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Radical Copolymerization of Glycidyl Dienecarboxylates with Styrene

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Extensive studies of the copolymerization of glycidyl acrylate and methacrylate have been undertaken by several investigators in recent years.[1–3] In connection with these works, glycidyl dienecarboxylates such as glycidyl β-vinylacrylate (GV) and glycidyl sorbate (GS) were prepared and copolymerized with styrene in benzene at 60°C, using α,α′-azobisisobutyronitrile as an initiator. The monomer reactivity ratios (r_1, r_2) were determined by the intersection method of Mayo and Lewis[4] and by the method of Fineman and Ross.[5] Then, the Q and e values of both monomers were calculated from these experimental results by means of Alfrey and Price equation.[6] These

TABLE 1. MONOMER REACTIVITY RATIOS AND Q, e VALUES

M_1	M_2	Fineman-Ross Method		Intersection Method		Q	e
		r_1	r_2	r_1	r_2		
Styrene	GV	0.12	4.97	0.13 ± 0.02	4.99 ± 0.14	4.79	−0.05
Styrene	GS	0.81	0.47	0.88 ± 0.07	0.51 ± 0.06	0.56	0.18

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1) Y. Iwakura, T. Kurosaki and N. Nakabayashi, *Makromol. Chem.*, **46**, 570 (1961).

2) Y. Iwakura and K. Matsuzaki, *Kobunshi Kagaku* (*J. High Polymers*), **17**, 187 (1960).

3) J. A. Simms, *J. Appl. Polymer Sci.*, **5**, 58 (1961).

4) F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944).

5) M. Fineman and S. D. Ross, *J. Polymer Sci.*, **5**, 259 (1950).

6) T. Alfrey and C. C. Price, *ibid.*, **2**, 101 (1947).

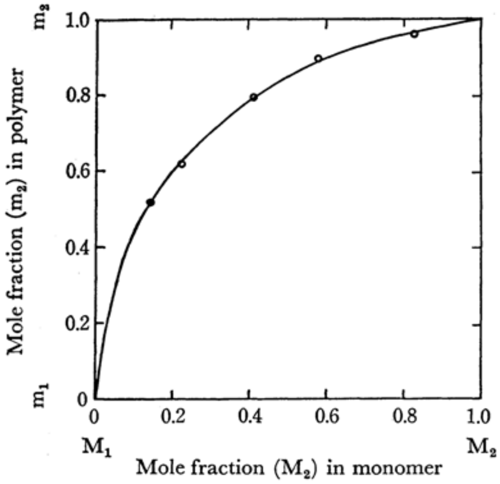

Fig. 1. Styrene - glycidyl β-vinylacrylate.

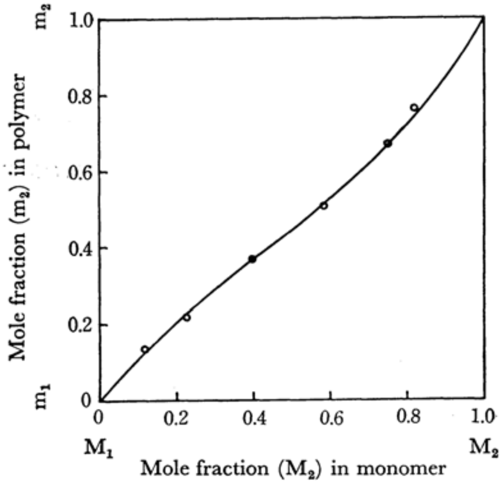

Fig. 2. Styrene - glycidyl sorbate.

values are listed in Table 1. The copolymer composition curves for GV and GS are shown in Figs. 1 and 2. It was found that the apparent rate of copolymerization of GV with styrene was somewhat slow in the region rich in charged styrene components, whereas the situation was reversed in the copolymerization of GS. The copolymer composition curve of GV shows that GV is reactive and is well-incorporated into a copolymer in the monomer mixture richer in styrene components. The copolymer composition curve of GS runs nearly along the 45° line and copolymerization will produce a copolymer possessing almost the same composition as the monomer mixture even at a high conversion.

It has been reported[7] that the replacement of the β-hydrogen of *n*-butyl acrylate by a methyl group brought about a serious decrease in the Q value from 0.50 to 0.007. The difference in Q value between GV and GS is presumably attributable to the same effect in the δ-methyl substitution system. Although the e value was also decreased by β-substitution in the case of butyl acrylate, no influence on the e value by δ-substitution in diene derivatives has been reported in the literature. The small increase in e value by δ-substitution therefore remained unexplained.

Copolymer were found to be soluble in benzene, tetrahydrofuran, dioxane, dimethylformamide, chloroform, and acetone, and insoluble in methanol, *n*-hexane, and water. The copolymers of GV containing a larger amount of GV were gummy materials, however, the other copolymers were white powder.

The infrared absorptions of $\nu_{C=O}$ and δ_{CH} of the *trans*-double bond in the copolymer appeared at 1730 and 970 cm^{-1} and at 1735 and 970 cm^{-1} in the copolymers of GV and GS, respectively. The absorption peaks arising from the phenyl ring of copolymer were exhibited at 1600, 1500, 760, and 700 cm^{-1}. The fact that the absorption maxima of the epoxide group[8] appeared at 900 and 840 cm^{-1} proved that the epoxide ring still remained unattacked in the copolymer. The epoxide contents in copolymers determined by titration corresponded substantially well to those calculated from elemental analyses.

Experimental

Synthesis of β-Vinylacrylic Acid. The procedure of Glushkov[9] was modified for the preparation of β-vinylacrylic acid. Malonic acid (250 g, 2.40 mol) was dissolved in pyridine (350 m*l*). Into the solution, kept at 75—80°C, acrolein (100 m*l*, 1.51 mol) was then added under stirring, drop by drop. The reaction mixture was stirred for 15 min, and then 75 m*l* of acrolein was added, drop by drop. After a few minutes interval, an additional 25 m*l* of acrolein was added to the mixture. After the mixture had been stirred for 30 min, it was poured onto crushed ice and acidified gradually wish 175 m*l* of concentrated sulfuric acid. Yellowish crystals were precipitated in a pulpy state by acidification. The crystals were filtered and washed with cold water. The filtrate was extracted three times with methylene chloride (each 300 m*l*), and the combined extract was dried over sodium sulfate. Yellowish crystals were obtained by the evaporation of the solvent. All the crystals were recrystallized from water, in the presence of hydroquinone as an inhibitor, to yield 66 g (28%) of the product melting at 68.5—70.5°C (lit.,[10] 72°C)

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7) L. J. Young and C. C. Kennedy, in "Copolymerization," ed. by G. E. Ham, Interscience Pub., New York (1964), p. 845.

8) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," p. 118, John Wiley & Sons, Inc., New York (1964).

9) R. G. Glushkov and O. Yu. Magidson, *Med. Prom. SSSR*, **16**, No. 3, 27 (1962); *Chem. Abstr.*, **58**, 442c (1963).

10) I. E. Muskat, B. C. Becker, and J. S. Lowenstein, *J. Am. Chem. Soc.*, **52**, 326 (1930).

in the form of needles. Crude crystals seemed to be pure enough for the synthesis of acid chloride. Recrystallization would cause a loss of β-vinylacrylic acid by thermal polymerization.

Synthesis of β-Vinylacryloyl Chloride. β-Vinylacryloyl chloride was synthesized from β-vinylacrylic acid and thionyl chloride in a 68% yield by the method described by Alder.[11] The boiling point was 42—44°C/10 mmHg.

Synthesis of Glycidyl β-Vinylacrylate (GV). In a four-necked flask there was placed glycidol in dry tetrahydrofuran, plus a small amount of an inhibitor. Equimolar amounts of triethylamine and β-vinylacryloyl chloride, each diluted with dry tetrahydrofuran, were added separately through two dropping funnels. Care had to be taken to maintain the reaction mixture in a condition with a slight excess of amine and to keep it below 10°C with an ice bath. After the addition had been completed, the mixture was stirred for 1 hr; the resultant triethylamine hydrochloride was removed by filtration, and the filtrate was dried over sodium sulfate. The product was obtained by distillation under a high vacuum in a 44% yield. The boiling point was 72—73°C/0.4 mmHg. If the bath temperature was raised above 120°C, distillation was impossible because of the thermal polymerization of the liquid phase. IR absorption bands: ν C=O 1715, ν C=C 1640, 1600; *trans*-conjugated diene δ CH 1015; epoxide 905, 840; terminal vinyl δ CH 930 cm^{-1}. λ_{max} 245 mμ in tetrahydrofuran.

Found: C, 62.57; H, 6.61%. Calcd for $C_8H_{10}O_3$: C, 62.32; H, 6.54%.

Synthesis of Sorboyl Chloride. A 500 m*l* flask was charged with 168 g (1.5 mol) of sorbic acid. Phosphorus pentachloride (312 g, 1.5 mol) was then vigorously blended in, portion by portion, using a glass rod. The reaction mixture was liquefied within a short time as the reaction proceeded. After the addition, the hydrogen chloride thus formed was purged from the reaction mixture with an aspirator. The product was separated from phosphorus oxychloride by distillation under reduced pressure with a small amount of a polymerization inhibitor such as *N*-phenyl-β-naphthylamine and purified by redistillation to give a fraction boiling at 70—72.5°C/10 mmHg and weighing 136 g (70% yield[12]). If the bath temperature was raised to over 110°C, the contents of the reaction flask suddenly became a black resinous material.

Synthesis of Glycidyl Sorbate (GS). Glycidyl sorbate was prepared by a method analogous to that used for GV. Toluene was used as the solvent in this case. The precipitated triethylamine hydrochloride was removed by filtration. The crude filtrate showed two carbonyl absorptions at 1720 and 1740 cm^{-1} in the infrared spectrum. The absorption of a higher frequency would indicate the existence of an isomer formed by the migration of the double bond to glycidyl 3,5-hexadienoate in the course of reaction. The crude reaction mixture was then heated together with a small amount of benzylamine at 90°C for 3 hr in order to bring about isomerization to a conjugated structure. The treatment was continued until the absorption at 1740 cm^{-1} disappeared. The solution thus treated was washed successively with dilute sulfuric acid, a sodium bicarbonate solution, and water, and then dried. After the removal of the toluene, vacuum distillation was repeated three times to give GS boiling at 100—102°C/0.3 mmHg[13] in a 42% yield. λ_{max} 259 mμ in tetrahydrofuran.

Found: C, 64.53; H, 7.06%. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19%.

Copolymerization. Polymerization experiments were carried out at 60°C in sealed tubes (10 m*l*) under a nitrogen atmosphere and using α,α′-azobisisobutyronitrile as an initiator. About 2 g of a mixture of precisely weighed styrene and GV was diluted with benzene (5 m*l*; in the case of GS, 2 m*l*) and sealed. The solution was then kept at 60°C for 15—28 hr. The polymer solution was poured into methanol, and the precipitated polymer was collected by filtration and reprecipitated, chloroform being used as the solvent and methanol as the non-solvent. The purified polymers were dried *in vacuo*, and the composition of the copolymer was determined by elemental analyses.

Determination of Epoxide Values. About 300mg of a copolymer sample was precisely weighed and dissolved in 25 m*l* of a HCl-dimethylformamide solution in a glass-stoppered flask.[14] The solution was then kept at 60°C for 64 hr. After the solution had been cooled to room temperature, calcium carbonate (0.5 g), starch solution (1.0 m*l*), and a fluorescein solution (5 drops) were added and the mixture was titrated by a standard silver nitrate solution. The epoxide value was calculated by subtracting the blank titer obtained under the same condition but without a sample.

The epoxy contents of the copolymers are as follows:

Copolymer	From elemental analyses:	From epoxide value:
Styrene-GV	89.1 mol%	84 mol%
Styrene-GS	21.7 mol%	21 mol%

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[11] K. Alder, M. Schumacher and O. Wolff, *Ann.*, **564**, 79 (1949).

[12] T. E. Jones and C. O. Wilson, *J. Am. Pharm. Assoc.*, **42**, 342 (1953).

[13] Y. Iwakura, N. Nakabayashi and M. H. Lee, *Makromol. Chem.*, **78**, 157 (1964).

[14] L. Shechter, J. Wynstra and R. P. Kurkjy, *Ind. Eng. Chem.*, **48**, 94 (1956).