		Stages of Decomposition	DSC
	T_{10}	T_{50}		T_g (°C)
Poly(MPA)	383.3	433.3	Two	74
Poly(GMA)	390.4	421.4	Single	76
Poly(MOPA)	375.0	410.0	Single	58
Copoly(MPA–GMA)	300.0	355.5	Two	—
Copoly(MOPA–GMA)	350.0	375.0	Single	70

T_{10} and T_{50} represent decomposition temperatures at 10° and 50°C, respectively.
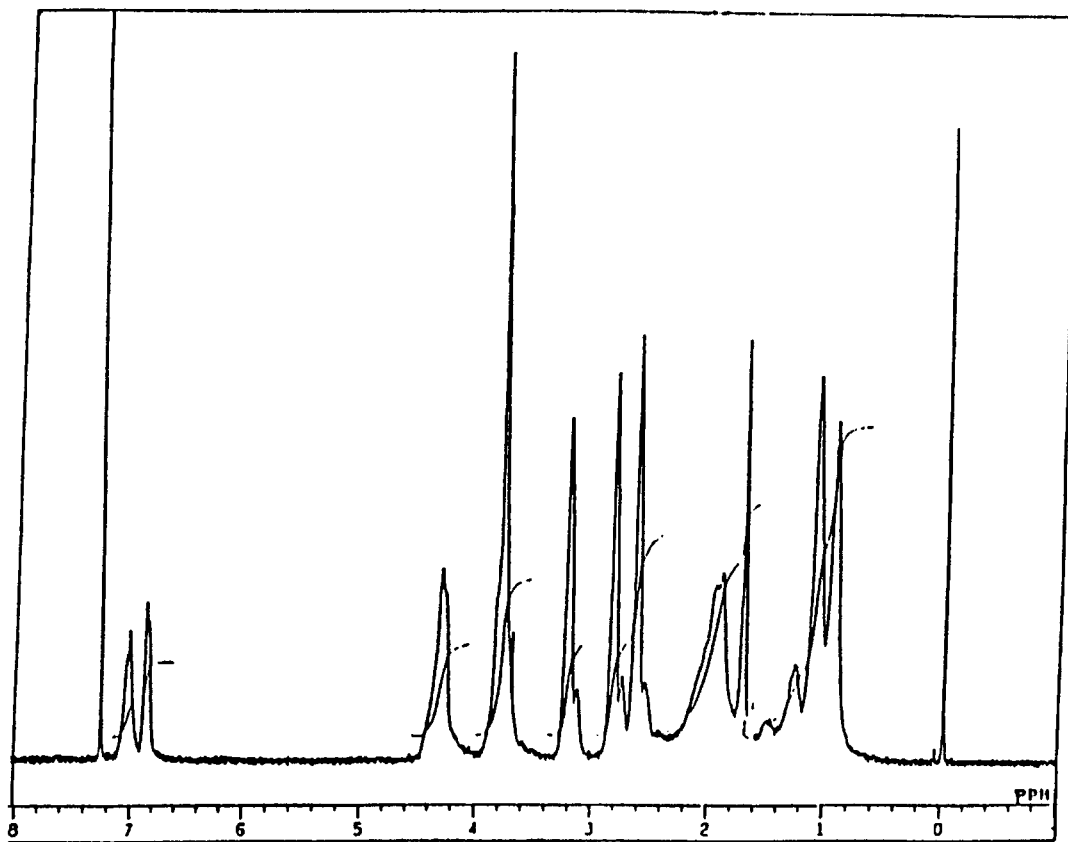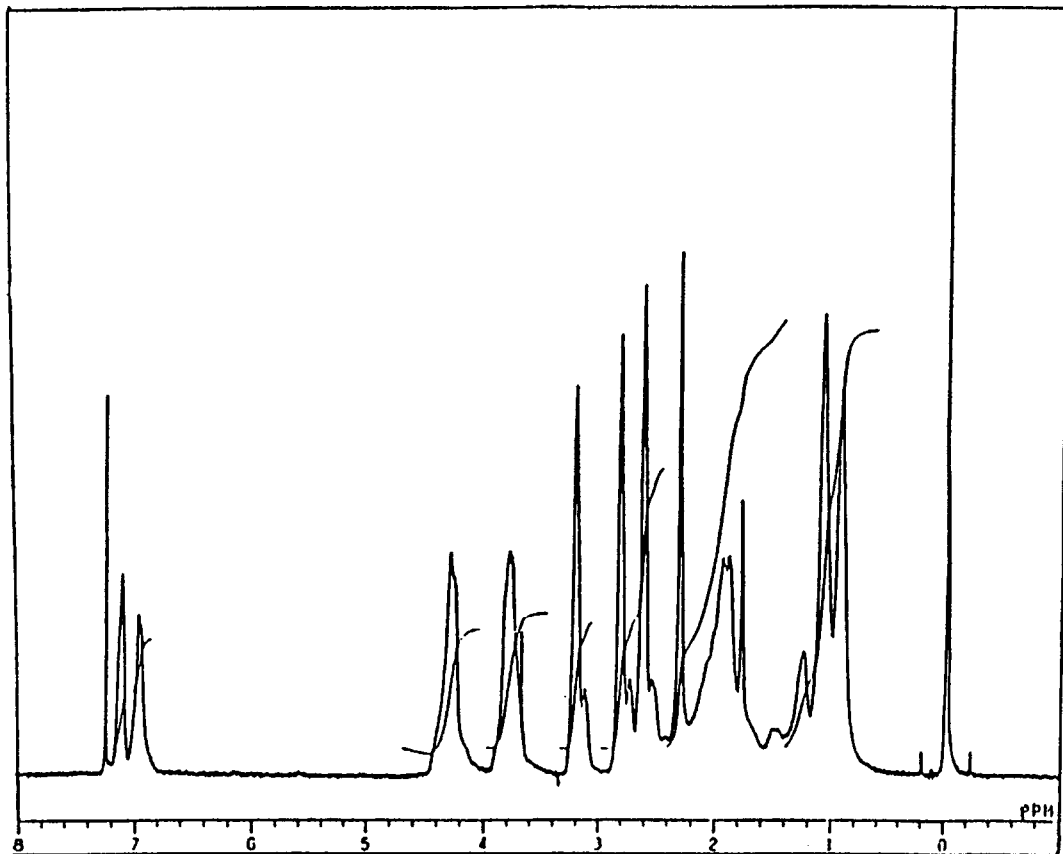
Figure 2 ¹H-NMR spectrum of (a) copoly(MPA–GMA) (39 : 61) and (b) copoly(MOPA–GMA) (39 : 61).
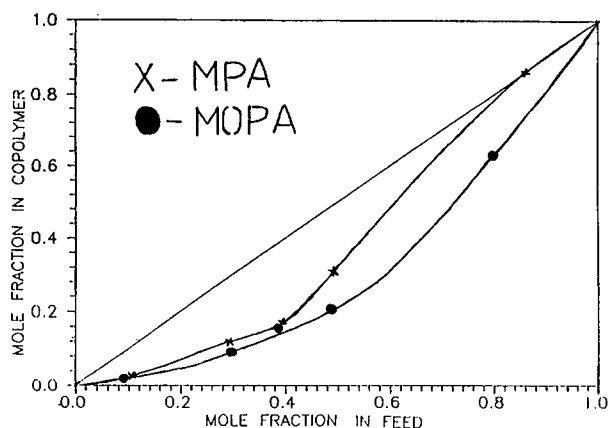
Figure 3 Feed versus copolymer composition curves of copoly(MPA–GMA) system and copoly(MOPA–GMA) system.

$$\frac{\text{Intensity of aromatic protons } (I_A)}{\text{Intensity of alifatic protons } (I_a)} = \frac{4m_1}{6m_1 + 10m_2}$$

where m_1 = MPA or MOPA and m_2 = GMA. This equation was deduced from the fact that there were

10 protons each in MPA or MOPA and GMA, whereas MPA or MOPA contain only 4 aromatic protons. From this and $m_2 = 1 - m_1$, we have

$$m_1 = \frac{5I_A}{2I_A + 2I_a}$$

A plot of feed (M_1) versus copolymer composition (m_1) gives the kinetic behavior of the monomers during copolymerization (Fig. 3).

Determination of Reactivity Ratios

To understand the copolymerization behavior, the reactivity ratios were calculated by the Fineman-Ross (F-R),[19] Kelen-Tudos (K-T)[20] (Table III), and extended Kelen-Tudos (ex-K-T)[21,22] (Table IV) methods. Figures 4 and 5 represent the K-T and extended K-T plots of copoly(MPA–GMA) and copoly(MOPA–GMA) systems. The 95% confidence intervals were also calculated as per the procedure given by Kelen-Tudos.[23] The comparisons of the

Table III   F-R and K-T Parameters for Copoly(MPA–GMA) and Copoly(MOPA–GMA) Systems

System	X	Y	G	F	η	ξ
Copoly(MPA–GMA)	0.12	0.03	−4.09	0.49	−1.83	0.22
	0.42	0.14	−2.64	1.26	−0.88	0.42
	0.65	0.21	−2.51	2.04	−0.66	0.53
	0.97	0.44	−1.21	2.10	−0.31	0.54
	6.17	6.23	5.18	6.12	0.65	0.78
Copoly(MOPA–GMA)	0.11	0.02	−4.66	0.51	−1.71	0.19
	0.43	0.11	−3.66	1.77	−0.92	0.44
	0.63	0.19	−2.72	2.12	−0.63	0.49
	0.97	0.27	−2.68	3.52	−0.47	0.61
	4.00	1.65	1.57	9.71	0.13	0.81

Table IV   Ex K-T Parameters for Copoly(MPA–GMA) and Copoly(MOPA–GMA) Systems

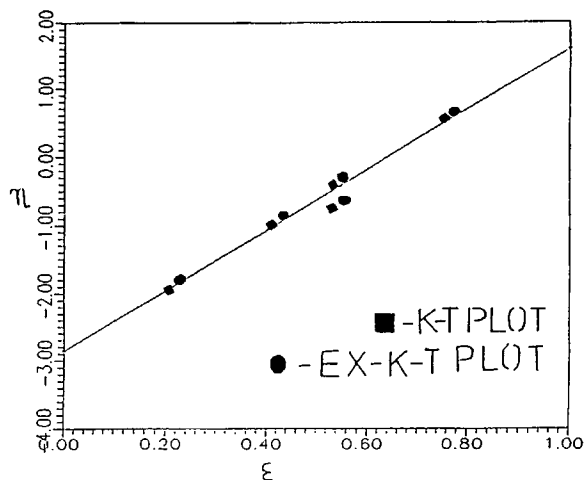| System	T_1	T_2	Z	F	G	η	ξ
Copoly(MPA–GMA)	0.03	0.11	0.23	0.54	−4.27	−1.81	0.23
	0.04	0.12	0.31	1.39	−2.76	−0.86	0.43
	0.04	0.13	0.30	2.25	−2.63	−0.64	0.55
	0.05	0.11	0.45	2.24	−1.25	−0.30	0.55
	0.07	0.07	1.00	6.12	5.19	0.65	0.77
Copoly(MOPA–GMA)	0.04	0.17	0.19	0.59	−5.02	−1.59	0.19
	0.04	0.15	0.23	1.99	−3.89	−0.85	0.44
	0.06	0.21	0.27	2.51	−2.96	−0.58	0.49
	0.04	0.15	0.26	3.97	−2.84	−0.43	0.61
	0.09	0.22	0.38	11.23	1.69	0.12	0.81

Figure 4 K-T and ex-K-T plots of copoly(MPA–GMA) system.
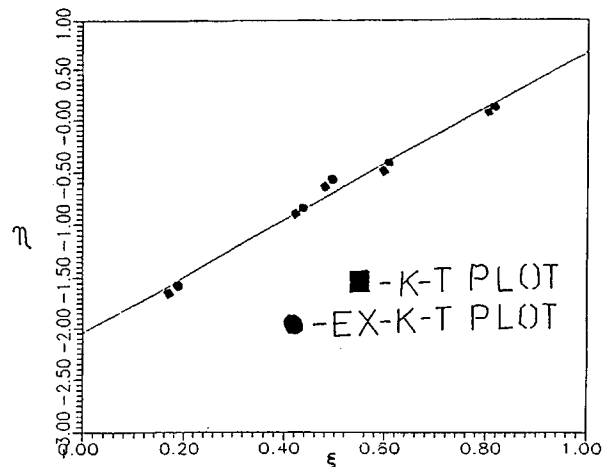

Figure 5 K-T and ex-K-T plots of copoly(MOPA–GMA) system.

reactivity ratios by these methods were tabulated in Table V.

Adhesive Studies

The results of the adhesive studies (Table VI) indicate that the adhesive prepared from co-

poly(MOPA–GMA) has a better adhesion property with a maximum of 1.9 N/mm at 50°C. The results from the table further show that the adhesives prepared from this copolymer were having better tackiness than even "fevicol" at 28°C which was commercially available. The poor adhesive property was perhaps due to its high T_g value (74°C) for copoly(MPA–GMA).

Table V Comparison of Reactivity Ratios by Different Methods

System	Method	r_1	r_2	$1/r_1$	$1/r_2$
Copoly(MPA–GMA)	F-R	1.65 ± 0.41	5.02 ± 1.27	0.61	0.20
	K-T	1.59 ± 0.62	4.89 ± 1.09	0.63	0.20
	ex-K-T	1.60 ± 0.70	5.19 ± 1.31	0.63	0.19
Copoly(MOPA–GMA)	F-R	0.65 ± 0.18	4.73 ± 0.87	1.53	0.21
	K-T	0.71 ± 0.36	4.87 ± 0.82	1.42	0.21
	ex-K-T	0.67 ± 0.30	5.24 ± 0.80	1.50	0.19

Table VI Peel Strength of Adhesives in N/mm

Type of Adhesive	28°C	50°C	90°C	100°C	110°C
Fevicol	0.3 (24)	—	—	—	—
Copoly(MOPA–GMA)	—	1.9 (96)	1.4 (24)	0.4 (24)	0.9 (24)
Copoly(MPA–GMA)	—	0.1 (96)	0.0 (24)	0.1 (24)	0.2 (24)

Curing agent: Diethanolamine; solvent: Chloroform. The figures given in parentheses indicate curing time in hours.

CONCLUSIONS

The results of the reactivity ratios obtained by F-R, K-T, and ex-K-T methods were in good agreement with each other. The second monomer GMA has a higher reactivity ratio than both MPA and MOPA, which means that the copolymer is always richer in GMA. This was also confirmed by $1/r_2$ values (<1).

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