

Synthesis, Characterization, Reactivity Ratios by Nuclear Magnetic Resonance Spectroscopy, and Application of (2,5-Dichlorophenyl acrylate-co-glycidyl methacrylate) Polymers as Adhesives for the Leather Industry

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ABSTRACT: 2,5-Dichlorophenyl acrylate (DPA)-co-glycidyl methacrylate (GMA) polymers having five different compositions were synthesized in 1,4-dioxane using benzoyl peroxide as a free-radical initiator at $70 \pm 0.5^\circ\text{C}$. Using $^1\text{H-NMR}$ spectroscopy, the composition of the two monomers in the copolymers was calculated by comparing the integral values of the aromatic and aliphatic proton peaks. The reactivity ratios were calculated by Fineman-Ross ($r_1 = 0.31$ and $r_2 = 1.08$), Kelen-Tudos ($r_1 = 0.40$ and $r_2 = 1.15$), and extended Kelen-Tudos ($r_1 = 0.39$ and $r_2 = 1.16$) methods. The nonlinear error-in-variables model was used to compare the reactivity ratios. The copolymers were characterized by ^1H and proton decoupled $^{13}\text{C-NMR}$ spectroscopies. Gel permeation chromatography was performed for estimating the M_w and M_n and M_w/M_n of the poly(DPA)

and copolymers (DPA-co-GMA: 09 : 91 and 50 : 50). Thermal stability of the homo- and copolymers was estimated using TGA [poly(DPA) > DPA-co-GMA (50 : 50) > DPA-co-GMA (09:91)], while DSC was utilized for determining the glass transition temperature. T_g increased with increased DPA content in the copolymer. The 50 : 50 mol % copolymer was chosen for curing with diethanolamine in chloroform. The cured resins were tested for the adhesive properties on leather at different temperatures (50, 90, 100, and 110°C). The resin cured at 50°C exhibited a maximum peel strength of 1.6 N/mm, revealing a good adhesive behavior. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1167–1174, 2006

Key words: adhesives; copolymerization; NMR; Kelen-Tudos

INTRODUCTION

Phenyl acrylates, the phenolic esters of acrylic acid, are a class of reactive monomers because of the presence of the aromatic ring. Initiators for photochemical polymerization,¹ pharmacologically active polymers,² and side chain liquid crystalline polymers³ are some of the applications in which phenyl-acrylate-based copolymers have been successfully employed.

Halogenated phenyl acrylates are a special class of activated monomers whose incorporation into the aromatic ring provides the facility for further modification with a wide range of reagents.^{4,5} The copolymers based on 2,4,5-trichlorophenyl acrylate have been utilized for synthesizing electroactive polymers and for the preparation of polymeric reagents carrying piperazine, isonitrile functionalities,^{6,7} etc. The activated acrylates were extensively employed in peptide synthesis.⁸ Phenyl acrylates and divinylbenzene crosslinked copolymers were also utilized in the prep-

aration of polymer supports for various chemical reactions.⁹ Copolymers synthesized from 2,4,6-tribromophenyl acrylate showed higher reactivity, perhaps due to the presence of electronegative bromine atoms in the aromatic ring.¹⁰

Epoxy adhesives have attained popularity in recent times because of their superior performance in many applications.¹¹ Schlack¹² described the preparation of the first epoxide adhesive from epichlorohydrin and bisphenol A, which was cured with an equivalent amount of amines, diamines, or polyamines. Casten¹³ cured these resins with phthalic anhydride and reported excellent adhesion to glass, porcelain, and metal. The development of epoxy resins as commercial adhesives took place when araldite¹⁴ was introduced based on Casten's work. De Bruyne¹⁵ demonstrated that the hydroxyl content greatly influences the addition of epoxide resins and tested a series of epoxides having different hydroxyl contents after curing them with phthalic anhydride. These findings were confirmed by May,¹⁶ who varied the hydroxyl content of the epoxide system by replacing a part of the phthalic anhydride used as a curing agent by an equivalent amount of phthalic acid. The cure behavior and the relationship between structure and ultimate

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properties^{17,18} of the epoxy resins have also been studied. The presence of the epoxy group in glycidyl methacrylate (GMA) allows further experimental modification of the copolymers for various applications.^{19–21} Paul and Ranby²² synthesized methyl methacrylate–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 addition of a hydrogen-bond donor like phenol increases the rate of epoxy ring opening with DEA.

Currently adhesives based on acrylic copolymers are utilized in wood and leather industries because of their versatility and performance characteristics. The shoe industry uses polyurethane adhesives for making high-quality shoes, which are not only costly but also have poor storage stability. In continuation of our work on phenyl acrylates^{23,24} the present study was undertaken with a view to develop an alternative adhesive with better utility and multifunctional for adhesion to leather based on epoxy resins.

EXPERIMENTAL

Materials

Glycidyl methacrylate (Aldrich) was distilled in vacuo before use. Benzoyl peroxide (Fluka) was recrystallized with a 1 : 1 mixture of chloroform and methanol. Methanol, 1,4-dioxane, chloroform, and triethylamine (Fluka) were distilled and stored before use. Acrylic acid, diethanolamine (Fluka), and 2,5-dichlorophenol (Aldrich) were used as received without further purification.

Instruments

¹H- and ¹³C-NMR spectra of the monomers and polymers were run on a Bruker 300-MHz spectrometer at room temperature using CDCl₃ as a solvent and tetramethylsilane as an internal reference. Proton-decoupled ¹³C-NMR spectra were run on a Bruker FT-NMR operating at 75.47 MHz under the same conditions. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed using Dupont 2000 in nitrogen at a heating rate of 10°C min⁻¹ for both TGA and DSC. Gel permeation chromatography was performed using a Shimadzu instrument. Tetrahydrofuran was the eluent at a flow rate of 0.3 mL min⁻¹ and polystyrene standards

TABLE I

	% Carbon	% Hydrogen	% Chlorine
Theoretical	49.79	2.77	32.69
Experimental	49.05	2.68	32.26

TABLE II
Copolymerization^a of DPA and GMA: Copolymer Composition and ¹H-NMR Data

Feed composition in mole fraction		Conversion (wt %)	¹ H-NMR data		Copolymer composition in mole fraction	
<i>M</i> ₁	<i>M</i> ₂		<i>I</i> _A	<i>I</i> _a	<i>m</i> ₁	<i>m</i> ₂
0.0930	0.9070	7.4	0.07	2.9	0.0702	0.9298
0.1946	0.8054	14.1	0.9	18.2	0.1477	0.8523
0.2924	0.7076	9.3	1.9	16.8	0.2982	0.7018
0.4955	0.5045	8.7	0.7	4.4	0.3886	0.6114
0.6994	0.3006	3.5	4.0	15.3	0.5412	0.4588

^a Temperature, 70 ± 0.5 °C; solvent, 1,4-dioxane; benzoyl peroxide, 0.5% w/w of monomers 1 and 2; nonsolvent; petroleum ether.

of different molecular weights were employed for calibration. The peel strength of the adhesive prepared from the copolymer compositions was tested by a Satra instrument at a humidity of 65% and a temperature of 20°C. The width and thickness of the specimen were 25 and 1 mm, respectively. The grip distance was maintained at 5 mm.

SYNTHESIS OF 2,5-DICHLOROPHENYL ACRYLATE

Acryloyl chloride was prepared by reacting acrylic acid with benzoyl chloride by following the procedure of Stampel et al.²⁵ 2,5-Dichlorophenyl acrylate (DPA) was synthesized by reacting 2,5-dichlorophenol with acryloyl chloride in the presence of triethylamine. In a typical experiment, phenol (0.1 mol) and 100 mL chloroform were taken in a three-neck RB flask fitted with a stirrer, thermometer, and dropping funnel. Acryloyl chloride (0.12 mol) in 25 mL of chloroform was added dropwise through the dropping funnel while the temperature was maintained between 0 and 5 °C. The addition was carried out for 45 min and then the reaction mixture was stirred for 1 h and left overnight. The unreacted phenol was removed by washing with 10% NaOH solution. Traces of water were removed by treatment with anhydrous Na₂SO₄. The solvent was finally removed by evaporation to obtain pure monomer. The monomer was yellow in color and the yield was ~90%.

Characterization

Elemental analysis (Table I) and ¹H- and ¹³C-NMR spectroscopies characterized the monomer.

Elemental analysis

NMR spectroscopy

¹H-NMR (δ, ppm): 8.7–7.1 (aromatic, 3H) and 6.5–5.8 (CH₂ = CH, 3H).

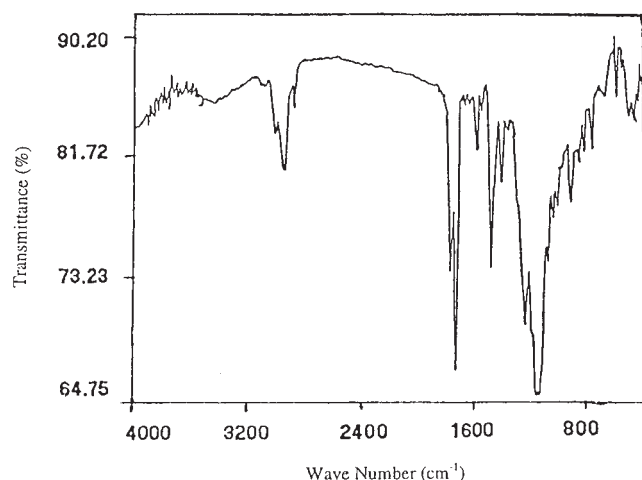


Figure 1 Infrared spectrum of (DPA-co-GMA) polymer (50 : 50).

^{13}C -NMR (δ , ppm): 132.10 (CH_2), 121.13 ($=\text{CH}$), 162.14 ($\text{C}=\text{O}$, ^{13}C), 150.12 (^{13}C), 124.70 (^{23}C and ^{63}C), 129.44 (^{33}C), 128.54 (^{43}C) and 132.11 (^{33}C).

Polymerization

Copolymers of DPA and GMA were prepared by polymerizing calculated amounts of the two monomers

using 0.5% benzoyl peroxide (based on the weight of monomer) as the initiator. The monomers were dissolved in 50 mL of 1,4-dioxane taken in the standard polymerization tube (100 mL). Oxygen-free nitrogen was passed into the reaction tube for about 3 min and after being sealed the tube was placed in a thermostat maintained at 70 ± 0.5 °C. Polymerization was carried to <15% conversion. The polymers were then precipitated by pouring into excess methanol. They were then redissolved in chloroform and precipitated in methanol. The resulting white precipitate was dried in vacuo at 40°C for 15 h (94%). The experimental details of copolymerization are given in Table II.

High conversion of copolymers

After the copolymer composition was ascertained using ^1H -NMR spectroscopy, the 50 : 50 copolymer was synthesized to high conversion using 1.5% benzoyl peroxide under the same conditions explained earlier for 72 h to obtain maximum yield (~80%).

Curing and estimation of peel strength

Curing of the epoxy group of the GMA was done by using 40% diethanolamine (based on the GMA content of the copolymer) and 10 mL of chloroform as a sol-

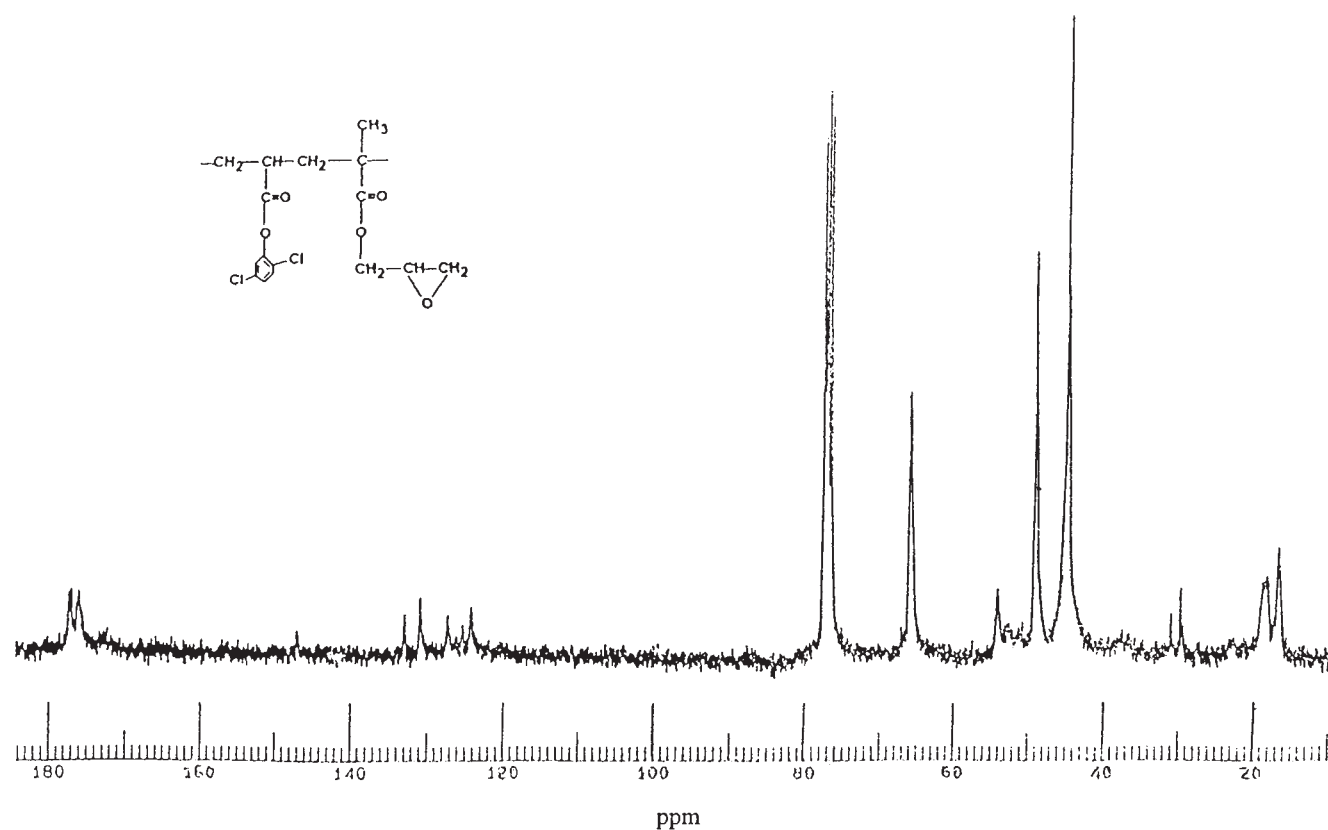


Figure 2 ^{13}C -NMR spectrum of (DPA-co-GMA) polymer (09 : 91).

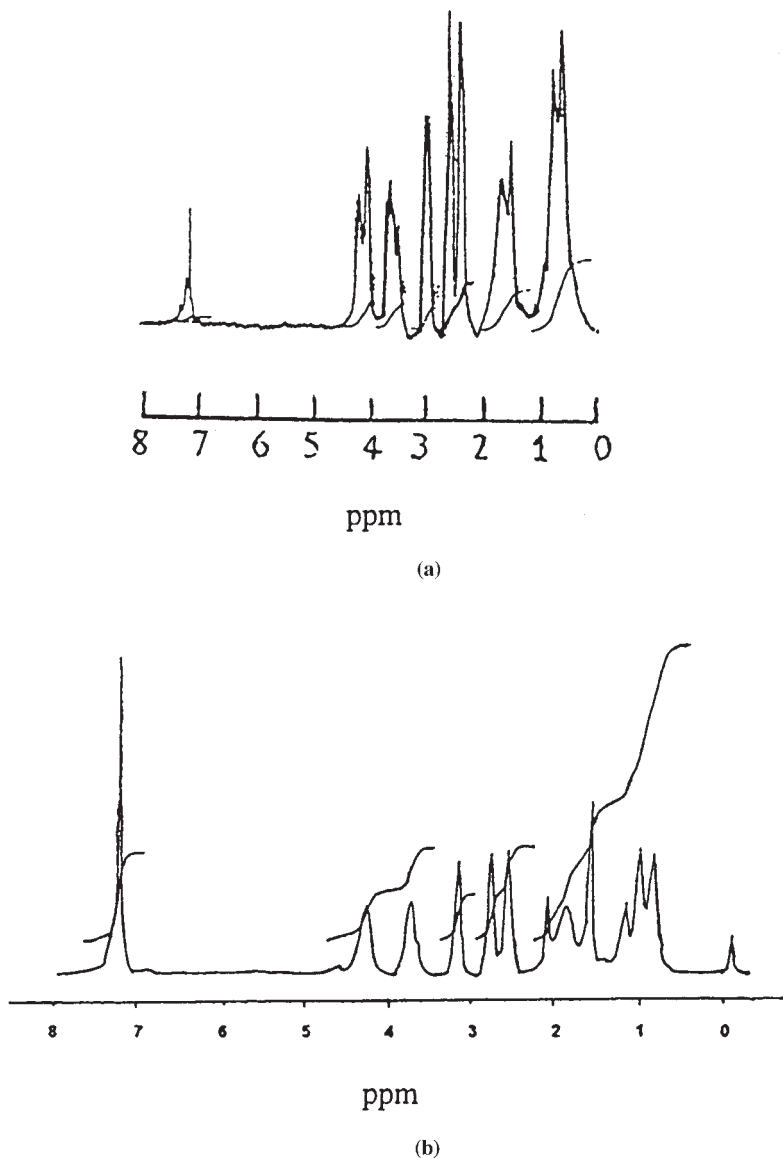


Figure 3 (a) $^1\text{H-NMR}$ spectrum of (DPA-co-GMA) polymer (09 : 91). (b) $^1\text{H-NMR}$ spectrum of (DPA-co-GMA) polymer (29 : 71).

vent. Cow leather strips measuring 15×2.5 cm were used for estimating the peel strength of the adhesives prepared after removing the grain manually using No. 80 emery paper. Approximately 0.75 g of the adhesive was applied for an area of 7.5×2.5 cm at one end of the buffed surface of each strip so that pores, if any, are completely filled, forming a uniform layer of adhesive. After the adhesive film was dried to a condition where there was still some tackiness, the coated surface of the two leather strips should 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 (96 h at 50°C and 24 h at 90, 100, and 110°C) and the peel strength of the adhesives on leather was estimated.

RESULTS AND DISCUSSION

Infrared spectroscopy

The infrared spectrum of (DPA-co-GMA) polymer (50 : 50) is shown in Figure 1. The vibrations at 3100, 3005, 1767, 1580, 1475, and 1452 cm^{-1} correspond to the aromatic $-\text{CH}$ stretching, $\text{C}=\text{O}$ stretching, and aromatic $\text{C}=\text{C}$, while the vibrations appearing at 2995, 2974, 2952, 2854, 1730, and 909 cm^{-1} represent the methyl stretching, $\text{C}=\text{O}$ stretching, and epoxy ring of the GMA unit. The appearance of a band at 1767 cm^{-1} for the aromatic $\text{C}=\text{O}$ is due to the high electronegativity of the chlorine atoms present in the phenyl ring. The $-\text{CO}$ of both monomers is seen at 1215 cm^{-1} . The vibration at 759 cm^{-1} represents the characteristic disubstitution in the phenyl ring.

TABLE III
F-R and K-T Parameters for (DPA-co-GMA)
Polymer System

X	Y	G	F	η^a	ξ^a
0.1025	0.0755	-1.2556	0.1393	-1.3376	0.1484
0.2416	0.1733	-1.1526	0.3369	-1.0144	0.2965
0.4132	0.4249	-0.5593	0.4019	-0.4656	0.3345
0.9822	0.6356	-0.5631	1.5177	-0.2430	0.6550
2.3267	1.1796	0.3542	4.5892	0.0657	0.8516

^a $\alpha = 0.7994$.

¹³C-NMR spectroscopy

The ¹³C-NMR spectrum of (DPA-co-GMA) polymer (09 : 91) is shown in Figure 2. The carbonyl group of the DPA unit appears at 176.99 ppm, while the backbone carbons give a sharp signal at 48.82 ppm. The aromatic carbons are observed at 147.50 (¹C), 124.79 (²C and ⁶C), 130.84 (³C), 132.13 (⁴C), and 132.95 (⁵C) ppm, respectively. The ester carbonyl of the GMA is seen at 176.09 ppm, while -OCH₂ and backbone carbons of the same unit gave very sharp peaks at 65.90 and 44.63 ppm. The two peaks at the far end of the spectrum at 18.29 and 16.74 ppm represent the α -methyl carbon of the GMA, which is sensitive to tacticity. The α -methyl group shifts have been associated with three possible species of substituents in a polymer by way of isotactic (meso, m), syndiotactic (racemic, r), and heterotactic triads of monomer units. With increasing strength of magnetic field, differences in chemical shift may allow resolution of tetrad sequences of monomer units appearing as fine structure on the m and r resonances. The fine structure on the α -methyl spectra of the mm, mr, and rr triad peaks split into further peaks associated with the pentad sequence at high magnetic field.

Copolymer composition

The ¹H-NMR spectra of (DPA-co-GMA) polymer (09 : 91) and (29 : 71) are shown in Figure 3(a,b). The composition of the DPA in the copolymer was determined using ¹H-NMR data by comparing the integral values of aromatic and aliphatic protons as shown:

$$\frac{\text{Integral value of aromatic protons } (I_A)}{\text{Integral value of aliphatic protons } (I_a)} = \frac{3m_1}{3m_1 + 10m_2}$$

The equation is derived from the fact that DPA contains 3 aromatic and 3 aliphatic protons, while GMA has 10 aliphatic protons. From this and $m_2 = 1 - m_1$, we have

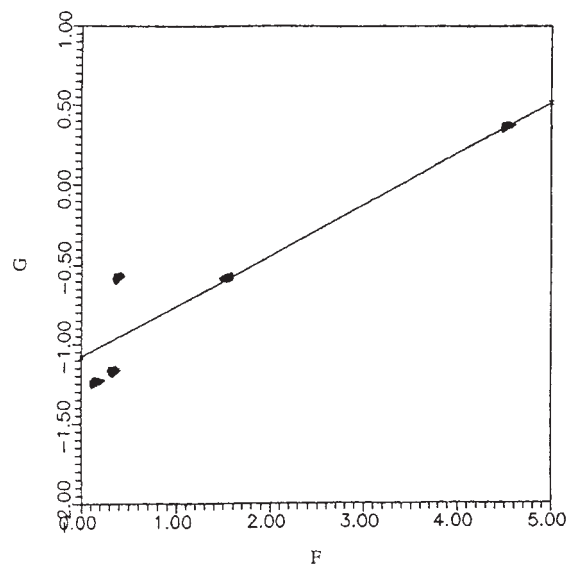


Figure 4 F-R plot of G vs. F for (DPA-co-GMA) polymer system.

$$m_1 = \frac{10I_A}{7I_A + 3I_a}$$

By making use of the above equation, the composition of DPA in the copoly(DPA-GMA) was estimated.

Calculation of reactivity ratios

Fineman-Ross method²⁶

Fineman and Ross utilized a graphical method for evaluating the reactivity ratios r_1 and r_2 of a given pair

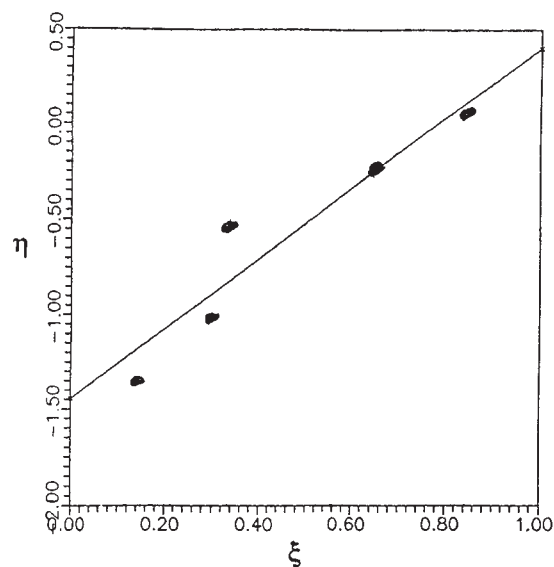


Figure 5 K-T plot of η vs. ξ for (DPA-co-GMA) polymer system.

TABLE IV
Extended K-T Parameters for (DPA-co-GMA)
Polymer System

$\tilde{\alpha}_1$	$\tilde{\alpha}_2$	G	F	η^a	ξ^a
0.0565	0.0767	-1.2691	0.1423	-1.3190	0.1479
0.1095	0.1526	-1.1809	0.3536	-1.0064	0.3013
0.0946	0.0920	-0.5585	0.4007	-0.4576	0.3283
0.0714	0.1104	-0.5751	1.5831	-0.2393	0.6588
0.0288	0.0569	0.3594	4.7247	0.0648	0.8521

^a $\alpha = 0.8199$.

of monomers. A plot of G vs. F is a straight line whose slope gives r_1 and the intercept gives $-r_2$. Here,

$$G = x(y - 1)/y$$

and

$$F = x^2/y,$$

where x and y are given by

$$x = M_1/M_2 \text{ and } y = m_1/m_2, \text{ where}$$

M_1 and M_2 = mole fraction of monomers 1 and 2 in feed

and

m_1 and m_2 = mole fraction of monomers 1 and 2 in copolymer.

Table III gives F-R parameters for the (DPA-co-GMA) polymer system. The reactivity ratios obtained by this method are $r_1 = 0.31 \pm 0.23$ and $r_2 = 1.07 \pm 0.52$, where r_1 is the reactivity ratio of DPA and r_2 is that of GMA. Figure 4 shows the F-R plot of G vs. F for the (DPA-co-GMA) polymer system.

Kelen-Tudos method²⁷

The Fineman-Ross method described above does not give equal weighting to the experimental points and does not allow for a nonlinear dependence of the error on the composition. Consequently, it gives erroneous results. To overcome this drawback the following linear equation was proposed by Kelen and Tudos.

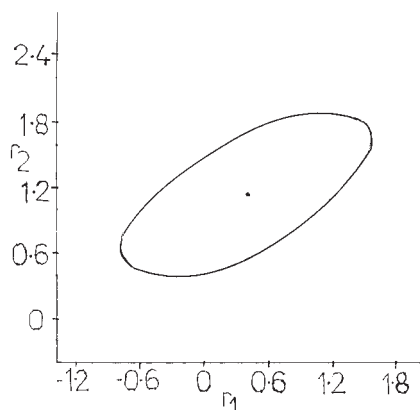


Figure 6 Nonlinear error-in-variable model for (DPA-co-GMA) system.

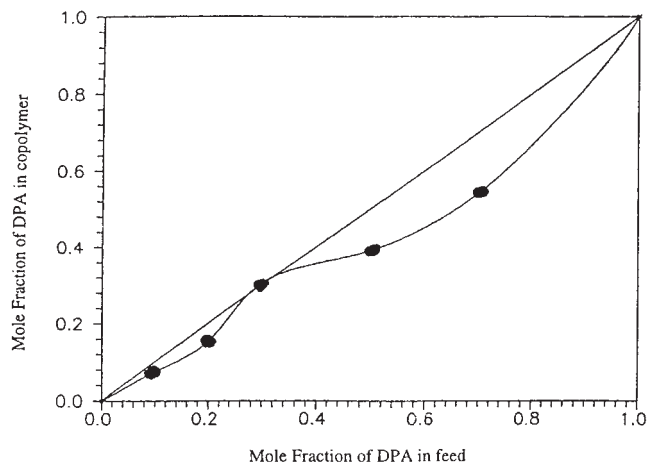


Figure 7 Feed vs. copolymer composition curve for (DPA-co-GMA) polymer system.

$$G/(\alpha + F) = (r_1 + r_2/a)(F/\alpha + F) - r_2/a,$$

where $a = F_{\min} F_{\max}^{1/2}$ obtained from the experimental data.

$$G = x(y - 1)/y \text{ and } F = x^2/y.$$

By introducing $\eta = G/(\alpha + F)$ and $\xi = F/(\alpha + F)$ the above equation changes to

$$\eta = r_1\xi - r_2/\alpha(1 - \xi).$$

The value of the reactivity ratios will be distributed between 0 and 1. A plot of η versus ξ gives a straight line having the value of r_1 at the intercept when $\xi = 1$ and the value of $-r_2/\alpha$ as the intercept at $\xi = 0$.

The Kelen-Tudos parameters are provided in Table III. The reactivity ratios obtained by this method are r_1 (DPA) = 0.40 ± 0.80 and r_2 (GMA) = 1.153 ± 0.6 . Figure 5 gives the Kelen-Tudos plot of η vs. ξ for the (DPA-co-GMA) polymer system.

Extended Kelen-Tudos method^{28,29}

In the extended Kelen-Tudos method instead of $x = M_1/M_2$, an average value of x is used. Walling and Briggs have used a constant z given by

$$z = \log(1 - \tau_1)/\log(1 - \tau_2),$$

where τ_1 and τ_2 are partial molar conversion given by

$$\tau_2 = w(\mu + x)/(\mu + y)/100$$

$$\tau_1 = 193_2 y/x,$$

TABLE V
Comparison of Reactivity Ratios of (DPA-co-GMA)
Polymers by Different Methods

Method	r_1	r_2	$1/r_2$
Fineman-Ross	0.31 ± 0.23	1.08 ± 0.52	0.90
Kelen-Tudos	0.40 ± 0.80	1.15 ± 0.56	0.90
Ex. Kelen-Tudos	0.39 ± 0.81	1.16 ± 0.58	0.90

TABLE VI
Thermal Properties and Molecular Weight Data

Polymer	Composition	TGA data (°C)		DSC data (°C)	M_w ($\times 10^3$)	M_n ($\times 10^3$)	M_w/M_n
		T_{10}	T_{50}				
Poly(DPA)	—	286	408	55	5.2	0.83	6.25
DPA-co-GMA	09:91	280	390	60	56.92	46.83	1.22
DPA-co-GMA	50:50	290	395	75	78.05	38.18	2.04

Note. T_{10} and T_{50} represent the temperature at which 10 and 50% weight loss of the respective polymers takes place.

where $w = \text{wt conversion}$ and $\mu = Mw_2/Mw_1$ of the monomers, respectively. $x = y/z$.

But $F = x^2/y$ and $G = x(y - 1)/y$.

By substituting x for x , we get

$F = y/z^2$ and $G = (y - 1)/z$.

The rest of the calculation is similar to the Kelen-Tudos method, i.e.,

$\eta = G/(\alpha + F)$ and $\xi = F/(\alpha + F)$,

where $\alpha = F_{\min} F_{\max}^{1/2}$.

The extended Kelen-Tudos parameters are provided in Table IV. The r_1 (DPA) and r_2 (GMA) values obtained by this method are 0.39 ± 0.81 and 1.16 ± 0.58 , respectively. The 95% confidence intervals were calculated as per the procedure given by Kelen and Tudos.³⁰ The nonlinear error-in-variable method using a computer program (PREVM)³¹ was used to compare the reactivity ratios and draw an elliptical model (Fig. 6).

Reactivity ratios and copolymerization behavior

The copolymer behavior plot for this system is shown in Figure 7. DPA has a reactivity of 0.40 ± 0.80 whereas GMA has a reactivity of 1.15 ± 0.56 (K-T method). Here k_{22}/k_{21} (r_2) prevails over k_{11}/k_{12} (r_1). Hence, the propagation reaction $\sim M_2M_2^*$ and $\sim M_1M_2^*$ will be preferred over $\sim M_2M_1^*$ and $\sim M_1M_1^*$. Therefore, the probability of M_2 (GMA) entering the copolymer chain is higher compared to M_1 (DPA). The copolymer formed therefore naturally will be richer in M_2 (GMA) all the time. This is also confirmed by the value of $1/r_2 < 1$ (Table V).

Thermal properties

The TGA and DSC data of poly(DPA) and (DPA-co-GMA) polymers are provided in Table VI. Poly(DPA) has a T_g of 55°C, while the T_g values of poly(4-methoxy phenyl acrylate), poly(2-hydroxyethyl acrylate), poly(methyl acrylate), poly(methyl methacrylate), and poly(styrene) are reported in the literature³² as 51, 55, 10, 105, and 100°C, respectively. Because of the presence of the ester group, which separates the phenyl ring from the backbone, the T_g of poly(DPA) is much less than that of poly(methyl methacrylate) and poly(styrene).

Molecular weight determination

The molecular weights determined by GPC for the poly(DPA) and (DPA-co-GMA) polymers having different compositions are provided in Table VI. Poly(DPA) shows a very high polydispersities of 6.25, which may be due to "auto acceleration," while the (DPA-co-GMA) polymers show narrow poly disparities.

Application of the copolymers as leather adhesives

The (50 : 50) copolymer was chosen for studying the adhesive property. These were crosslinked using 40% diethanolamine (based on the weight of GMA) in chloroform. The peel strength of the adhesive was 1.6, 1.0, 0.6, and 0.2 N/mm at 50, 90, 100, and 110 °C, respectively. The peel strength of the adhesive was maximal at 50 °C exhibiting high adhesive behavior.

CONCLUSIONS

The conclusions that can be drawn from the present study are as follows:

1. The results of the reactivity ratios obtained by Fineman-Ross, Kelen-Tudos, and extended Kelen-Tudos methods were in excellent agreement with each other.
2. GMA has a higher reactivity ratio than DPA, which means the copolymer is always richer in GMA. This is also confirmed by $1/r_2$ values, which are < 1 .
3. The adhesive prepared from this copolymer is found to possess a good peel strength compared to commercial Fevicol SR 998 and hence the possibility of using this adhesive in leather industry can be explored.

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