## Reactive Monomers Derived from p-Vinylbenzoic Acid

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The preparation and the application of reactive polymers have been studied in our laboratory.<sup>1,2)</sup> Generally, reactive polymers can be obtained by the polymerization of so-called reactive monomers, which have a carbon-carbon double bond, and another functional group, such as epoxide, aziridine or isocyanate.

The present paper will describe the preparation of new reactive monomers derived from p-vinylbenzoic acid.<sup>3,4</sup> Jäger's method was adopted for preparing the acid in this report.

Glycidyl p-Vinylbenzoate.— $p-\beta$ -Bromoethylbenzoic acid (I) was prepared by the procedure of Foreman.<sup>5)</sup> I was treated with potassium hydroxide in ethanol in order to obtain potassium p-vinylbenzoate (II). The reaction of II and epichlorohydrin using triethylbenzylammonium chloride as a catalyst produced glycidyl p-vinylbenzoate (III), which was then distilled at 115.5—116.5°C/0.1 mmHg. The yield was 71%.

Found: C, 70.63; H, 6.01. Calcd. for  $C_{12}H_{12}O_3$ : C, 70.57; H, 5.92%.

The infrared absorption spectrum showed carbon-carbon double-bond bands at 1629, 987 and 918 cm<sup>-1</sup>, epoxide at 907 and 839 cm<sup>-1</sup>, carbonyl at 1720 cm<sup>-1</sup> and p-phenylene at 856 cm<sup>-1</sup>. The epoxide content was 98.0%.

When the radical polymerization of III was carried out, linear poly-III was obtained; it had a  $\eta_{sp}/c$  value of 0.20 (0.2 g./100 ml. dioxane at 30.0°C), and the epoxide content of the polymer was 96.0%. The copolymerization of III (M<sub>2</sub>) with styrene (M<sub>1</sub>) was also studied. The monomer reactivity ratios were as follows:  $r_1$ =0.40±0.02, and  $r_2$ =0.95±0.10 (at 70.0±0.1°C). Alfrey-Price's Q and e values were 1.18 and 0.18 respectively. Nucleophilic reagents such as hydrogenchloride and alkyl amine, could easily be added to epoxy groups in the poly-III and the copolymer.

p-Vinylphenylisocyanate. — This compound<sup>6></sup> (b. p. 40.5—41.5°C/0.1 mmHg) was obtained through the acid chloride and the acid azide. The isocyanate gave a homopolymer with a vinyl group by means of the anionic polymerization of the isocyanate group at a low temperature. The radical polymerization, on the other hand, brought about one with a isocyanate group.

The details will be pulished in a short time.

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<sup>1)</sup> Y. Iwakura, T. Kurosaki and N. Nakabayashi, Makromol. Chem., 44/46, 570 (1961).

Y. Iwakura, N. Nakabayashi and H. Suzuki, ibid., 78, 168 (1964).

<sup>3)</sup> S. Merill, J. Org. Chem., 26, 1301 (1961).

<sup>4)</sup> P. Jäger and E. S. Waight, J. Chem. Soc., 1963, 1339.

<sup>5)</sup> E. L. Foreman and S. M. McElvain, J. Am. Chem. Soc., 62, 1435 (1940).

<sup>6)</sup> U. S. Pat. 2468713 (1949).