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4-CHLOROPHENYL ACRYLATE AND GLYCIDYL METHACRYLATE COPOLYMERS: SYNTHESIS, CHARACTERIZATION, REACTIVITY RATIOS, AND APPLICATION

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Key Words: 4-Chlorophenyl Acrylate, Glycidyl Methacrylate, Reactivity Ratios and Adhesives

ABSTRACT

4-Chlorophenyl acrylate (CPA) and glycidyl methacrylate (GMA) copolymers having different copolymer compositions were synthesized in 1,4-dioxane using benzoyl peroxide as initiator at 70 ± 0.5°C. Using ^{1}H-NMR spectroscopy, the composition of the two monomers in the copolymers were calculated by comparing the integral values of the aromatic and alifatic proton peaks. The reactivity ratios (average $r_1 = 0.03 \pm 0.04$ and $r_2 = 2.27 \pm 0.55$) were calculated by Fineman-Ross, Kelen-Tudos and extended Kelen-Tudos methods. The copolymers were characterized by ^{1}H and proton decoupled ^{13}C-NMR spectroscopies. Gel permeation chromatography was employed for estimating the M_w and M_n and M_w/M_n of the homo- and co-polymers. Thermal analysis showed copoly(CPA-GMA) (49:51) to be less stable (345°C) than poly(CPA) (417°C) at 50°C. DSC was utilized in determining the glass transition temperature. The 49:51 copolymer was chosen for making adhesives by curing with

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diethanolamine in chloroform. The cured resins were tested for the adhesion properties on leather-leather bonding at 50° and 90°C. It was found that the resin cured at 90°C exhibited a maximum peel strength of 1.1 N/mm, revealing a good adhesive behavior.

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 polymers [3] are some of the applications in which phenyl acrylate based copolymers are successfully employed. The incorporation of halogen atoms into the aromatic ring in phenyl acrylates provide a labile leaving group 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 [6], for the preparation of polymeric reagents carrying piperazine, isonitrile functionality's, etc. [7, 8] and extensively employed in peptide synthesis [9]. Divinylbenzene crosslinked phenyl acrylate copolymers are also utilized in the preparation of polymer supports for various chemical reactions [10]. Copolymers synthesized from 2,4,6-tribromophenyl acrylate showed higher reactivity due to the presence of electronegative bromine atoms in the aromatic ring [11]. Epoxy adhesives have attained popularity in recent times because of their superior performance in many industrial applications [12]. Paul Schlack [13] described the preparation of the first epoxide adhesive from epichlorohydrin and bisphenol-A which was cured with an equivalent amount of mono-, di- or poly-amines. Piere Casten [14] 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 Araldite [15] was introduced based on Casten's work. De Bruyne [16] has demonstrated and May [17] confirmed later 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. The cure behavior and the relationship between structure and ultimate properties of the epoxy resins have also been studied [18, 19]. Paul and Ranby [20] synthesized MMA-GMA copolymers of low molecular weight and modified it by opening the oxirane ring of the GMA by reaction with diethanolamine (DEA). They also found that the addition of a hydrogen-bond donor like phenol increases the rate of epoxy ring opening with DEA. The presence of epoxy group in GMA allows experimentally to modify the copolymers further for various applications [21-23].

Aim of the Investigation

At present, adhesives based on acrylic copolymers are utilized in wood and leather industries because of their versatility and performance characteristics. The shoe industry for making high quality shoes uses polyurethane adhesives which are not only costly but also have poor storage stability. In continuation of our work on phenyl acrylates [24], the present study was undertaken with a view to develop an alternative adhesive with better utility and multifunctional for adhesion to different surfaces, e.g., leather to leather, leather to rubber, rubber to rubber and leather to metal.

EXPERIMENTAL

Materials

Glycidyl methacrylate (Aldrich) was distilled under *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 4-chlorophenol (Aldrich) were used as received without further purification.

Instruments

^{1}H and ^{13}C-NMR spectra of the monomers, homo- and co-polymers were run on a Bruker 300 MHz spectrometer at room temperature using $CDCl_3$ as a solvent and tetramethyl silane (TMS) as internal reference. Proton decoupled ^{13}C-NMR spectra was 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 atmosphere with a heating rate of 10°C min^{-1} for 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 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 Monomer

Acryloyl chloride was prepared by reacting acrylic acid with benzoyl chloride by following the procedure given earlier [24]. CPA was synthesized by reacting 4-chlorophenol with acryloyl chloride in the presence of triethylamine. In a typical experiment, phenol (0.1 mole) and 100 mL chloroform were taken in a three-necked round-bottom flask fitted with a stirrer, thermometer and a dropping funnel. Acryloyl chloride (0.12 mole) 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 for 45 minutes, then the reaction mixture was stirred for 1 hour and left overnight. The unreacted phenol was removed by washing with 10% NaOH solution. Traces of water present were removed by treating with anhydrous Na_2SO_4. The solvent was finally removed by evaporation to obtain yellow monomer. yield was -90%.

Characterization

The monomer was characterized by microelemental analysis, ^1H and ^{13}C-NMR spectroscopes.

Elemental analysis ($C_9H_7O_2Cl$)

	% Carbon	% Hydrogen
Theoretical	59.19	3.84
Experimental	58.87	3.74

NMR Spectroscopy

^1H-NMR (δ, ppm): 7.5-7.0 (4H), 6.7-5.9 (3H)

^{13}C-NMR (δ, ppm): 132.70 (CH_2), 127.30 (=CH),164.00 (C=O), 148.80 (^1C), 122.72 (^2C & ^6C), 129.20 (^3C & ^5C), 130.90 (^4C)

Polymerization

Homo- and co-polymers of CPA and GMA were prepared by polymerizing 10 g of the monomers for homopolymers and using calculated amounts of the two monomers for copolymerization, using 0.5% benzoyl peroxide (based on the weight of monomer and solvent) as the initiator. The monomer/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 minutes. The tube after sealing was placed in a thermostat maintained at 70 ± 0.5°C. Polymerization was continued to obtain < 15% conversion, diluted in chloroform and precipitated by pouring into excess methanol. Filtered, redissolved in chloroform and again reprecipitated into excess methanol. The resulting white precipitate was dried *in vacuo* at 40°C for 15 hours (94%). The experimental details of copolymerization are provided in Table 1.

Adhesion and Estimation of Peel Strength Property

After ascertaining the copolymer composition using ^{1}H-NMR spectroscopy, the 50:50 copolymer was synthesized to high conversion by using 1.5% benzoyl peroxide under the same conditions as explained earlier for 72 hours to get maximum yield (~90%). 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 solvent. Cow leather strips measuring 15 x 2.5 cm were used for estimating the peel strength of the adhesives prepared after removing the grain manually using No. 80 emery paper, ~0.75 g of the adhesive was applied for an area of 7.5 x 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

TABLE 1. Copolymerization[a] of CPA and GMA: Copolymer Composition and ^{1}H-NMR Data

Feed composition in Mmole Fraction		Conversion	^{1}H-NMR data		Copolymer Composition in Mole Fraction	
CPA (M_1)	GMA (M_2)	Wt %	I_A	I_a	m_1	m_2
0.4935	0.5065	12.2	1.5	12.7	0.2447	0.7553
0.5920	0.4080	8.7	0.6	4.1	0.2966	0.7024
0.7047	0.2953	7.9	2.3	12.9	0.3397	0.6603
0.7940	0.2060	9.0	2.8	12.1	0.4118	0.5882
0.8390	0.1610	14.2	2.7	9.8	0.4647	0.5353

[a] Temperature: 70 ± 0.5°C; Solvent: 1,4-dioxane; Benzoyl peroxide: 0.5% w/w of monomers 1 and 2; non-solvent: Petroleum ether

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 hours at 50°C and 24 hours at 90°C) and the peel strength of the adhesives on leather was estimated.

RESULTS AND DISCUSSION

Infra-Red Spectroscopy

The IR spectrum of copoly(CPA-GMA) (84:16) showed vibrations at 3220, 3100, 3065, 1756, 1554, and 1489 cm^{-1} corresponding to the aromatic -CH stretching, C=O stretching and the aromatic C=C, while the vibrations appearing at 2952, 2924, 2854, 1728 and 908 cm^{-1} represent the methyl stretch-ing, C=O stretching and the epoxy ring of the GMA unit.

^{13}C-NMR Spectroscopy

The ^{13}C-NMR spectra of copoly(CPA-GMA) (84:16) is shown in Figure 1. The carbonyl group of the CPA unit appears at 176.90 ppm, while the backbone CH_2 gave a sharp signal at 44.40 ppm. The aromatic carbons appear as sharp lines. The peak at 150.70 ppm corresponds to ^{1}C atom of the phenyl ring which is adjacent to ester group. The electronegativity of chlorine atom present in ^{4}C causes downfield shift at 131.50 ppm. The aromatic carbons ^{3}C & ^{5}C and ^{2}C & ^{6}C are observed at 127.45 and 122.75 ppm, respectively. The presence of GMA in the copolymer is confirmed by observing ester carbonyl at 172.75 ppm, while -OCH_2 and backbone carbons of the same unit gave very sharp peaks at 65.75 and 48.00 ppm. The group of broad peaks at the far end of the spectrum at 20.80 and 18.30 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 meso (m) and racemic (r) resonance's. 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.

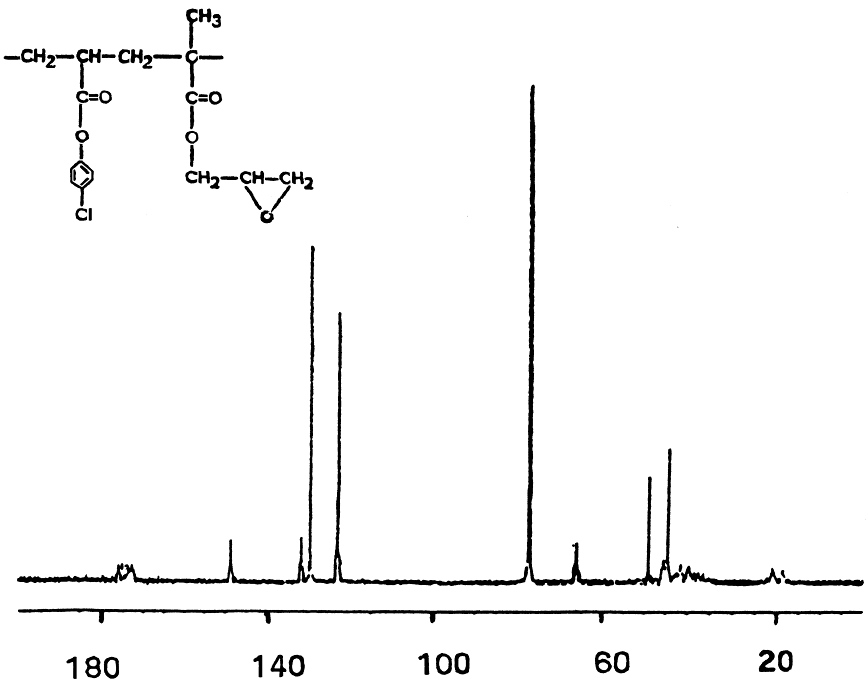


Figure 1. ^{13}C-NMR spectrum of copoly(CPA-GMA) (84:16).

Copolymer Composition

The ^{1}H-NMR spectra of copoly(CPA-GMA) (49:51) is shown in Figure 2. The composition of the CPA in the copolymer was determined using ^{1}H-NMR data by comparing the integral values of aromatic and alifatic protons as shown below:

$$\frac{\text{Integral value of aromatic protons } (I_A)}{\text{Integral value of alifatic protons } (I_a)} = \frac{4\ m_1}{3\ m_1 + 10\ m_2}$$

The equation is derived from the fact that CPA contains 4 aromatic and 3 aliphatic protons, while GMA has 10 alifatic protons. From this and $m_2 = 1\text{-}m_1$, we have

$$m_1 = \frac{10\ I_A}{7\ I_A + 4\ I_a}$$

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

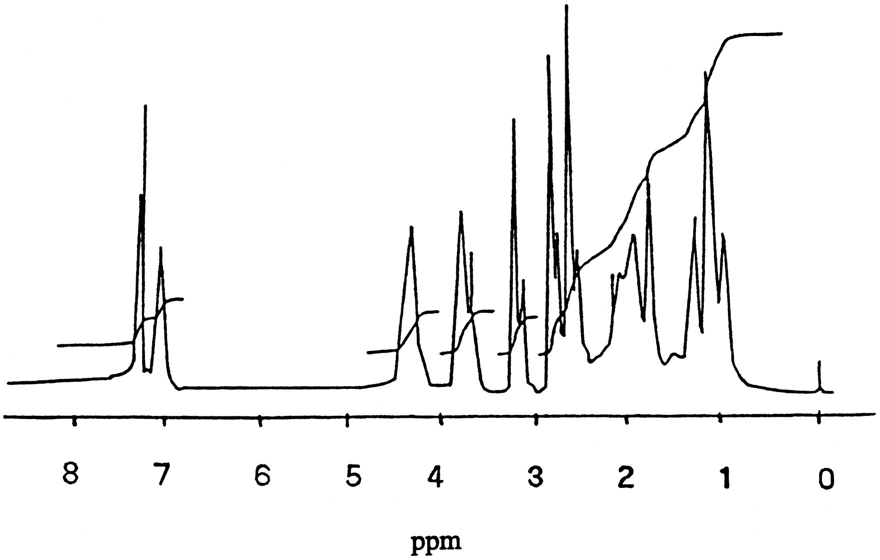
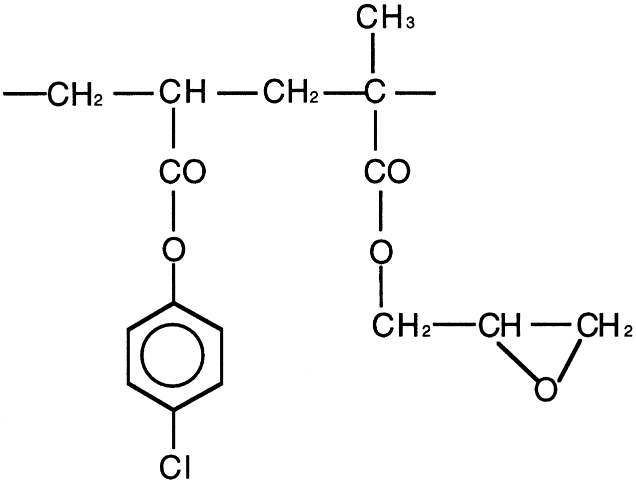


Figure 2. ^{1}H-NMR spectrum of copoly(CPA-GMA) (49:51).

The structure of the copolymer is shown below:



Calculation of Reactivity Ratios

Fineman-Ross method [25]

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

$x = M_1/M_2$ and $y = m_1/m_2$, where
M_1 and M_2 = mole fraction of monomers 1 and 2 in feed
m_1 and m_2 = mole fraction of monomers 1 and 2 in copolymer

Table 2 gives F-R parameters for the copoly(CPA-GMA) system. The reactivity ratios obtained by this method are $r_1 = 0.04 \pm 0.04$ and $r_2 = 2.35 \pm 0.74$ where r_1 is the reactivity ratio of CPA and r_2 that of GMA.

Kelen-Tudos Method [26]

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

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

where $\alpha = \sqrt{F_{min} \cdot F_{max}}$. is obtained from the experimental data and

TABLE 2. F-R and K-T Parameters for Copoly(CPA-GMA) System

X	Y	G	F	η^a	ξ^a
0.9743	0.3240	-2.0331	2.9302	-0.1626	0.2343
1.4510	0.4217	-1.9901	4.9929	-0.1366	0.3428
2.3864	0.5145	-2.2522	11.0695	-0.1091	0.5362
3.8544	0.7001	-1.6511	21.2200	-0.0536	0.6891
5.2112	0.8681	-0.7917	31.2822	0.0194	0.7657

[a] $\alpha = 9.5741$

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

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 vs 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 for copoly(CPA-GMA) system are provided in Table 2. The reactivity ratios obtained by this method are r_1 (CPA)= 0.03 ± 0.05 and r_2 (GMA)= 2.187 ± 0.5. Figure 3 gives the Kelen-Tudos plot of η vs ξ for the copoly(CPA-GMA) system.

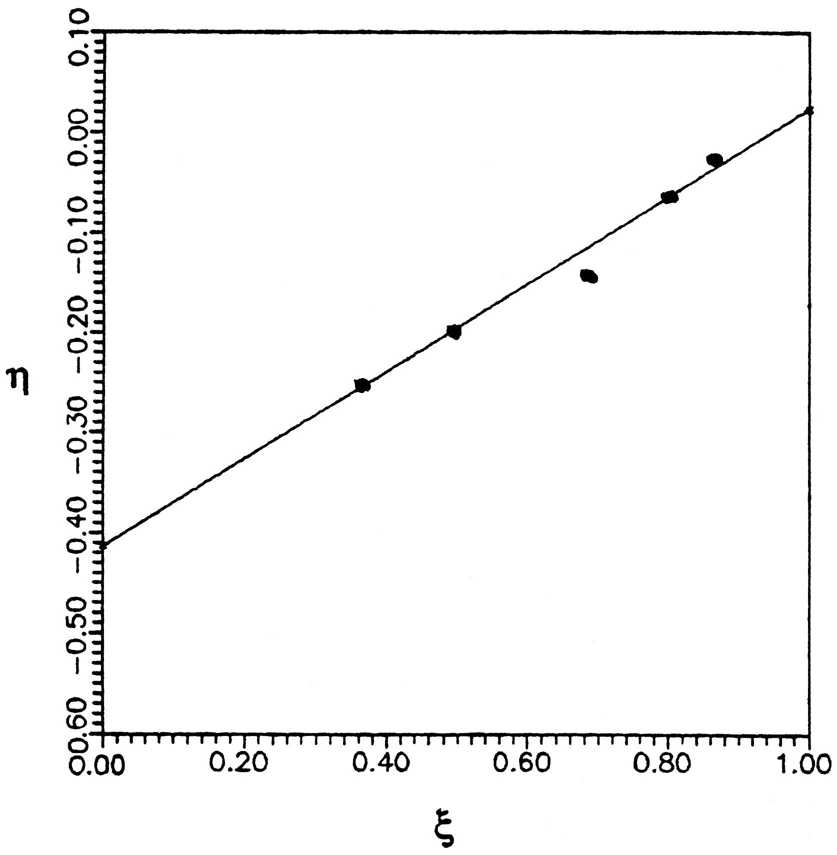


Figure 3. K-T plot of η vs. ξ for copoly(CPA-GMA) system.

Extended Kelen-Tudos method [27,28]

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:

$$z = \log(1-\Im_1)/\log(1-\Im_2)$$

where $\Im_1$ and $\Im_2$ are partial molar conversion given by

$$\Im_2 = w\,(\mu+x)/(\mu+y)/100$$
$$\Im_1 = \Im_2\, y/x$$

where w = 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 z for x, we get,

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

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

$$\eta = G/(\alpha+F) \text{ and } \xi = F/(\alpha+F)$$

where $\alpha = \sqrt{F_{min.}\,F_{max}}$.

The extended Kelen-Tudos parameters for copoly(CPA-GMA) are provided in Table 3. The r_1 (CPA) and r_2 (GMA) values obtained by this method are 0.02 ± 0.03 and 2.29 ± 0.41, respectively. The 95% confidence intervals were also calculated as per the procedure given by Kelen-Tudos [29]. The average of the reactivity ratios given in the abstract was obtained by taking the values of F-R, K-T and extended K-T methods (Table 4).

Reactivity Ratios and Copolymerization Behavior

The copolymer behavior plot for this system is shown in Figure 4. 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

TABLE 3. Extended K-T Parameters for Copoly(CPA-GMA) System

$\Im_1$	$\Im_2$	G	F	η^a	ξ^a
0.0645	0.1939	-2.1864	3.3889	-0.1268	0.1966
0.0470	0.1616	-2.1192	5.6619	-0.1086	0.2901
0.0417	0.1933	-2.4503	13.1018	-0.0909	0.4861
0.0512	0.2819	-1.8894	27.7890	-0.0454	0.6673
0.0860	0.5164	-1.0652	56.6249	-0.0151	0.8034

$^a\alpha = 13.8526$

of M_2 (GMA) entering the copolymer chain is higher as compared to M_1 (CPA). Therefore, the copolymer formed naturally will be richer in M_2 (GMA) all the time.

Thermal Properties

The TGA and DSC data of poly(CPA) and copoly(CPA-GMA) are provided in Table 5.

In the Table, T_{10} and T_{50} refer to the temperature for 10% and 50% weight loss of the respective homo- and co-polymers. Because of the presence of ester carbonyl (COO) which separates the phenyl ring from backbone carbons, the Tg of copoly(CPA-GMA) is much less (75°C) than poly(phenyl methacrylate) (110°C), poly(styrene, isotactic and atacatic) (100°C) and higher than that of poly(phenyl acrylate) (57°C), poly(4-methoxyphenyl acrylate (51°C) and poly(methyl methacrylate, isotactic) (38°C) which are reported in the literature [30].

TABLE 4. Comparison of Reactivity Ratios of Copoly(CPA-GMA) by Different Methods

Method	r_1	r_2
Fineman-Ross	0.04 ± 0.04	2.35 ± 0.74
Kelen-Tudos	0.03 ± 0.05	2.19 ± 0.50
Ex. Kelen-Tudos	0.01 ± 0.03	2.28 ± 0.41
Average	0.03 ± 0.04	2.27 ± 0.55

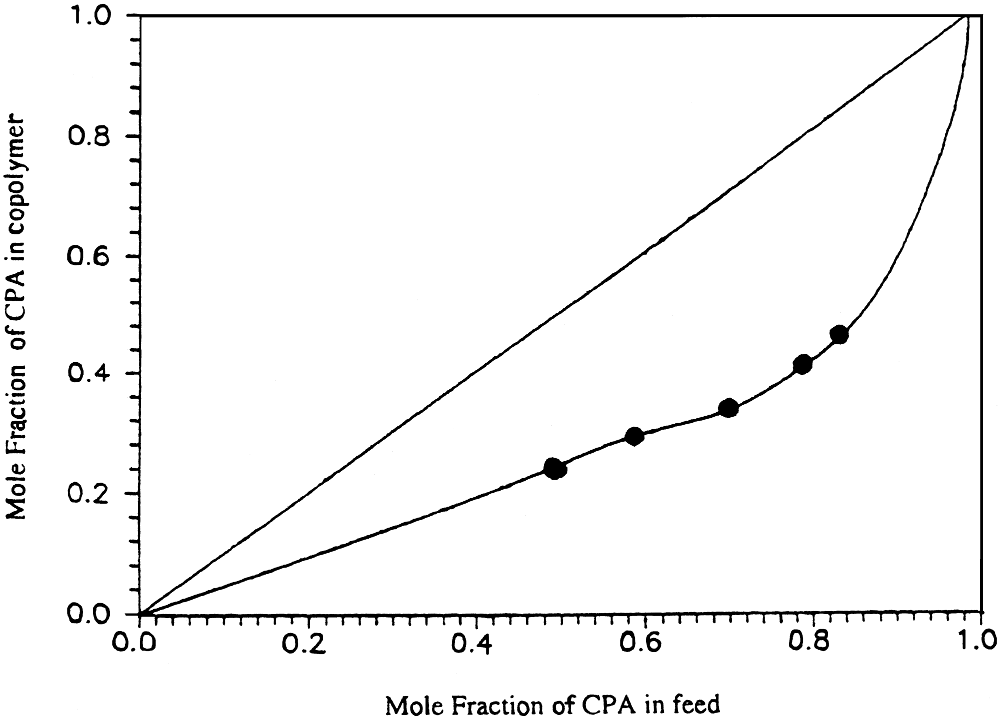


Figure 4. Feed vs. copolymer composition curve for copoly(CPA-GMA) system (●—●) and ideal copolymer composition ($r_1 = r_2$) curve (—).

Molecular Weight Determination

The molecular weights determined by GPC for the poly(CPA) and copoly(CPA-GMA) having different compositions are provided in Table 5. The high polydispersity of 5.4 for poly(CPA) may be perhaps due to autoacceleration. In the case of copoly(CPA-GMA), the polydispersity value of above 2 suggests that termination may take place by coupling mechanism.

Application of the Copolymers as Leather Adhesives

The (50:50) copolymer was chosen for studying the leather adhesive property. These were crosslinked using 40% diethanolamine (based on the weight of GMA) in chloroform. The peel strength of the adhesive were 0.7, and 1.1 N/mm at 50, and 90°C, respectively. These adhesives showed better adhesion characteristics than even commercially available adhesive. Fevicol SR 998 at room temperature which showed a peel strength of 0.3 N/mm.

TABLE 5. TGA, DSC and GPC Data of Poly(CPA) and Copoly(CPA-GMA)

	(°C)			Molecular Weight x 10^3		
Polymer	T_{10}	T_{50}	T_g	Mw	Mn	Mw/Mn
Poly(CPA)	360	417	63	8.4	1.5	5.4
Copoly(CPA-GMA)(49:51)	295	345	75	132	54	2.5
Copoly(CPA-GMA) (84:16)	...	...	..	29	13	2.1

CONCLUSION

The results of the reactivity ratios obtained by Fineman-Ross, Kelen-Tudos and extended Kelen-Tudos methods were in excellent agreement with each other. GMA has a higher reactivity ratio than CPA which means the copolymer is always richer in GMA. The adhesive prepared from this copolymer is found to possess a good peel strength compared to commercial Fevicol SR 998. Hence, the possibility of using this adhesive in leather industry can be explored.

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