Synthesis and characterization of glycidyl methacrylate–styrene copolymers and determination of monomer reactivity ratios

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Copolymers of glycidyl methacrylate (GMA) and styrene were prepared in the presence of 2,2'-azobisisobutyronitrile in chlorobenzene. The polymers were characterized by infra-red and ^{13}C nuclear magnetic resonance spectroscopy. The percentage of GMA present in the copolymers was established by elemental analysis. The copolymerization reactivity ratios were calculated using the Kelen–Tudos method. Molecular weights, glass transition temperatures and thermal properties were determined by gel permeation chromatography, differential scanning calorimetry and thermogravimetric analysis, respectively.

(Keywords: glycidyl methacrylate; styrene; copolymerization; characterization; reactivity ratios)

INTRODUCTION

The conventional epoxidized resin adhesives generally have a molecular weight in the range of 5000 and are based on phenolic intermediates. They do not have necessary colour stability and possess only a few terminal epoxy groups and require polar solvents for solubilization. These difficulties were overcome by taking glycidyl methacrylate (GMA), an epoxide containing vinyl and acrylate as comonomer[1]. Copolymers based on GMA have applications in biology for the binding of drugs and biomolecules[2] and in electronics industries as negative electron-beam resists[3]. Our interest is to develop an adhesive for leather-to-leather and leather-to-rubber bonding using GMA copolymers.

In the present paper the synthesis and characterization of glycidyl methacrylate–styrene (GMA–STY) copolymers and the reactivity ratios determined by the Kelen–Tudos method[4], which is an extension of the method of Fineman and Ross[5], are reported. The curing studies and applications of the copolymers as adhesives will be reported elsewhere.

EXPERIMENTAL

Materials

2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from chloroform and petroleum ether mixture and dried in vacuum for 24 h. Chlorobenzene, methanol, chloroform and tetrahydrofuran were used as received. Styrene (Aldrich) and GMA (Fluka) were distilled under reduced pressure before use.

Copolymerization

Appropriate quantities of GMA and STY with chlorobenzene (monomer/solvent = 2/5 w/v) and AIBN were placed in a standard reaction tube 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°C. Copolymerization was allowed to proceed to about 10% conversion (*Table 1*). The copolymer was precipitated in excess methanol, filtered off using a No. 4 sintered glass crucible and washed repeatedly with fresh methanol to ensure complete removal of unreacted monomers, AIBN and chlorobenzene. It was then dried in a vacuum oven at 40°C for 24 h.

CHARACTERIZATION

Elemental analysis

Micro-elemental analysis of the copolymers was carried out at the Regional Sophisticated Instrumentation Centre (RSIC), Central Drug Research Institute (CDRI), Lucknow, India.

I.r. spectroscopy

A Shimadzu-408 i.r. spectrometer was used. Thin films of poly(GMA)and copoly(GMA–STY), 45:55 mol%, were prepared from chloroform solution of concentration 0.1 g ml^{-1}. The solutions were cast on a clean glass plate at room temperature. After the solvent was evaporated completely the resultant films were dried under vacuum at 25°C for 24 h to remove trace amounts of solvent before characterization.

^{13}C n.m.r. spectroscopy

Fourier-Transform (*FT*) ^{13}C n.m.r. spectra were recorded using a Bruker-CXP 22.64 MHz spectrophotometer. Homo- and copolymer samples were examined as 15–20% (w/v) solutions of $CDCl_3$ using tetramethylsilane (TMS) as internal reference.

Gel permeation chromatography

The weight- and number-average molecular weights of the copolymers were determined by gel permeation chromatography (g.p.c.), using tetrahydrofuran as eluent.

Thermogravimetric analysis

Thermogravimetric analysis (t.g.a.) curves were recorded with a Du Pont micro-thermobalance. An aliquot

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Table 1 Copolymerization of GMA (1) and STY (2) at 60°C[a]

Sample No.	Mole fraction of GMA in feed, M_1	Copolymer conversion (wt%)	Elemental analysis: epoxide oxygen (wt%)	Mole fraction of GMA in copolymer, dM_1	Molecular weight by g.p.c. $\bar{M}_w \times 10^3$	$\bar{M}_n \times 10^3$	$\bar{M}_w/\bar{M}_n$
1	0.09	7.62	2.54	0.18	8.46	6.50	1.31
2	0.20	9.51	3.80	0.28			
3	0.30	9.73	4.77	0.35			
4	0.40	8.82	5.98	0.46	9.18	6.32	1.45
5	0.50	9.23	6.36	0.49			
6	0.60	9.64	7.24	0.58	8.92	6.37	1.37
7	0.70	9.56	7.82	0.63			
8	0.80	10.00	8.93	0.75			
9	0.90	10.52	9.95	0.86			
10	1.00	40.00	11.12	0.99	4.83	3.12	1.55

[a] Solvent: chlorobenzene. Catalyst: AIBN 2% (based on the total weight of the monomers and solvent). M/S = 2/5 (w/v)

Table 2 Kelen and Tudos parameters[a]

Sample No.	$X=\frac{M_1}{M_2}$	$Y=\frac{dM_1}{dM_2}$	$G=\frac{X(Y-1)}{Y}$	$F=\frac{X^2}{Y}$	$\xi=\frac{F}{\alpha+F}$	$\eta=\frac{G}{\alpha+F}$
1	0.0989	0.2195	−0.3517	0.0446	0.0550	−0.4334
2	0.2500	0.3889	−0.3928	0.1607	0.1732	−0.4235
3	0.4286	0.5385	−0.3673	0.3411	0.3079	−0.3315
4	0.6667	0.8519	−0.1159	0.5218	0.4049	−0.0900
5	1.0000	0.9608	−0.0408	1.0408	0.5758	−0.0226
6	1.5000	1.3810	0.4138	1.6293	0.6800	0.1727
7	2.3333	1.7027	0.9629	3.1974	0.8065	0.2428
8	4.0000	3.0000	2.6667	5.3333	0.8743	0.4371
9	9.0000	6.1429	7.5349	13.1860	0.9450	0.5400

[a] $\alpha=\sqrt{(F_{min}F_{max})}=0.7669$. M_1 = mole fraction of GMA in feed. M_2 = mole fraction of styrene in feed. dM_1 = mole fraction of GMA in copolymer. dM_2 = mole fraction of styrene in copolymer

sample weighing 5 mg was used at a temperature rise of 20°C min^{-1} for poly(GMA) and copoly(GMA–STY) (50:50 mol%) and 10°C min^{-1} for polystyrene using a nitrogen atmosphere.

Glass transition temperature

The glass transition temperatures of poly(GMA) and copoly(GMA–STY) (10:90 mol%) were determined by differential scanning calorimetry (d.s.c.) with a Du Pont micro-thermobalance. Samples of 15 mg were used at a temperature rise of 10°C min^{-1} in the presence of air.

RESULTS AND DISCUSSION

Copolymerization of GMA and STY was carried out in chlorobenzene at 60°C in the presence of AIBN under a nitrogen atmosphere. All systems were polymerized to low conversions, usually about 10%. The composition of monomer mixtures and the resulting copolymers obtained by elemental analysis are summarized in *Table 1*. The curve in *Figure 1* represents the mole fraction of GMA in the feed vs. that in the copolymer. This figure suggests a strong tendency for alternation with an azeotropic composition about 50 mol% of GMA.

Copolymerization reactivity ratios

The reactivity ratios of GMA and STY were estimated by the graphical method according to the Kelen–Tudos[4] (KT) equation:

$$\eta = r_1\xi - \frac{r_2}{\alpha}(1-\xi)$$

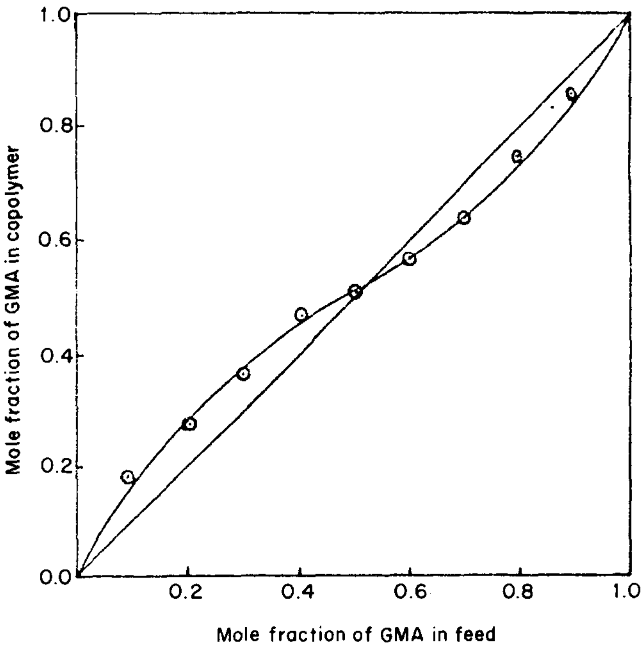


Figure 1 Plot of mole fraction of GMA in the feed vs. that in the copolymer

Here r_1 and r_2 are the reactivity ratios relating to monomer 1 (GMA) and monomer 2 (STY) respectively; η, ξ and α are mathematical functions of G and F as defined and recorded in *Table 2*. A typical plot is shown in *Figure 2*. The intercepts at $\xi=0$ and $\xi=1$ give $-r_2/\alpha$ and r_1 respectively. The reactivity ratios with 95%

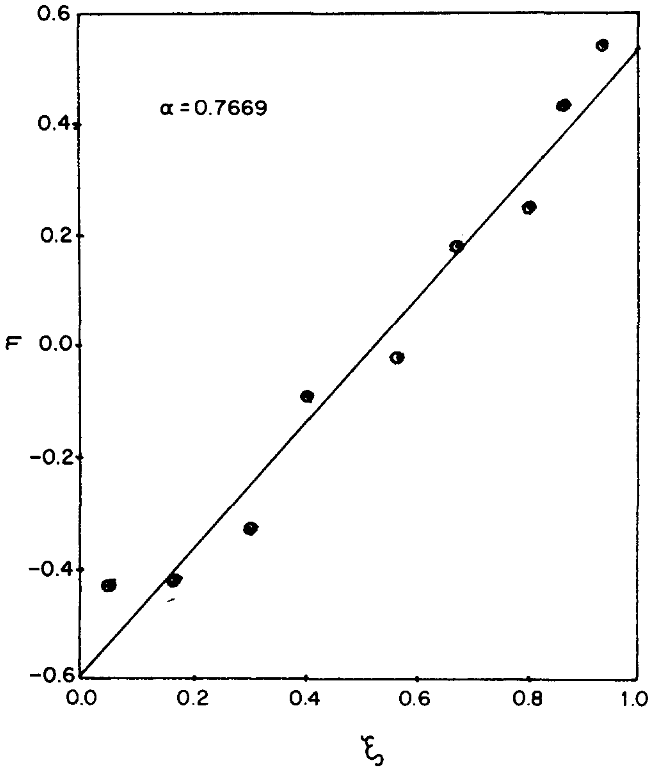


Figure 2 Plot of η vs. ξ for copolymerization reactivity ratio determination by Kelen and Tudos method

confidence limits are:

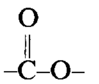
$$r_1 = 0.53 \pm 0.11 \qquad r_2 = 0.45 \pm 0.09$$

These values have good agreement with the reported values[6]:

$$r_1 = 0.54 \pm 0.004 \qquad r_2 = 0.44 \pm 0.007$$

I.r. spectroscopy

The i.r. spectra of poly(GMA) and copoly(GMA—STY) show absorption bands typical of the constituent monomeric units and their relative intensity depending on composition. Absorptions at 905 cm^{-1} in both *Figures 3a* and *3b* indicate the presence of epoxy groups in the polymers. Absorptions at 1720–1740 cm^{-1} corresponds to the



$$\overset{\displaystyle O}{\overset{\|}{-C}}-O-$$

of GMA. The peaks at 750 cm^{-1} in *Figure 3b* were due to the five adjacent aromatic C–H bending modes of styrene. The $-CH_3$ group of GMA absorbs at 1470–1430 cm^{-1} in both homo- and copolymer. The aromatic stretching mode absorbs at 3030 cm^{-1}.

^{13}C n.m.r. spectroscopy

The ^{13}C n.m.r. spectra of poly(GMA) (*Figure 4*) and copoly(GMA–STY) (50:50 mol%) (*Figure 5*) were recorded using a Bruker-CXP in $CDCl_3$. The chemical shifts were assigned from the off-resonance H-decoupled spectra of GMA in which peaks due to carbon atoms attached to none, one, or two hydrogen atoms will appear as a singlet, doublet, or triplet respectively. The ^{13}C n.m.r. spectra for poly(STY) was reported earlier[7]. Chemical shift assignments for copoly(GMA–STY) were assigned based on the chemical shifts observed for the respective homopolymers. All these chemical shifts are presented in *Table 3*. In poly(GMA), C3, C4, C6 and C7 are sensitive to tacticity. In copoly(GMA–STY), C1, C2, C4 and C5 of the GMA unit and C8 and C9 of the STY unit are sensitive to tacticity.

Molecular weights

The number- and weight-average molecular weights of poly(GMA) and three samples of different compositions of copoly(GMA–STY) were determined by g.p.c. Molecular-weight data of the samples are given in *Table 1*. The polydispersity ($\bar{M}_w/\bar{M}_n$) of these copolymers is almost close to 1.50. In the homopolymerization of styrene the polymeric radicals undergo mainly recombination[8]. The theoretical value of $\bar{M}_w/\bar{M}_n$ for polymer produced via radical recombination and radical disproportionation are 1.5 and 2.0 respectively[9]. The $\bar{M}_w/\bar{M}_n$ in copolymerization is also known to depend on the chain termination mechanism in the same way as it does in homopolymerization. The value of $\bar{M}_w/\bar{M}_n$ is 1.55 for poly(GMA), and, compared to that of the copolymers, suggests that there is a strong tendency for radical recombination to terminate the polymeric chains.

Glass transition temperature

The glass transition temperatures of poly(GMA) and copoly(GMA–STY) were determined by d.s.c. with a Du Pont micro-thermobalance. The T_g of poly(GMA) is 76°C and that of copoly(GMA–STY) (10:90 mol%) is 82°C. The T_g of poly(STY) was well established as 100°C. Since the T_g of poly(STY) is well above room temperature, the polymer film obtained from the uncured copolymer of any composition would be brittle in nature. The curing of the epoxy groups of the copolymers with

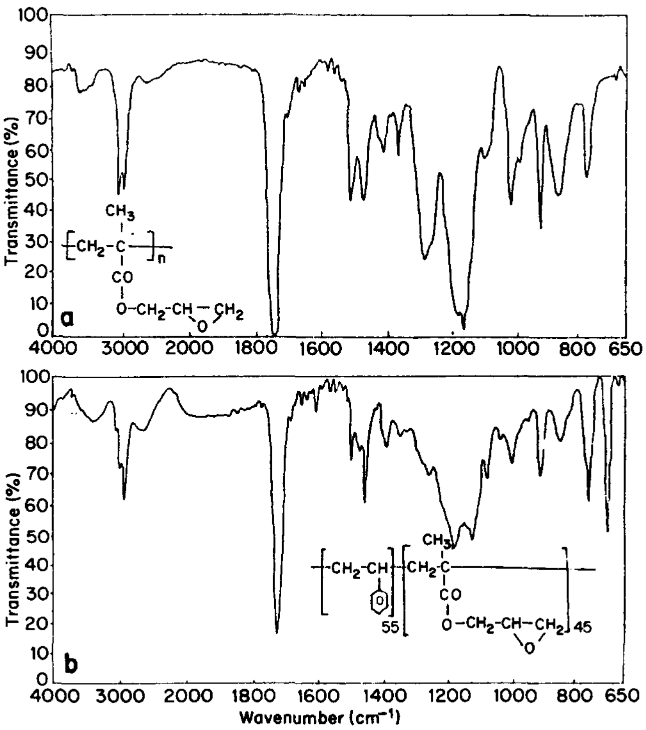


Figure 3 (a) I.r. spectrum (cast film) of poly(GMA). (b) I.r. spectrum (cast film) of copoly(GMA–STY) (45:55 mol%)

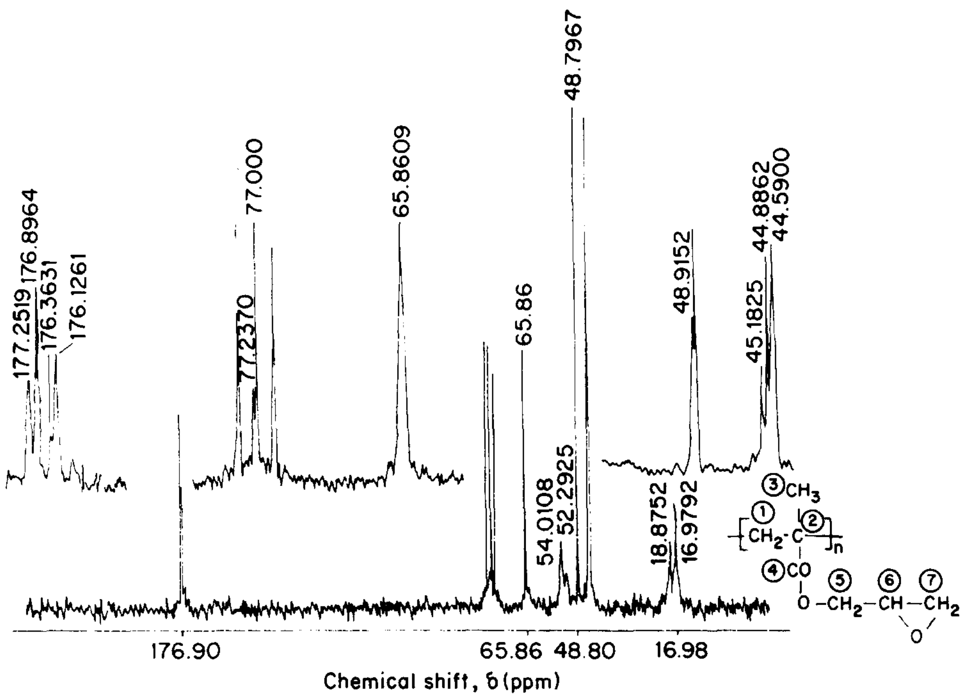


Figure 4 ^{13}C n.m.r. spectrum of poly(GMA)

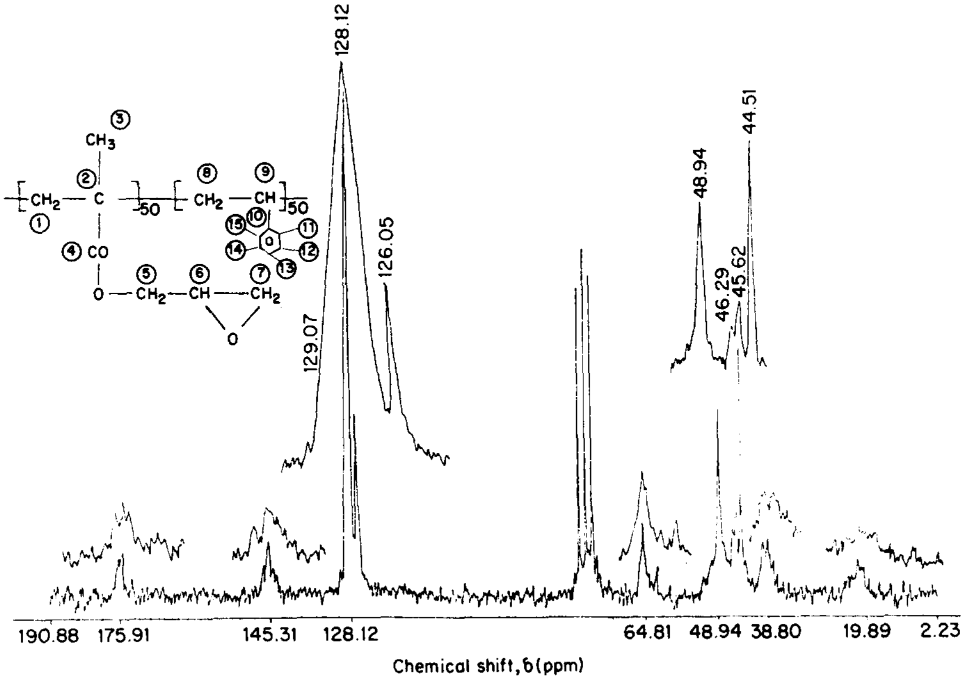


Figure 5 ^{13}C n.m.r. spectrum of copoly(GMA–STY) (50:50 mol%)

Table 3 Chemical shifts (ppm)

Sample	C1	C2	C3	C4	C5	C6	C7	C8	C9	Aromatic C10–15
GMA	124.83	135.34	17.21	165.86	64.38	48.42	43.71			
Poly(GMA)	52.29	54.01	18.75 16.97	177.19 176.90 176.36 176.13	65.80	48.92 48.80	45.18 44.89 44.59			
Copoly(GMA–STY)	50.77 50.22 49.90	61.94	19.89	176.53 175.91 175.53	64.82 64.62	48.94	44.51	46.29 45.62	39.63 39.02 38.80 38.43	146.44 145.31 144.70 128.12 129.07 126.05

Table 4 Differential thermogravimetric analysis data of poly(GMA), poly(STY) and copoly(GMA–STY)

	Temperatures at different percentage weight loss (°C)								
Sample	10%	20%	30%	40%	50%	60%	70%	80%	90%
Poly(GMA)	305	335	365	380	395	405	415	425	445
Poly(STY)	400	425	435	445	455	465	495	–	–
Copoly(GMA–STY)	355	380	395	405	410	415	425	430	445

plasticizers and/or flexibilizers and the application of these copolymers in the leather industry will be reported elsewhere.

Thermogravimetric analysis

T.g.a. curves for poly(GMA), poly(STY) and copoly(GMA–STY) (50:50 mol%) were obtained and the results of the differential thermogravimetric analysis are presented in *Table 4*. In poly(GMA) first degradation occurs at 360°C (28%) and second degradation occurs at 435°C. Poly(STY) was found to be stable to heat up to 500°C and maximum degradation (71%) occurs at 500°C. In copoly(GMA–STY) only one degradation occurs at 440°C. In both poly(GMA) and copoly(GMA–STY) 90% weight loss was observed at 445°C. The kinetics of thermal degradation of poly(GMA) and copoly(GMA–STY) will be reported elsewhere. For polystyrene it has been reported already[10].

The thermal stability of poly(GMA) has been improved by the copolymerization of GMA with styrene. The stabilization can be further improved by crosslinking the epoxy groups present in the poly(GMA) and copoly(GMA–STY) with common epoxy curing agents such as amines, acid anhydrides, etc., to form a three-dimensional network.

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REFERENCES

1 Simms, J. A. *J. Appl. Polym. Sci.* 1961, **5**, 58
2 Kalal, J. *J. Polym. Sci., Polym. Symp. Edn.* 1978, **62**, 251
3 Feit, E. D., Wurtz, M. E. and Kammlott, G. W. *J. Vac. Sci. Technol.* 1978, **15**, 944
4 Kelen, T. and Tudos, F. *J. Macromol. Sci.–Chem.* (*A*) 1975, **9**, 1
5 Fineman, M. and Ross, S. D. *J. Polym. Sci.* 1950, **5**, 259
6 Sorokin, M. F. and Kochnov, I. M. *Vysokomol. Soedin* 1964, **6**, 793
7 Reddy, B. S. R., Arshady, R. and George, M. H. *Macromolecules* 1983, **16**, 1813
8 Bevington, J. C., Melville, H. W. and Taylor, R. P. *J. Polym. Sci., Polym. Chem. Edn.* 1954, **12**, 449
9 Brandrup, J. and Immergut, E. H. (Eds.), 'Polymer Handbook', Second Edn., Wiley Interscience, New York, 1975
10 Soundararajan, S., Reddy, B. S. R., Rajadurai, S. and Thyagarajan, G. *J. Appl. Polym. Sci.* 1987, **34**, 247