

Synthesis, Spectral Properties, and Thermal Properties of Homo- and Copolymers of 3,5-Dimethylphenyl Acrylate with Glycidyl Methacrylate and Determination of Reactivity Ratios

P. S. VIJAYANAND, R. ARUNPRASATH, R. BALAJI, S. NANJUNDAN

Department of Chemistry, College of Engineering, Anna University, Madras-600 025, India

Received 3 May 2001; accepted 10 December 2001

ABSTRACT: The new acrylic monomer, 3,5-dimethylphenyl acrylate, was synthesized by reacting 3,5-dimethylphenol dissolved in ethyl methyl ketone (EMK) with acryloyl chloride in the presence of triethylamine. The homopolymer and copolymers of different feed compositions of 3,5-dimethylphenyl acrylate and glycidyl methacrylate were synthesized using free radical polymerization in ethyl methyl ketone solution at $70 \pm 1^\circ\text{C}$ using benzoyl peroxide as initiator. The copolymers were characterized by Fourier transform infrared (FTIR), ^1H nuclear magnetic resonance (NMR), and ^{13}C -NMR spectroscopic techniques. The molecular weight (\bar{M}_n and \bar{M}_w) and polydispersity index of the polymers were determined using gel permeation chromatograph. The glass transition temperatures of the polymers were determined by differential scanning calorimeter. Thermogravimetric analysis of the polymers was performed in air. The solubilities of the polymers were tested in various polar and nonpolar solvents. Copolymer compositions were determined using ^1H -NMR spectra. The monomer reactivity ratios were determined by the application of conventional linearization methods such as Fineman-Ross, Kelen-Tüdös, and extended Kelen-Tüdös. The peel strength of the leather adhesives prepared from the copolymers was also determined. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2261–2270, 2002

Key words: 3,5-dimethylphenyl acrylate; glycidyl methacrylate; thermal properties; NMR; adhesives

INTRODUCTION

Polymer supports based on glycidyl methacrylate (GMA) are found to have versatile application due to the preference of the oxirane group.¹ Copolymers based on GMA have applications in biology for the binding of drugs and biomolecules,² and in electron industries as negative electron beam re-

sists.³ Epoxy group containing compounds are used as excellent thermosetting adhesives that are heat resistant and decrease the flow cracking in the manufacture of semiconductor device packaging,^{4–6} Ultraviolet (UV) radiation curing surface coatings,⁷ and matte coatings that prevents from corrosion.⁸ Substituted phenyl acrylate and GMA copolymers are used as adhesive on leather to leather bonding and leather to rubber bonding having a maximum peel strength, and also for antireflective coating.^{9,10}

The accurate estimation of copolymer composition and determination of monomer reactivity ra-

Correspondence to: S. Nanjundan (snanjundan@yahoo.com).

Journal of Applied Polymer Science, Vol. 85, 2261–2270 (2002)
© 2002 Wiley Periodicals, Inc.

tio is significant for tailor making copolymers. In the past few decades, $^1\text{H-NMR}$ spectroscopic analysis has been established as a powerful tool for the estimation of copolymer composition.^{11–15} The present paper reports the synthesis, characterization, and determination of reactivity ratios for the comonomers 3,5-dimethylphenyl acrylate (DMPA) and GMA. Thermal properties of all the polymers were analyzed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

EXPERIMENTAL

Materials

3,5-Dimethylphenol (Lancaster) was used as such without purification. GMA (Emerk) was purified by distillation under reduced pressure.¹⁶ Benzoyl peroxide (BPO) was recrystallized from a chloroform–methanol (1:1) mixture. All the solvents were purified by distillation prior to their use.

Synthesis of DMPA

Acryloyl chloride was prepared from acrylic acid and benzoyl chloride using the procedure of Stampel.¹⁷ For the synthesis of 3,5-dimethylphenyl acrylate, 3,5-dimethylphenol (15 g, 0.12 mol) and triethylamine (18.8 mL, 0.13 mol) were dissolved in 250 mL of ethyl methyl ketone, and taken in a two-necked round-bottom flask fitted with a mechanical stirrer. To the other neck a dropping funnel was fitted. The reaction mixture was stirred in an ice bath of 0–5°C. To the well-cooled reaction mixture, acryloyl chloride (11.00 mL, 0.13 mol) dissolved in 25 mL of ethyl methyl ketone was added dropwise through the dropping funnel over a period of 30 min. After the addition, the reaction mixture was stirred for 1 h. Then the ice bath was removed and the reaction mixture was stirred well at room temperature for a further period of 1 h. Then the precipitated triethylammonium chloride was filtered off and the solvent in the filtrate was removed using a rotary evaporator. The residue obtained was dissolved in ether and was washed with 0.1% solution of sodium hydroxide twice and then with distilled water. The ether solution was dehydrated using anhydrous sodium sulfate. The ether solution was then evaporated to get a crude 3,5-dimethylphenyl acrylate, which was purified by reduced pressure distillation. Yield 18 g (72%).

The formation of the monomer was confirmed by elemental analysis, FTIR, and $^1\text{H-NMR}$ spectra.

Elemental analysis (%): C = 74.65 (Found), 74.98 (Calcd); H = 6.54 (Found), 6.86 (Calcd); IR cm^{-1} : 3080 (=C–H), 2980 and 2891 (C–H stretching), 1735 (C=O), 1631 ($\text{CH}_2=\text{C}<$), 1600, 1490, 1470 (aromatic C=C), 1375 ($-\text{CH}_3$ bending), 1125 (C–O), 780 and 697 (C–H out-of-plane bending).

$^1\text{H-NMR}$ ppm: 6.88–6.31 (3H) (Ar-H), 6.00–5.99 (2H) ($\text{CH}_2=\text{C}$), 5.95 (1H) (=CH–), 2.30 and 2.23 (6H) (Ar- CH_3).

Homopolymerization of DMPA

One gram of the monomer, DMPA and 50 mg of benzoyl peroxide were dissolved in 10 mL of ethyl methyl ketone (EMK) in a polymerization tube, and oxygen-free nitrogen gas was purged through the solution for 20 min. Then the solution was thermostated at $70 \pm 1^\circ\text{C}$. After 8 h the polymer was precipitated by adding the reaction mixture to methanol. The polymer was purified by repeated reprecipitation by methanol from a solution of the polymer in EMK. The polymer was filtered and washed with methanol and dried in vacuum at 50°C for 24 h. Yield is 70%.

Copolymerization of DMPA with GMA

Predetermined quantities of DMPA, GMA with EMK, and benzoyl peroxide were taken in a standard reaction tube (100 mL), and the mixture was purged with oxygen free nitrogen for 30 min. The tube was tightly sealed and immersed in a thermostated water bath maintained at $70 \pm 1^\circ\text{C}$. To follow the copolymer equation, the conversions were restricted to less than 10%. After the required time, the reaction mixture was poured into excess methanol. The precipitated polymer was filtered off and purified by repeated reprecipitation from chloroform solution using methanol and finally dried in a vacuum oven at 50°C for 24 h.

Measurements

Elemental analysis was performed with a Perkin-Elmer C-H analyzer. Infrared spectra were recorded with a Nicolet 360 FTIR ESP spectrophotometer as KBr pellets. $^1\text{H-NMR}$ spectra of all the monomer and polymer samples were run on a Bruker 270 MHz FT-NMR spectrometer at room temperature using CDCl_3 and tetramethylsilane (TMS) as a solvent and an internal standard re-

Table I Composition Data of Free Radical Copolymerization of DMPA(1) with CMA(2) in EMK Solution at 70°C

| Copolymer | M_1^a | Conversion (%) | Intensities of Protons | | C | m_1^a | m_2^b |
|-----------|---------|----------------|------------------------|-----------|--------|---------|---------|
| | | | I_{Ar} | I_{Ali} | | | |
| 1 | 0.1621 | 8.72 | 1.1679 | 96.912 | 0.0120 | 0.0398 | 0.9602 |
| 2 | 0.3548 | 7.52 | 3.1370 | 94.132 | 0.0333 | 0.1097 | 0.8903 |
| 3 | 0.4914 | 8.50 | 5.017 | 91.034 | 0.0551 | 0.1803 | 0.8197 |
| 4 | 0.6600 | 9.25 | 8.852 | 89.460 | 0.0989 | 0.3191 | 0.6809 |
| 5 | 0.8002 | 9.17 | 12.883 | 81.637 | 0.1578 | 0.4997 | 0.5003 |
| 6 | 0.9026 | 8.84 | 16.127 | 72.513 | 0.2224 | 0.6901 | 0.3090 |

^a M_1 and m_1 are the mole fraction of DMPA in the feed and copolymer respectively.

^b m_2 mole fraction of GMA in the copolymer.

spectively. The proton decoupled ^{13}C -NMR spectrum was run on the same instrument operating at 22.63 MHz at room temperature and the chemical shifts were recorded under similar conditions. The molecular weights (\bar{M}_n and \bar{M}_w) were determined using Waters 501 gel permeation chromatograph. Tetrahydrofuran was used as an eluent and polystyrene standards were employed for calibration. Thermogravimetric analysis was performed with Mettler TA 3000 thermal analyzer in air atmosphere at a heating rate of 15°C/min. The glass transition temperature was determined with a Perkin-Elmer DSC d7 differential scanning calorimeter at a heating rate of 10°C/min in air. The peel strength of adhesives prepared from the copolymers was estimated using Satra AM I and II.

Estimation of Peel Strength of Adhesives

Three poly(DMPA-co-GMA) samples having different compositions (0.1:0.89, 0.18:0.82, and 0.32:0.68) were chosen in order to study the adhesive property on leather. The copolymers were individually crosslinked using 40% ethanolamine (based on the weight of GMA in chloroform). Cow side leathers of length 15 cm and breadth 2.5 cm were used for determining the peel strength of adhesives prepared. After the grains of the leather were removed with the help of Emery paper, 0.75 g of adhesive was applied uniformly over an area of 7.5×2.5 cm at one end of the buffed surface of each strips. The adhesive film was allowed to dry and when it was still having some tackiness, the coated surfaces of the two leather strips were aligned face to face carefully such that there is no air bubble is trapped inside and the

free ends of the leather strips lie in the same direction. The effect of two different curing temperature (50 and 90°C) on the peel strength of leather to leather adhesive was determined.

RESULTS AND DISCUSSION

Poly(DMPA) was obtained by free radical solution polymerization of the monomer at $70 \pm 1^\circ\text{C}$ in EMK solvent using benzoyl peroxide as the initiator.

The copolymerization of DMPA with GMA in ethyl methyl ketone solution was studied in a wide composition interval with mole fractions of DMPA ranging from 0.15 to 0.9 in the feed. The reaction time was selected between 2.40 and 3 h to give conversions less than 10% by weight in order to satisfy in differential copolymerization equation. The data on the composition of the feed and the copolymers are presented in Table I.

The homopolymer and the copolymers were soluble in chloroform, acetone, dimethyl acetamide, dimethyl formamide, dimethyl sulfoxide, tetrahydrofuran, benzene, toluene, and xylene, but insoluble in n-hexane and the hydroxyl group containing solvents such as methanol and ethanol.

The IR spectrum of poly(DMPA) shows a peak at 3020 cm^{-1} due to the C—H stretching of the aromatic ring. The peaks at 2955, 2921, and 2876 cm^{-1} are attributed to the unsymmetrical and symmetrical C—H stretching of methylene and methyl groups. When compared to the monomer the ester carbonyl stretching is shifted to higher frequency and is observed at 1757 cm^{-1} . This is due to the loss of conjugation after polymerization

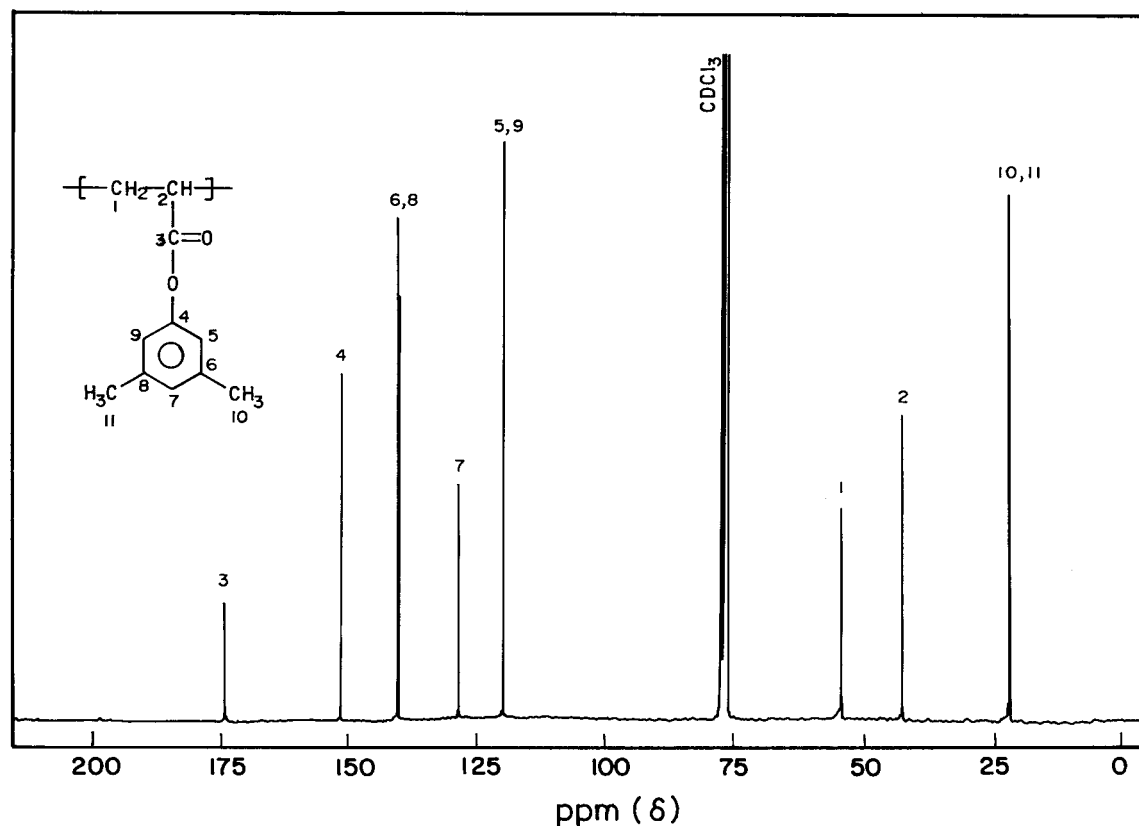


Figure 1 ^{13}C -NMR spectrum of poly(DMPA).

of the monomer. The ring stretching vibrations of the aromatic nuclei were at 1610, 1593, and 1480 cm^{-1} . The symmetrical bending vibrations of methyl group is seen at 1382 cm^{-1} . The peak at 1146 cm^{-1} is due to the C—O stretching. The C—H out of plane bending vibrations of the 1,3,5 trisubstituted aromatic nuclei are observed at 857 and 731 cm^{-1} .

The proton NMR spectrum of the homopolymer poly(DMPA) shows that the chemical shifts of the aromatic protons are shifted to upfield due to the electron donating methyl groups attached to the aromatic nucleus and they appear at 6.65 and 6.44 ppm. The methyne protons give a broad signal between 2.85 and 3.13 ppm. The methyl groups attached to the aromatic nucleus show signal at 2.24 ppm. The broad resonance signal shown between 1.86 and 1.12 ppm is due to the backbone methylene group.

The proton decoupled ^{13}C -NMR spectrum of the homopolymer is given in Figure 1. The ester carbonyl carbon shows resonance at 174.46 ppm. The aromatic carbon attached to the oxygen atom gave signal at 150.75 ppm. The aromatic carbon atoms to which methyl groups are attached gave

resonance signals at 139.83 and 139.56 ppm. The other aromatic carbons gave signals at 119.52 (C_9 and C_5) and 127.97 ppm (C_7). The backbone methylene and methyne carbons give signals at 59.84 and 44.95 ppm respectively. The peaks at 21.63 and 21.34 ppm are attributed to the methyl carbons attached to the aromatic nucleus.

The IR spectrum of the copolymer, poly(DMPA-co-GMA) (0.5; 0.5), shows a peak at 3047 cm^{-1} corresponding to the C—H stretching of aromatic system. The symmetrical and unsymmetrical stretching due to the methyl and methylene groups are observed at 2983 and 2853 cm^{-1} . The peak at 1732 cm^{-1} is attributed to the ester carbonyl stretching of both DMPA and GMA units. The aromatic C=C stretching are observed at 1600, 1567, 1475, and 1490 cm^{-1} . The symmetrical and asymmetrical bending vibrations of methyl groups is seen at 1375 and 1450 cm^{-1} respectively. The symmetrical stretching of the epoxy group is observed at 1250 cm^{-1} . Another band seen at 900 cm^{-1} is due to the asymmetric stretching of the epoxy group. Another band due to the epoxide referred to as the "12 micron" band appears at 850 cm^{-1} . The C—O stretching is ob-

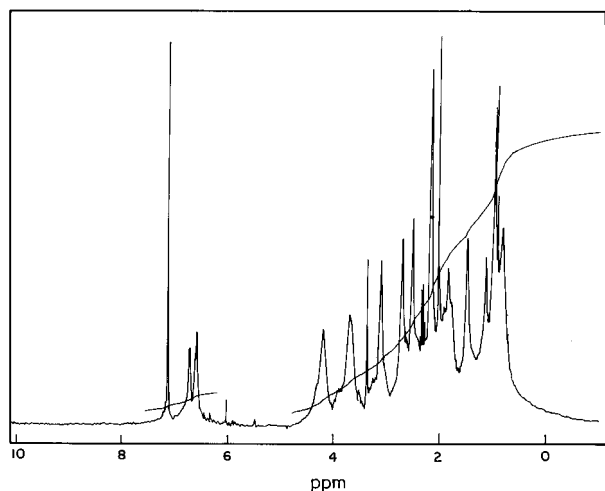


Figure 2 $^1\text{H-NMR}$ spectrum of poly(DMPA-co-GMA) (0.1097; 0.8903).

served at 1145 cm^{-1} . The C—H out-of-plane bending vibrations of the aromatic nuclei are observed at 836 and 735 cm^{-1} .

The proton NMR spectrum of the copolymer poly(DMPA-co-GMA) (0.1097; 0.8903) is shown in

Figure 2. The chemical shifts assignments for the copolymers were based on the chemical shifts observed for the respective homopolymers. The aromatic protons show signals at 6.78 and 6.55 ppm. The spectrum shows two signals at 4.13 and 3.71 ppm due to the ester $-\text{CH}_2\text{O}$ group. The peak at 3.15 ppm is due to the methyne proton of the epoxy group. The methylene protons of the epoxy show signal at 2.73 and 2.52 ppm. The signals obtained at 2.13 and 2.03 ppm are due to the methyl groups attached to the aromatic nucleus. The methylene and methyne groups of the backbone show a broad signal between 1.14 and 1.88 ppm. The signals obtained at 0.78 and 0.91 ppm are due to the α -methyl protons of the DMPA unit.

The proton decoupled $^{13}\text{C-NMR}$ spectrum of poly(DMPA-co-GMA) (0.1803; 0.8197) is shown Figure 3. It shows resonance signals at 176.15 and 173.96 ppm due to the ester carbonyl carbon of DMPA and GMA units. The aromatic carbon attached to the oxygen atom shows resonance signal at 152.08 ppm. The other aromatic carbon signals are observed at 139.83 ppm (C_6 and C_8),

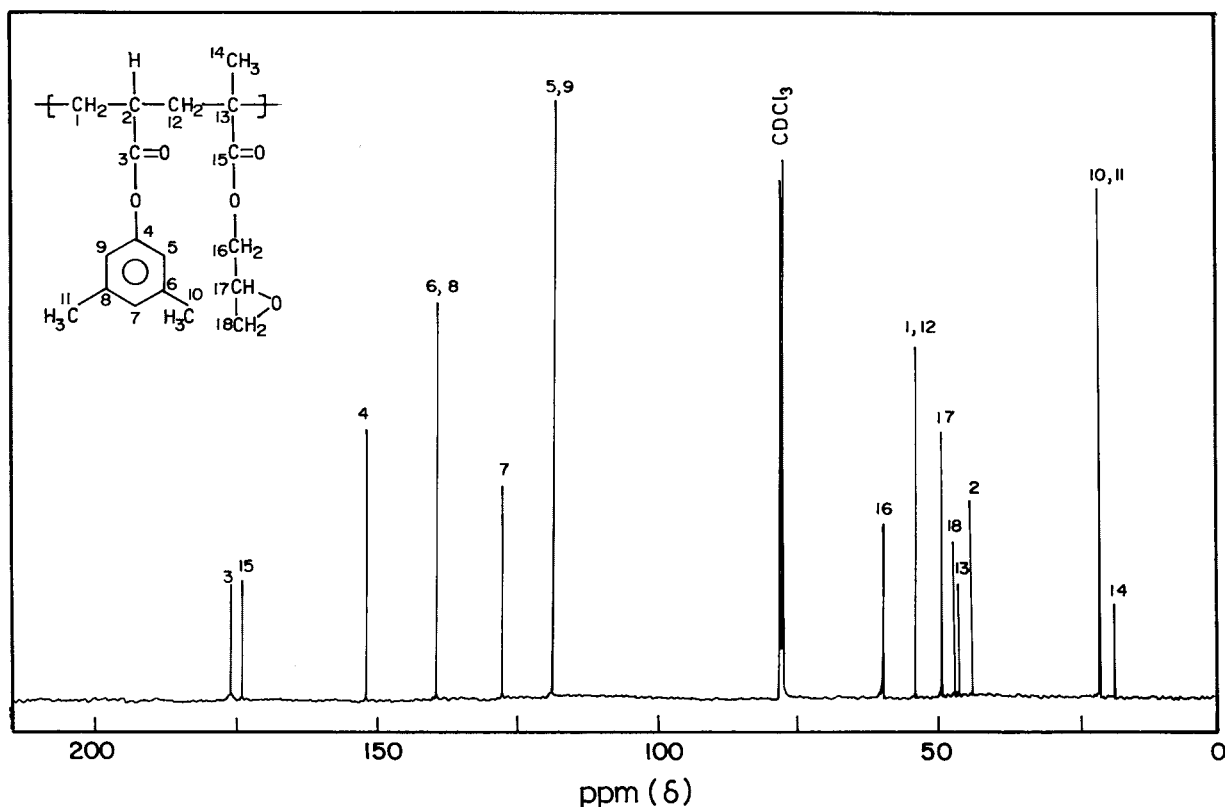


Figure 3 $^{13}\text{C-NMR}$ spectrum of poly(DMPA-co-GMA) (0.1803; 0.8197).

Table II Molecular Weight Data of Homo and Copolymers of DMPA and GMA

| Polymer | m_1^a | $\bar{M}_w \times 10^{-4}$ | $\bar{M}_n \times 10^{-4}$ | \bar{M}_w/\bar{M}_n |
|-------------------|---------|----------------------------|----------------------------|-----------------------|
| Poly(DMPA) | 0.0000 | 3.35 | 2.01 | 1.67 |
| Poly(DMPA-co-GMA) | 0.0398 | 3.80 | 1.96 | 1.94 |
| | 0.1097 | 3.69 | 1.98 | 1.86 |
| | 0.1803 | 3.55 | 1.88 | 1.89 |
| | 0.3191 | 3.51 | 1.91 | 1.84 |
| | 0.4997 | 3.24 | 1.78 | 1.82 |
| | 0.6901 | 3.19 | 1.81 | 1.76 |
| Poly (GMA) | 1.0000 | 4.02 | 2.04 | 1.97 |

^a m_1 is the mole fraction of DMPA in the copolymer.

127.97 ppm (C_7), 119.52, and 119.42 ppm (C_9 and C_5). The methylenoxy group flanked between the carbonyl group and methylene carbon of GMA unit show signal at 66.6 ppm. The epoxy ring methyne and methylene carbon of GMA unit show signal at 49.12 and 46.41 ppm respectively. The signal due to the backbone methylene, methyne, and tertiary carbon atoms are observed at 54.12, 42.2, and 44.35 ppm, respectively. The methyl group attached to the aromatic nuclei show signal at 21.62 ppm. The α -methyl group of GMA unit shows resonance signal at 18.32 ppm.

Molecular Weights

The number and weight average molecular weights of poly(DMPA), poly(GMA), and six samples of copolymers determined by gel permeation chromatography are presented in Table II. The polydispersity index of poly(DMPA) and poly(GMA) are 1.67 and 1.97 respectively. The theoretical value of \bar{M}_n/\bar{M}_w for polymers produced

via radical combination and disproportionation are 1.5 and 2.0 respectively.¹⁸ In the homopolymerization of GMA the growing chains undergo termination mainly by disproportionation.¹⁹ The polydispersity value of poly(DMPA) suggest that there is a strong tendency for chain termination by recombination. The values of \bar{M}_n/\bar{M}_w in copolymerization is also known to depend on chain termination in the same way as in homopolymerization.²⁰ The values of \bar{M}_n/\bar{M}_w of the copolymers suggest that for most of the copolymers the tendency for chain termination by disproportionation is more than that for recombination and the copolymer having a mole fraction 0.6901 with respect to DMPA has nearly the same tendency for termination by recombination and disproportionation.

Glass Transition Temperature

The glass transition temperature (T_g) of the copolymers were determined using differential

Table III TGA and DSC Data for DMPA-GMA copolymer system

| Polymers | m_1 | m_2 | IDT ^a | Temperature at Weight Loss (°C) | | | | | T_g (°C) |
|-------------------|--------|--------|------------------|---------------------------------|-----|-----|-----|-----|------------|
| | | | | 10% | 30% | 50% | 70% | 90% | |
| Poly(GMA) | 0.0000 | 1.000 | 188 | 260 | 292 | 308 | 322 | 372 | 74 |
| Poly(DMPA-co-GMA) | 0.0398 | 0.9602 | 191 | 263 | 294 | 312 | 327 | 374 | 73 |
| | 0.1097 | 0.8903 | 194 | 266 | 296 | 316 | 331 | 376 | 70 |
| | 0.1803 | 0.8197 | 200 | 268 | 299 | 323 | 339 | 378 | 67 |
| | 0.3191 | 0.6809 | 206 | 270 | 303 | 330 | 348 | 383 | 61 |
| | 0.4997 | 0.5003 | 212 | 272 | 306 | 337 | 356 | 388 | 50 |
| | 0.6901 | 0.3090 | 233 | 279 | 322 | 356 | 378 | 412 | 35 |
| Poly(DMPA) | 1.0000 | 0.0000 | 254 | 307 | 337 | 375 | 400 | 443 | 11 |

^a IDT is initial decomposition temperature.

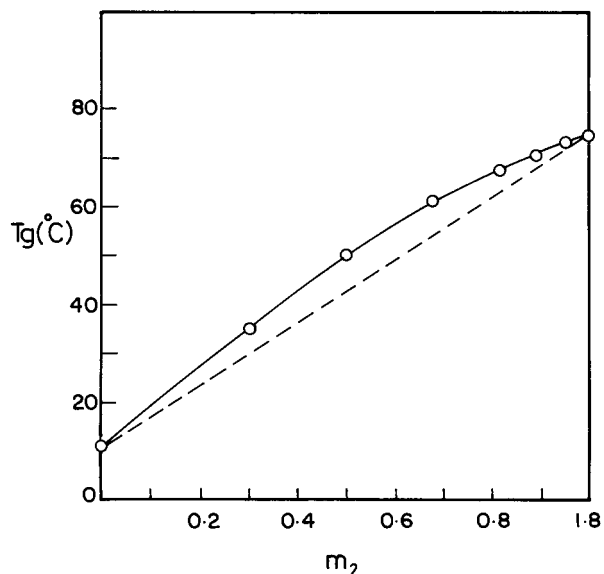


Figure 4 Variation of T_g with composition of poly-(DMPA-co-GMA) system.

scanning calorimeter and the data are presented in Table III. All the prepared copolymers show a single T_g , showing the absence of formation of mixture of homopolymers or a block copolymer. The T_g of poly(DMPA) is 11°C. The T_g of poly(GMA) is 74°C.²¹ The variation of T_g of copolymers with the mole fractions of DMPA unit in the copolymer is shown in Figure 4.

Thermogravimetric Analysis

TGA curves for poly(DMPA), poly(GMA), and a sample of poly(DMPA-co-GMA) (0.5; 0.5) are shown in Figure 5. The results of the differential thermogravimetric analysis are presented in Table III. The thermograms clearly indicate that poly(DMPA-co-GMA) undergo two stage decomposition, while poly(GMA) and poly(DMPA) undergoes single stage decomposition. The initial decomposition temperature of poly(DMPA), poly(DMPA-co-GMA) and poly(GMA) are 254, 212, and 188°C. For DMPA, poly(DMPA-co-GMA) (0.5: 0.5) and poly(GMA) 50% weight loss was observed at 375, 337, and 308°C. TGA results indicate that the thermal stability of the copolymer increases with increase in DMPA content in the copolymer.

Copolymer Composition

The chemical structure of copolymers may be represented as in Scheme 1. The average composition

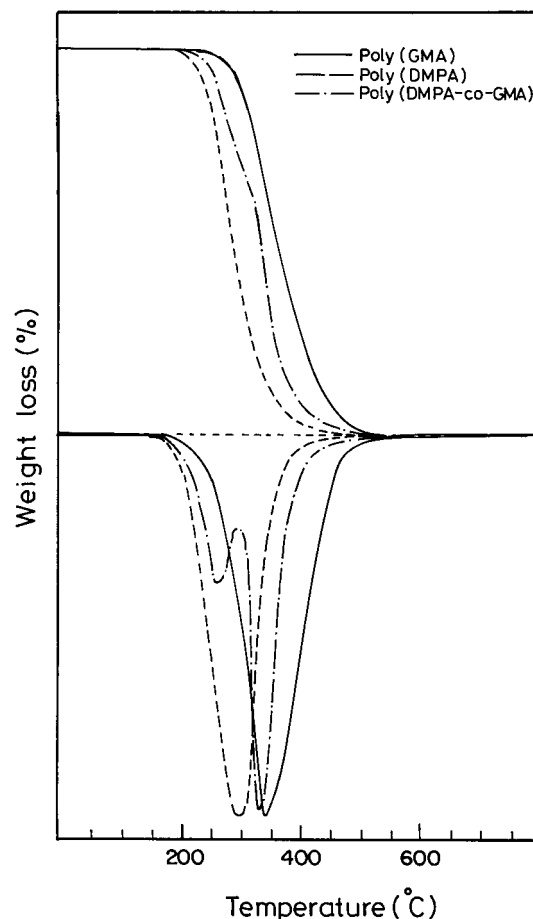
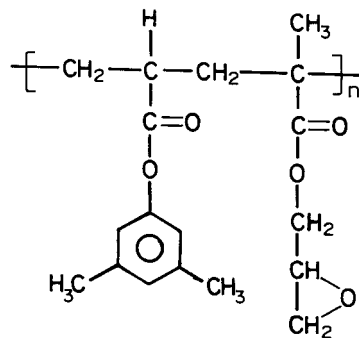


Figure 5 TGA curves for poly(GMA), poly(DMPA-co-GMA) (0.5; 0.5), and poly(DMPA).

of the copolymer samples were determined from the corresponding $^1\text{H-NMR}$ spectra. The assignment of the resonance peaks in the $^1\text{H-NMR}$ spectrum leads to the accurate evaluation of the content of each kind of monomeric unit incorporated into the copolymer chains. Thus, the mole fraction



Scheme 1 Chemical structure of poly(DMPA-co-GMA).

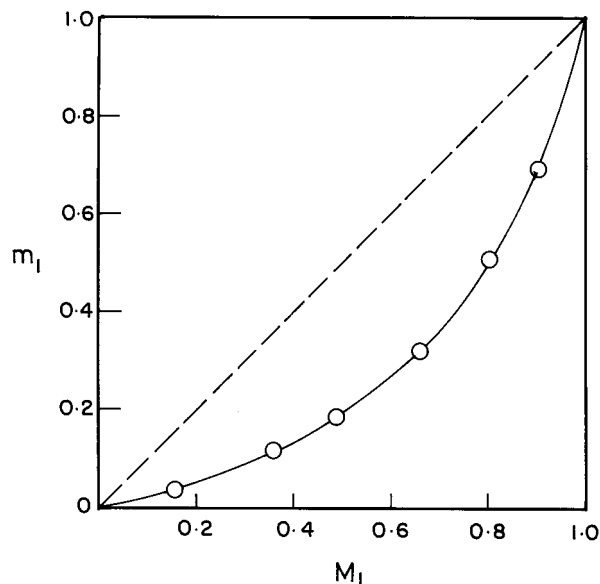


Figure 6 Copolymer composition diagram of poly-(DMPA-co-GMA) system.

of DMPA in the copolymer chain was calculated from measuring the integrated intensities of aromatic protons of DMPA and aliphatic protons of DMPA and GMA.

The following expression is used to determine the composition of copolymers. Let m_1 be the mole fraction of DMPA and $1 - m_1$ be that of GMA. DMPA contains 3 aromatic protons and 9 aliphatic protons and GMA contains 10 aliphatic protons.

$$C = \frac{\text{Intensities of aromatic protons } (I_{Ar})}{\text{Intensities of aliphatic protons } (I_{Ali})}$$

$$= \frac{3m_1}{9m_1 + 10(1 - m_1)}$$

which on simplification gives

$$m_1 = \frac{10C}{3 + C}$$

From eq. (2), the mole fraction of DMPA in the copolymers were determined by measuring the intensity of aromatic proton signals and aliphatic proton signals. Table I gives the values of C and the corresponding mole fractions of DMPA in the copolymers. The plot of mole fractions of DMPA (M_1) in the feed Vs that in the copolymer (m_1) is shown in Figure 6. It indicates that the composition of DMPA in the copolymer is always lower than that in the feed.

Reactivity Ratios

From the monomer feed ratios and the copolymer compositions, the reactivity ratio of DMPA and GMA were determined by the application due to Fineman–Ross Method (F-R),²² Kelen–Tüdös (K-T),²³ and extended Kelen–Tüdös (Ext.K-T)²⁴ methods. The F-R and K-T parameters for the copolymers are presented in Table IV and that for Ext.K-T are shown in Table V. The values from the F-R plot, K-T, and Ext.K-T plots (Fig. 7) are presented in the Table VI. The value of r_1 is less than 1 and that of r_2 is greater than 1, which indicates that the presence of higher amount of GMA units in the copolymer than that in the feed. However, the product of r_1 and r_2 is more than 1, which indicates that the system leads to random distribution of the monomer units with longer sequence of the GMA units in the copolymer chain.

Application of the Copolymers as Leather Adhesives

Poly(DMPA-co-GMA) samples having three different compositions—0.11:0.89, 0.18:0.82, and

Table IV F-R and K-T Parameters for the Copolymerization of DMPA with GMA

| Copolymers | $F = M_1/M_2$ | $f = m_1/m_2$ | $H = F^2/f$ | $G = F(f - 1)/f$ | $\eta = G/(\alpha + H)^a$ | $\xi = H/(\alpha + H)^a$ |
|------------|---------------|---------------|-------------|------------------|---------------------------|--------------------------|
| 1 | 0.1934 | 0.0414 | 0.9034 | -4.4780 | -0.6579 | 0.1327 |
| 2 | 0.5499 | 0.1232 | 2.4544 | -3.9135 | -0.4683 | 0.2937 |
| 3 | 0.9661 | 0.2199 | 4.2444 | -3.4272 | -0.3377 | 0.4182 |
| 4 | 1.9411 | 0.4691 | 8.0321 | -2.1968 | -0.1576 | 0.5764 |
| 5 | 4.0050 | 0.9988 | 16.0592 | -0.0048 | -0.0002 | 0.7312 |
| 6 | 9.2669 | 2.2680 | 38.5645 | 5.1053 | 0.1148 | 0.8612 |

^a $\alpha = (H_{\min} \times H_{\max})^{1/2} = 5.9024$.

Table V Extended K-T Parameters from DMPA-GMA Copolymer System

| Parameters | Copolymer System | | | | | |
|------------|------------------|---------|---------|---------|---------|---------|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| ζ_2 | 0.1028 | 0.1097 | 0.1468 | 0.1992 | 0.2444 | 0.2936 |
| ζ_1 | 0.0220 | 0.0246 | 0.0334 | 0.0481 | 0.0610 | 0.0706 |
| Z | 0.2051 | 0.2144 | 0.2205 | 0.2219 | 0.2246 | 0.2106 |
| \bar{F} | 0.2019 | 0.5746 | 0.9973 | 2.1140 | 4.4470 | 10.5735 |
| H | 0.9842 | 2.6802 | 4.5228 | 9.5269 | 19.7997 | 50.2070 |
| G | -4.6738 | -4.0896 | -3.5379 | -2.3925 | -0.0053 | 5.8253 |
| η | -0.5832 | -0.4212 | -0.3062 | -0.1445 | -0.0002 | 0.1018 |
| ξ | 0.1228 | 0.1228 | 0.3915 | 0.5754 | 0.7380 | 0.8772 |

^a $\alpha = 7.0295$ and $\mu = 0.8068$.

0.32:0.68—were chosen for studying the adhesive property on leather. All these copolymer samples were individually crosslinked with 40% ethanolamine (based on the weight of GMA) in chloroform. The peel strength for the adhesives prepared from the copolymers containing 68, 82, and 89% GMA were 0.45, 0.60, and 0.7 N/mm at 50°C, respectively. The corresponding values for these adhesives at 90°C are 0.65, 0.90, and 1.15 N/mm, respectively. The peel strength was enhanced with the increase in epoxy group content in the copolymers. All these compositions showed good adhesive characteristics even at room temperature.

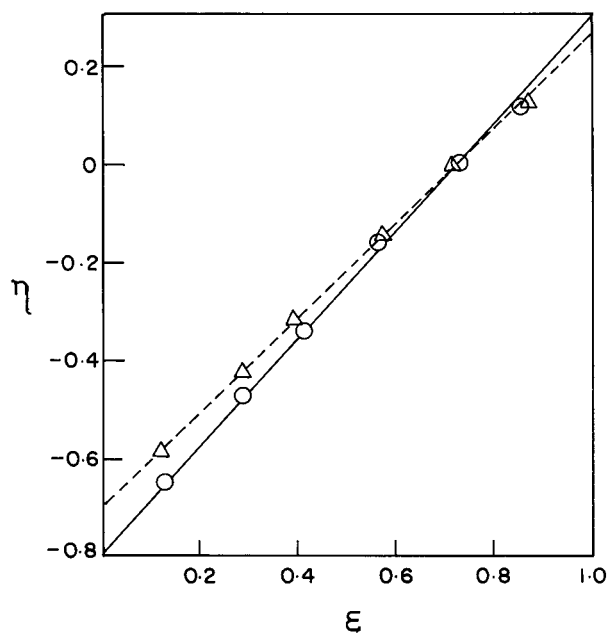


Figure 7 K-T(O) and Ext.K-T(Δ) plot for poly(DMPA-co-GMA) system.

CONCLUSIONS

Poly(DMPA) and the copolymers of DMPA with GMA were synthesized by free radical solution polymerization. Characterization of poly(DMPA) and poly(DMPA-co-GMA) were performed with IR, ¹H-NMR, and ¹³C-NMR spectroscopic techniques. The homopolymer and copolymer are soluble in chloroform, acetone, dimethyl acetamide, dimethylformamide, dimethyl sulfoxide, tetrahydrofuran, benzene, toluene, xylene, and insoluble in *n*-hexane and hydroxyl-group containing solvents such as methanol and ethanol. Thermogravimetric analysis indicated that the thermal stability of the copolymers increases with the increase of DMPA units in the copolymer. GPC data showed the value of polydispersity index of poly(DMPA), poly(DMPA-co-GMA), and poly(GMA), suggest a strong tendency for chain termination by disproportionation in most of the cases and that the tendency increases with increasing GMA content in the feed. The copolymer composition was calculated by ¹H-NMR analysis of the polymers. The reactivity ratios were determined by F-R, K-T, and Ext K-T methods and the graphical values obtained are in good agreement. The r_1 value is less than 1 and r_2 value greater than 1, indicating that GMA is more reactive than DMPA. The value of the product of r_1 and r_2 is more than 1, which indicating that there is random distribution with longer sequence of GMA units in the copolymer chain. The adhesives prepared from poly(DMPA-co-GMA) with ethanolamine as crosslinking agent and applied on leather had good peel strength at 50 and 90°C. These copolymers showed good adhesive character even at room temperature.

Table VI Copolymerization Parameters for the Free Radical Copolymerization of DMPA with GMA

| Methods | r_1^a | r_2^a | $r_1 \times r_2$ | $1/r_1$ | $1/r_2$ |
|-----------------|---------|---------|------------------|---------|---------|
| Fineman–Ross | 0.2875 | 4.652 | 1.3374 | 3.4782 | 0.2149 |
| Kelen–Tüdös | 0.2925 | 4.648 | 1.3595 | 3.4188 | 0.2151 |
| Ext Kelen–Tüdös | 0.2913 | 4.7528 | 1.3844 | 3.4328 | 0.2104 |

^a r_1 and r_2 are the reactivity ratios for DMPA and GMA respectively.

REFERENCES

- Kaidov, A. A.; Ericv, O. M. *Akad Nank Resp UzB* 1997, 11, 39.
- Kalal, J. *J Polym Sci Poly Sym Edn* 1978, 62, 251.
- Feit, E. D.; Wurtz, M. E.; Kammlott, G. W. *J Voc Sci Technol* 1978, 1, 944.
- Arshady, R.; Atherton, E.; Sheppard, K. C. *Tetrahedron Lett* 1979, 1521.
- Hiroshi, H.; Jun, T.; Mahi, N.; Katsuhide, A.; (Hitachi Chemical Co. Ltd. Japan). *Jpn Kokai Tokkyo Koho jp* 2000, 186, 268 (C1 C093178/04). 4 July 2000, *Appl* 1998/362, 425, 21 Dec 1998, 5pp (Japan).
- Kamalakannan, V.; Siddarthan, S.; Olivannan, M. S.; Rajendran, S. *Leather Sci* 1983, 30, 235.
- Kumar, R. N.; Kong, W.-C.; Abubakar, A. *J Coat Technol* 1999, 71, 896.
- Bandour, M.; Loutz, J. M.; Maetnes, D.; Van Kerckove, M. *FATIEPEC Congr* 1996, 23, 369–382.
- Vijayaraghavan, P. G.; Reddy, B. S. R. *J Macromol Sci Pure Appl Chem* 1999, A36(9), 1181.
- Jung, M.; Hong, S.; Baik, K. *Ger often De* 19.162663 (C1.C08F220/32), 21 Sep 2000, *KR Apl* 9,908,668, Mar 1999, pp 18.
- Grassie, N.; Torrence, B. J. D.; Fortune, J. D.; Gemel, L. D. *Polymer* 1965, 6, 653.
- Ivin, K. J.; Pitchumani, S.; Rami Reddy, C.; Rajadurai, S. *J Polym Chem Ed* 1982, 20, 277.
- Tacx, J. C. J. F.; Vander Velden, G. P. M.; German, A. L. *Polymer* 1988, 29, 1675.
- Tamizharasi, S.; Ganasundaram, P.; Reddy, B. S. R. *J Appl Polym Sci* 1997, 65, 1285.
- Balaji, R.; Sivakumar, N.; Nanjundan, S. *J Polym Mater* 2000, 17(2), 213.
- Aota, S.; Sanai, Y.; Matsumoto, A.; Kamachi, M. *Polym J* 1996, 28, 867.
- Stampel, G. M.; Cross, R. P.; Mariella, R. D. *J Am Chem Soc* 1950, 72, 2899.
- Teramachi, S.; Hasegara, A.; Atasuka, M.; Yamashita, A.; Takemoto, N. *Macromolecules* 1978, 11, 1206.
- Bevington, J. C.; Melville, H. W.; Taylor, R. P. *J Polym Sci Chem Edn* 1954, 12, 448.
- Melville, H. N.; Noble, B.; Watson, W. F. *J Polym Sci* 1949, 4, 629.
- Bandrup, J.; Immergut, E. H. *Polymer Handbook*, 2nd ed.; Wiley—Interscience: New York, 1976.
- Fineman, M.; Ross, S. D. *J Polym Sci* 1950, 5, 259.
- Kelen, T.; Tüdös, F. *J Macromol Sci Chem A* 1975, 9, 1.
- Kelen, T.; Tüdös, F.; Turesanyi, B.; Kennedy, J. P. *J Polym Sci Polym Chem* 1977, 15, 3041–3074.