

# Glycidyl Methacrylate and *N*-Vinyl-2-pyrrolidone Copolymers: Synthesis, Characterization, and Reactivity Ratios

S. SOUNDARARAJAN and B. S. R. REDDY\*

Central Leather Research Institute, Adyar, Madras-600 020, India

## SYNOPSIS

Free radical copolymerization of glycidyl methacrylate (GMA) and *N*-vinyl-2-pyrrolidone (VPD) was carried out using 2,2'-azobisisobutyronitrile (AIBN), in chloroform at 60°C. The polymers were characterized by IR and <sup>13</sup>C-NMR spectroscopic methods. The percentage composition of the copolymers were established by microelemental analysis and by <sup>13</sup>C-NMR spectroscopy. The copolymerization reactivity ratios were computed using the Fineman-Ross method, the Kelen-Tudos method, and the extended Kelen-Tudos method. The molecular weights of the copolymers were obtained by GPC measurements. Thermal properties of the homo- and copolymers were also studied by thermogravimetric analysis. The copolymers were tested as adhesives for leather-to-leather and leather-to-rubber bonding.

## INTRODUCTION

Conventional epoxidized resin adhesives generally have a molecular weight in the range of 4000–5000 and are based on phenolic intermediates. The main drawbacks of these adhesives are that they have only a few terminal epoxy groups in the polymer and also require polar solvents for solubilization. To overcome these shortcomings, glycidyl methacrylate (GMA), which contains an epoxide as well as vinyl functionality, has been used as a comonomer.<sup>1</sup> Copolymers of GMA have biological applications for the binding of drugs and biomolecules,<sup>2</sup> and in electronic industries, as negative electron beam resists.<sup>3</sup> *N*-vinyl-2-pyrrolidone (VPD) polymer has good properties such as biocompatibility, low toxicity, and film-forming and adhesive characteristics.<sup>4</sup> The main object of this present work is to develop an adhesive suitable for leather-to-leather and leather-to-rubber bonding using well-characterized GMA copolymers.

The present paper deals mainly with the synthesis and characterization of eight GMA-VPD copolymers of different composition by free radical polymerization and the reactivity ratios determined by the Fineman-Ross (F-R) method,<sup>5</sup> Kelen-Tudos (K-T) method,<sup>6</sup> and the extended K-T method,<sup>7</sup> and the applications of these copolymers as adhesives are also reported.

## EXPERIMENTAL

### Materials and Methods

2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from a chloroform and petroleum ether mixture and dried in a vacuum oven for 24 h. Chloroform (BDH), carbon tetrachloride (BDH), and tetrahydrofuran (Fluka) were used as received. GMA (Fluka) and VPD (Fluka) were distilled under reduced pressure before use.

### Copolymerization

Known mixtures of GMA (1), VPD (2), 2% AIBN, and chloroform (monomer/solvent: 1/2, w/v) as given in Table I were placed in a standard reaction

\* To whom correspondence should be addressed.

**Table I** Copolymerization of GMA-VPD by Elemental Analysis and  $^{13}\text{C}$ -NMR Spectroscopy

Sample No.	Mol Fraction of GMA in Feed ( $M_1$ )	Time in Min	Conversion (wt %)	Elemental Analysis (N%)	Intensity of $^6\text{C}$ of GMA	Intensity of $^9\text{C}$ of VPD	Mol Fraction of GMA in Copolymer by Elemental ( $m_1$ )	Mol Fraction of GMA in Copolymer by $^{13}\text{C}$ -NMR
1	0.10	55	18.3	5.16	—	—	0.53	—
2	0.20	48	18.1	3.89	0.6	0.35	0.64	0.63
3	0.30	45	19.1	3.16	1.85	0.75	0.70	0.71
4	0.40	41	16.8	2.19	0.80	0.25	0.79	0.76
5	0.50	36	19.1	1.84	—	—	0.82	—
6	0.60	30	18.2	1.34	1.35	0.25	0.87	0.86
7	0.70	25	20.2	—	1.55	0.18	—	0.90
8	0.80	20	21.5	—	1.60	0.10	—	0.94

Solvent: chloroform; temperature:  $60^\circ\text{C}$ . AIBN: 2% based on the total weight of the monomers and solvent; Monomer/solvent; 1/2 (w/v).

tube (100 mL), and the mixture was flushed with oxygen-free nitrogen for 10 min. The tube was then tightly sealed and immersed in a thermostatic water bath at  $60^\circ\text{C}$ . Copolymerization was allowed to proceed to about 15% conversion (Table I). The copolymer was precipitated in excess carbon tetrachloride and filtered off using a No. 4 sintered glass crucible and was washed repeatedly with fresh carbon tetrachloride to ensure the complete removal of residual monomers. It was then dried in vacuum oven at  $40^\circ\text{C}$  for 48 h.

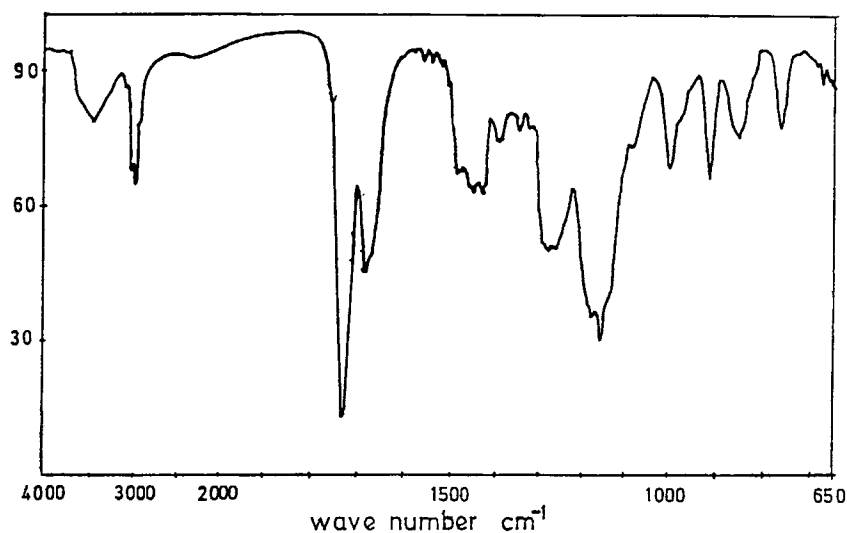
### Characterization

The copolymers were characterized by IR spectroscopy (Shimadzu-408 spectrometer) and  $^{13}\text{C}$ -NMR

spectroscopy (Brucker CXP 22.64 MHz FT-NMR). Microelemental analysis was carried out at the Regional Sophisticated Instrumentation Centre, Central Drug Research Institute, India. Molecular weights were obtained by gel permeation chromatography, and the thermal properties were studied using a DuPont 990 microthermobalance.

### RESULTS AND DISCUSSION

Eight copolymers of GMA-VPD having different copolymer compositions were prepared according to the experimental details given in Table I, using AIBN as initiator in chloroform solution under ni-



**Figure 1** IR spectrum of copoly(GMA-VPD) 50 : 50 mol %.

trogen atmosphere. The IR spectrum of the copolymer (50 : 50 mol %) is shown in Figure 1. Absorptions at 1735 and 906  $\text{cm}^{-1}$  were due to the ester and epoxy groups of GMA units, respectively. The peak at 1680  $\text{cm}^{-1}$  corresponds to the carbonyl group of VPD units.

The  $^{13}\text{C}$ -NMR spectra of poly(VPD) and poly(GMA) are shown in the Figures 2(a) and (b), respectively. Figure 2(c) is the spectrum of copoly(GMA-VPD) of 30 : 70 mol %. The assignments of the peaks were made with the off-resonance spectra of the homopolymers and are given in Table II. In Figure 2(b), a distinct peak appears at 65.86 ppm for the  $\text{OCH}_2$  carbon peak corresponding to poly(GMA), and in Figure 2(a), another distinct peak appears at 31.38 ppm for the  $-\text{CH}-$  (methine) carbon peak corresponding to the poly(VPD) unit. Thus, these two peak areas are best utilized in the copolymer spectra to determine the composition of the copolymers.

The percentage composition of the copolymers were also obtained by microelemental analysis (N%), and the results thus obtained were compared with the  $^{13}\text{C}$ -NMR method. The plot of the mol fraction of GMA in feed vs. that of GMA in copolymer is shown in Figure 3(a). There is no azeotropic composition, and the incorporation of GMA is always higher than VPD in all the copolymers.

Copolymerization reactivity ratios of GMA and VPD were determined using the data given in Table I by the F-R, K-T, and extended K-T methods.<sup>5-7</sup> The equations used are

$$G = r_1 F - r_2 \quad (\text{F-R equation})$$

$$\eta = r_1 \xi - r_2 / \alpha (1 - \xi) \quad (\text{K-T equation})$$

$r_1$  and  $r_2$  are the reactivity ratios relating to the monomers GMA and VPD, respectively.  $G$  and  $F$  are F-R parameters.  $\eta$ ,  $\xi$ , and  $\alpha$  are K-T parameters. The plot of  $G$  vs.  $F$  will give a straight line with  $r_1$  as the slope and  $-r_2$  as the intercept [Fig. 3(b)].  $\eta$ ,  $\xi$ , and  $\alpha$  are mathematical functions of  $G$  and  $F$  as defined and entered in Tables III and IV for K-T and extended K-T methods, respectively. The plot of  $\eta$  vs.  $\xi$  are also shown in Figures 3(c) and (d). For K-T methods, the  $r_1$  and  $r_2$  values could also be obtained by using the following equations:

$$r_1 = \left[ \frac{\sum \eta_i \xi_i \cdot \sum (1 - \xi_i)^2}{\sum \eta_i (1 - \xi_i) \cdot \sum \xi_i (1 - \xi_i)} \right] / D$$

$$r_2 = \alpha \left[ \frac{\sum \eta_i \xi_i \cdot \sum \xi_i (1 - \xi_i)}{\sum \eta_i (1 - \xi_i) \cdot \sum \xi_i^2} \right] / D$$

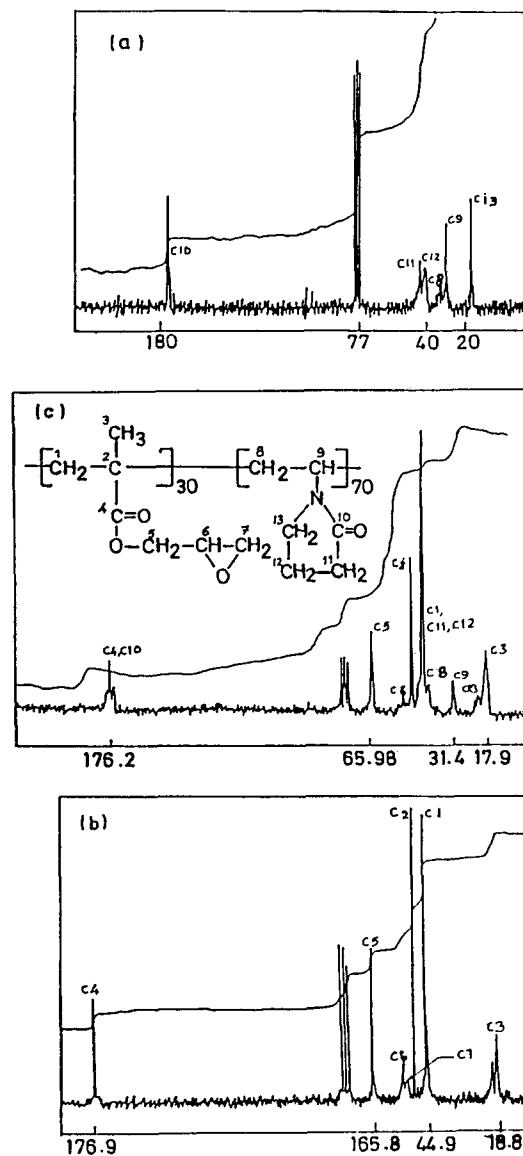


Figure 2  $^{13}\text{C}$ -NMR spectra of (a) poly(VPD), (b) poly(GMA), and (c) copoly(GMA-VPD) 30 : 70 mol %.

where  $D = \sum \xi_i^2 - \sum (1 - \xi_i)^2 - [\sum \xi_i (1 - \xi_i)]^2$ . In the K-T and extended K-T plots,  $r_1$  will be obtained as the intercept at  $\xi = 1$  and  $-r_2/\alpha$  will be obtained as the intercept at  $\xi = 0$ .

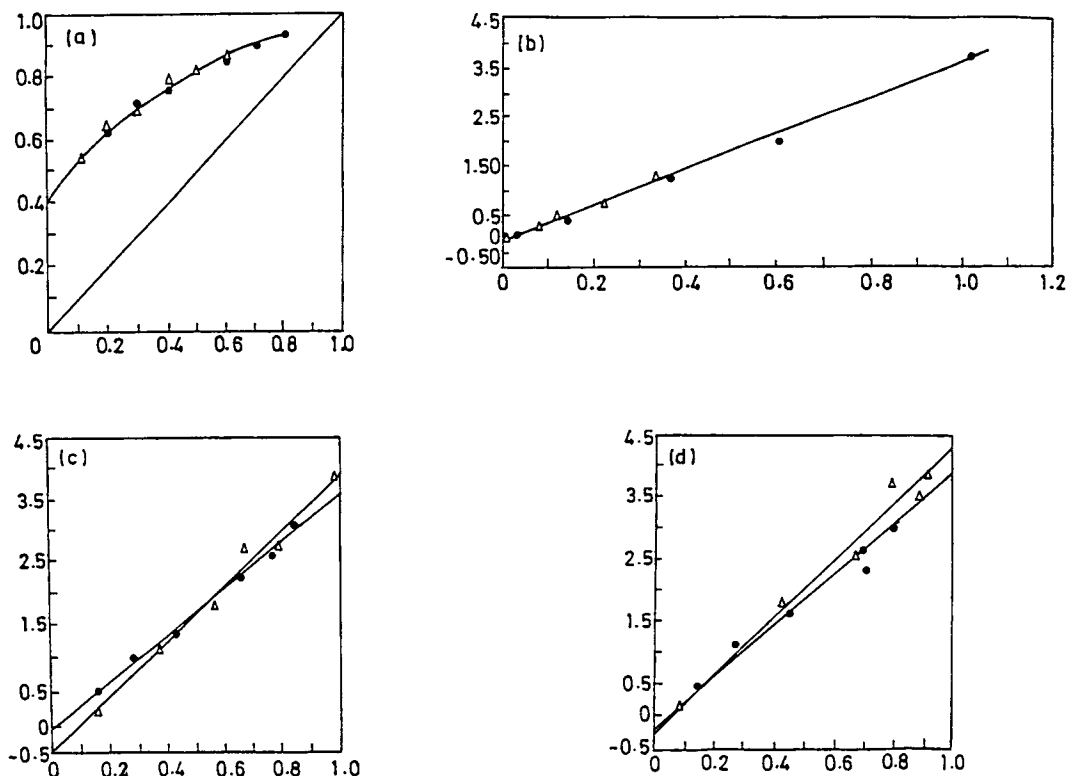
The 95% confidence intervals of the  $r_1$  and  $r_2$  are obtained by the following expressions:

#### (a) F-R Method<sup>8</sup>

$$\Delta r_1 = \pm \text{SE}(b) \times t_{0.95}$$

$$\Delta r_2 = \pm \text{SE}(b_0) \times t_{0.95}$$





**Figure 3** (a) Plot of mole fraction of GMA in feed ( $M_1$ ) vs. that of GMA in copolymer ( $m_1$ ); (b) F-R plot of  $G$  vs.  $F$ ; (c) K-T plot of  $\eta$  vs.  $\xi$ ; (d) extended K-T plot of  $\eta$  vs.  $\xi$ ; ( $\Delta$ ) elemental analysis; ( $\bullet$ )  $^{13}\text{C}$ -NMR.

more GMA units. This may be because the GMA monomer is more reactive towards the growing chain regardless of whether the radical end was derived from GMA or VPD. Therefore, in copolymerization, of these two monomers, the polymer is always richer in GMA up to 100% conversion of both monomers.

The correlation coefficients for F-R plots are .997 and .999 for elemental analysis and  $^{13}\text{C}$ -NMR data, respectively. In the K-T methods, the

$$\delta^{\square} = \Delta r_1 \cdot \Delta r_2 / r_1 \cdot r_2$$

and the K-T plots suggest that this system belongs to the I Class system (Table V). However, the

$$Q = \text{Exp}[-|\ln^{\alpha}/(r_1/r_2)|]$$

values for the K-T methods are very low. This suggests that the experiment is to be planned to take

**Table III** F-R and K-T Parameters for GMA-VPD System (Elemental Analysis)

Sample No.	$x = \frac{M_1}{M_2}$	$y = \frac{m_1}{m_2}$	$G = \frac{x \cdot (y - 1)}{y}$	$F = \frac{x^2}{y}$	$\eta = \frac{G}{(\alpha + F)}$	$\xi = \frac{F}{(\alpha + F)}$
1	0.1111	1.1277	0.0126	0.0109	0.1756	0.1529
2	0.2500	1.7778	0.1094	0.0352	1.1414	0.3669
3	0.4286	2.3333	0.2449	0.0787	1.7570	0.5647
4	0.6667	3.7619	0.4895	0.1181	2.7372	0.6607
5	1.0000	4.5556	0.7805	0.2195	2.7856	0.7835
6	1.5000	6.6923	1.2759	0.3362	3.2148	0.8471

$M_1$  = mol fraction of GMA in feed;  $M_2$  = mol fraction of VPD in feed;  $m_1$  = mol fraction of GMA in copolymer;  $m_2$  = mol fraction of VPD in copolymer;  $\alpha = \sqrt{F_{\min} + F_{\max}} = 0.0607$ .

**Table IV** Extended K-T Parameters for GMA-VPD System (Elemental Analysis)

	Sample No.					
	1	2	3	4	5	6
$\tau_2 = w(\mu + x)/(\mu + y)/100$	0.0830	0.0730	0.0742	0.0536	0.0637	0.0555
$\tau_1 = \tau_2 \cdot y/x$	0.8662	0.5195	0.4039	0.3026	0.2902	0.2476
$z = \log(1 - \tau_1)/\log(1 - \tau_2)$	22.5460	9.6612	6.7115	6.5387	5.2075	4.9827
$\bar{x} = y/z$	0.0500	0.1840	0.3477	0.5753	0.8748	1.3431
$F = y/z^2$	0.0022	0.0190	0.0518	0.0880	0.1680	0.2696
$G = (y - 1)/z$	0.0057	0.0805	0.1987	0.4224	0.6828	1.1424
$\alpha = \sqrt{F_{\min}} \times F_{\max} = 0.0245$						
$\xi = F/(\alpha + F)$	0.0832	0.4378	0.6793	0.7825	0.8729	0.9168
$\eta = G/(\alpha + F)$	0.2123	1.8507	2.6053	3.7566	3.5479	3.8857

$\mu = 111.16/142.16$  (mol wt 2/mol wt 1).

**Table V** Comparison of Reactivity Ratios of GMA-VPD System

Composition Obtained by	Method	$r_1$	$r_2$	$\delta^{\square}$	$Q$	$r$
Elemental analysis	F-R	$3.843 \pm 0.398$	$0.026 \pm 0.070$	—	—	0.997
	K-T	$3.875 \pm 0.510$	$0.029 \pm 0.038$	0.170	0.125	—
	Ex. K-T	$4.286 \pm 0.498$	$0.003 \pm 0.018$	0.609	0.033	—
$^{13}\text{C}$ -NMR spectroscopy	F-R	$3.661 \pm 0.190$	$0.056 \pm 0.097$	—	—	0.999
	K-T	$3.570 \pm 0.190$	$0.030 \pm 0.041$	0.069	0.042	—
	Ex. K-T	$3.92 \pm 0.230$	$0.002 \pm 0.030$	0.947	0.004	—

**Table VI** Percent Weight Loss and Temperature for Poly(GMA), Poly(VPD), and Copoly(GMA-VPD)

Sample	Temperatures at Different % Weight Loss ( $^{\circ}\text{C}$ ) (%)								
	10	20	30	40	50	60	70	80	90
Poly(GMA)	305	335	365	380	395	405	415	425	445
Poly(VPD)	78	342	384	408	426	431	438	441	450
Copoly(GMA-VPD)	275	345	370	388	405	415	430	438	450

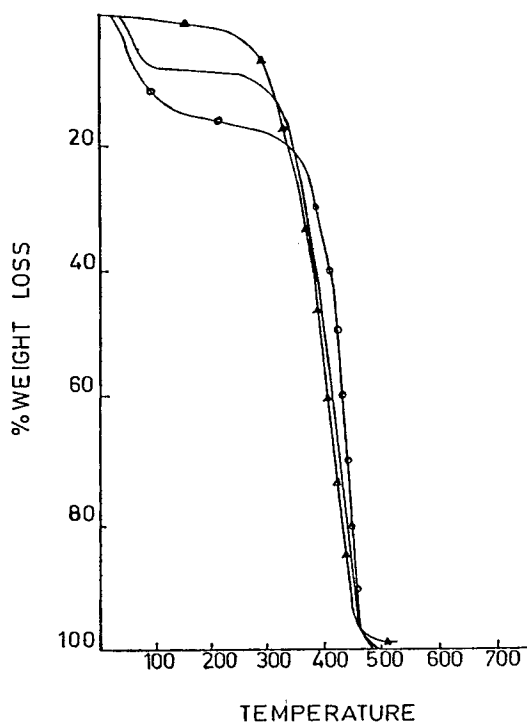
the VPD more in the feed to obtain better K-T plots.<sup>8</sup>

The weight and number average molecular weight ( $\bar{M}_w, \bar{M}_n$ ) of poly(GMA) are  $4.8 \times 10^4$  and  $3.1 \times 10^4$ , respectively. The  $\bar{M}_w$  and  $\bar{M}_n$  of copoly(GMA-VPD) of 10 : 90 mol % are  $1.2 \times 10^5$  and  $4.9 \times 10^4$ , respectively. Poly(VPD) is a sample obtained from Fluka having  $\bar{M}_w$ :  $3.6 \times 10^5$ . The polydispersity index value  $\bar{M}_w/\bar{M}_n$ , 1.55 and 2.46 of poly(GMA) and copoly(GMA-VPD), respectively, suggests the radical recombination and disproportionation mechanisms for the termination of the growing polymer radicals.<sup>11</sup>

The TGA curves of poly(GMA), poly(VPD), and copoly(GMA-VPD) (10 : 90 mol %) are obtained (Fig. 4), and the results of the thermogravimetric analysis are given in Table VI. In poly(VPD) and copoly(GMA-VPD), the first weight loss (degradation) occurs within  $100^{\circ}\text{C}$ . This may be due to the presence of moisture absorbed by VPD units. The second and major degradation starts around  $300^{\circ}\text{C}$ , and complete degradation takes place around  $460^{\circ}\text{C}$ . In poly(GMA), first degradation occurs at  $360^{\circ}\text{C}$  (28%) with complete degradation occurring at  $435^{\circ}\text{C}$ . The thermal stability of the polymers could be improved by employing suitable epoxy cur-

ing agents such as amines and anhydrides to form three-dimensional networks.

The copolymers were tested as adhesives for leather-to-leather and leather-to-rubber bonding with diethanolamine (DEA), as the curing agent. The results obtained are given in Table VII. As the amount of DEA increases, the peel strength of the bonds also increases. The reason may be due to the increase in the number of hydroxyl groups available for bonding both from DEA and the product formed on opening of epoxide ring, which improves the adhesion<sup>12</sup> by increasing the interaction between the polar group, and due to the increase in the cross-linking density, increasing the toughness of the cured epoxy network. An important variable in peel testing is the rate of separation. At low rates, the peel behavior is determined by viscoelastic flow and the peel force is strongly rate dependent. At high rates, little viscous deformation occurs and the peel strength becomes independent of rate and failure is usually interfacial, whereas at intermediate rates, a "slip-stick" failure mode is predicted.<sup>13</sup> The toughening properties of the adhesive also improved further by blending with rubbers like neoprene that are largely used in the shoe industry, and, hence, greater



**Figure 4** TGA curves for poly(GMA) ( $\Delta$ ), poly(VPD) ( $\oplus$ ), and copoly(GMA-VPD) (—) at 20°C/min.

**Table VII** Peel Strength Data of GMA-VPD Copolymers Cured with Diethanolamine for Leather-to-Leather and Leather-to-Rubber Bonding

Copolymer	DEA E.E	Peel Strength	
		L to L (PPI)	L to R (PPI)
GMA-VPD 10 : 90 Mol %	0.2	2	2
	0.4	3	2
	0.6	4	3
	0.8	5	3
	1.0	7	4
	1.2	10	5

L = leather; R = rubber; DEA = diethanolamine; E.E = epoxy equivalents; PPI = pounds per inch.

peel strength can be attained. This type of behavior has been reported earlier.<sup>12</sup>

## CONCLUSIONS

Eight copolymers of GMA-VPD were prepared using AIBN as catalyst in chloroform at 60°C. IR and <sup>13</sup>C-NMR spectroscopy reveals the presence of both monomeric constituents in the copolymer structure. The copolymer compositions determined by the <sup>13</sup>C-NMR method agree well with that of elemental analyses. The reactivity ratios obtained by the F-R, K-T, and extended K-T methods agree well with each other.  $r_1 = 3.8$  and  $r_2 = 0.03$  indicates that GMA is more reactive in the copolymerization and the copolymer structure will be random in nature. The feed vs. copolymer composition curve also confirm  $r_1 \gg 1$  and  $r_2 \ll 1$ . The  $\delta^{\square}$  values and the K-T plots suggest that this system belongs to the I Class system. However, the lowest Q values suggest that the experiments are to be preplanned. Thermal stability of the polymers are also good. The peel strength data shows that the copolymer cured with DEA can be used as adhesives for leather-to-leather and leather-to-rubber bondings.

One of the authors (S. S) is thankful to Dr. S. Rajadurai, Head of the Chemical Sciences Division of our institute, for his suggestions during the course of this work.

## REFERENCES

1. J. A. Simms, *J. Appl. Polym. Sci.*, **5**, 58 (1961).
2. J. Kalal, *J. Polym. Sci. Polym. Symp.* **62**, 251 (1978).

3. E. D. Felt, M. E. Wurtz, and G. W. Kammlott, *J. Vac. Sci. Technol.*, **15**, 944 (1978).
4. E. V. Hort and B. H. Waxman, in *Encyclopaedia of Chemical Technology*, H. Mark et al., Interscience, New York, 1983, Vol. 23, p. 967.
5. M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**, 259 (1950).
6. T. Kelen and F. Tudos, *J. Macromol. Sci. Chem.*, **A9**, 1 (1975).
7. F. Tudos, T. Kelen, B. Turcsanyi, and J. P. Kennedy, *J. Polym. Sci. Polym. Chem. Ed.*, **19**, 1119 (1981).
8. E. P. George, Box, W. G. Hunter, and J. S. Hunter, *Statistics for Experiments: An Introduction to Design, Data Analysis and Model Building*, Wiley, New York, 1978.
9. T. Kelen, F. Tudos, and T. Turcsanyi, *Polym. Bull.*, **2**, 71 (1980).
10. F. Tudos and T. Kelen, *J. Macromol. Sci. Chem.*, **A16**, 1283 (1981).
11. J. C. Bevington, H. W. Melville, and R. P. Taylor, *J. Polym. Sci. Polym. Chem. Ed.*, **14**, 463 (1954).
12. H. Mark et al., *Encyclopedia of Polymer Science and Engineering*, Wiley, New York, 1985, Vol. I, pp. 494, 566.
13. D. W. Aubrey, G. N. Welding, and T. Wang, *J. Appl. Polym. Sci.*, **13**, 2193 (1969).

Received January 21, 1990

Accepted August 21, 1990