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Two-stage Polymerization of (1,3-Dioxolan-4-yl)methyl Acrylate

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A monomer containing two different polymerizable functional groups is of interest from the viewpoint of the two-stage polymerization. Monomers containing a vinyl group and an epoxy group such as glycidyl methacrylate,[1,2] and monomers containing a vinyl group and a tetrahydrofuran ring such as tetrahydrofurfuryl methacrylate[3,4] have been investigated in detail. (1,3-Dioxolan-4-yl)methyl acrylate containing a vinyl group and a dioxolane ring appears to be a very interesting monomer, but it has been mentioned only briefly in two patents.[5]

The preparation, the structure and the two-stage polymerization of this monomer have been investigated in detail, and the findings will be described in this paper.

Experimental

1,2-Methyleneglycerol. This was prepared as a mixture with 1,3-methyleneglycerol according to the method of Hibbert and Carter.[6] From 175 g of paraformaldehyde and 525 g of glycerol, 309 g of a mixture of methyleneglycols was obtained (52%).

(1,3-Dioxolan-4-yl)methyl Acrylate (DA). Into a 1-liter three-necked flask equipped with a mechanical stirrer, a condenser and a thermometer, 300 g of methylene glycerol, 122 g of acrylic acid and 258 g of benzene were added. After 1 m*l* of concentrated sulfuric acid and 8.6 g of copper powder were added, the mixture was placed in an oil bath at 110°C. The solution was refluxed at about 88°C, and became yellow after 12 hr of heating and stirring. The unreacted 1,3-methyleneglycerol was removed by washing with saturated sodium chloride solution. Four washings with 50 g portions of

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1) T. Otsu, K. Goto and M. Imoto, *Kobunshikagaku*, **21**, 198 (1964).

2) I. M. Kochnow and M. F. Sorokin, *Vyskomol Soedin.*, **6**(5), 791 (1964); *Chem. Abstr.*, **61**, 5765 (1964).

3) I. Sakurada, K. Noma and Y. Ohfuji, *Kobunshikagaku*, **21**, 295 (1964).

4) I. Sakurada, K. Noma and Y. Ohfuji, *ibid.*, **21**, 481 (1964).

5) E. Ellery, Brit. Pat. 690709 (April 29, 1953) and Brit. Pat. 695633 (Aug. 12, 1953).

6) H. Hibbert and N. M. Carter, *J. Am. Chem. Soc.*, **50**, 3120 (1928).

the salt solution removed 275 g of 1,3-methyleneglycerol. Then benzene was distilled off at 20 mmHg in a water bath at 30°C, and finally 82 g of a colorless liquid was collected by distillation at 55—57.5°C/0.2—0.3 mmHg. Its infrared spectrum shows absorptions at 1705 and 1723 cm^{-1}, which indicate that this liquid is a mixture of acrylic acid and an acrylic acid ester. The liquid was dissolved in carbon tetrachloirde, and acrylic acid was extracted with a 5% sodium hydrogen carbonate solution. Ten washings removed all the acrylic acid in the mixture. The carbon tetrachloride solution was dried by use of anhydrous sodium carbonate. The solvent was removed under reduced pressure, and 34.5 g (19%) of DA was obtained by distillation at 60—64°C/ 0.8 mmHg. Found: C, 53.10; 53.14; H, 6.41; 6.43%. Calcd for $C_7H_{10}O_4$: C, 53.14; H, 6.37%.

Determination of Formaldehyde from DA. About 0.1 g of DA was accurately weighed, and was added to a 20% sulfuric acid solution. The solution was refluxed for one hour, and then was steam-distilled. About 300 m*l* of a distillate was collected, which was refluxed for one hour with 20 m*l* of a 7% hydroxylamine hydrochloride solution. After cooled to room temperature, the hydrochloric acid liberated was titrated with 0.1 N sodium hydroxide solution by use of a pH meter. Because of the very dilute concentration, the titration curve was not so sharp. Eighty-three percent of formaldehyde was detected. When authentic 1,3-dioxolane was subjected to this analysis, 0.88 mol of formaldehyde per mole of dioxolane was detected.

Free Radical Polymerization of DA. *In Toluene.* One gram of DA, 0.0197 g of azoisobutyronitrile, and 3 g of toluene were heated at 80°C under nitrogen atmosphere. After 5 min of heating, viscous materials precipitated as a lower layer. After two hours of heating, the precipitated polymer was separated by decantation. The polymer was dissolved in acetone and reprecipitated by addition of petroleum ether. This purification was repeated twice. White solids obtained were soluble in acetone or chloroform, and were hygroscopic. The surface became smooth upon absorption of moisture in air.

In Benzene. DA, 0.9458 g, was refluxed in 3 g of benzene with 0.0197 g of azoisobutyronitrile for 3 hr. Though the hot solution was transparent, a transparent polymer precipitated when the solution was cooled to room temperature. The polymer was separated by decantation, and was dissolved in acetone, but a fraction of the polymer was insoluble in acetone which corresponded to 17% of the monomer used. The acetone-soluble polymer was reprecipitated by addition of petroleum ether. The dissolution-reprecipitation was repeated twice. The polymer dried under reduced pressure weighed 0.689 g (73%), and resembled to the polymer obtained in toluene.

The viscosity of the polymer was determined in acetone at 30°C, and it was found that $[\eta]$ was 0.137. The application of the equations established for poly (methyl acrylate) ($[\eta]=1.49\times10^{-3}\times P^{0.52}$, acetone, 30°C)[7] and poly (ethyl acrylate) ($[\eta]=4.19\times10^{-4}\times P^{0.66}$, acetone, 30°C)[8] gave the molecular weights of 5.14×10^5 and 3.39×10^5, respectively. Therefore, it is likely that the molecular weight of the polymer obtained is about 10^5.

Second-stage Cationic Polymerization of Poly-(1,3-dioxolan-4-yl)methyl Acrylate. The polymer obtained by azoisobutyronitrile was subjected to a ring-opening polymerization.

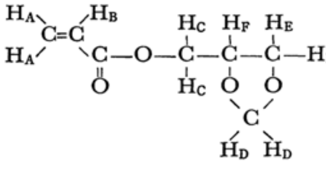
When the polymer was heated at 140°C with about 10 weight percent of *p*-toluenesulfonic acid, some reaction took place and the polymer became insoluble in acetone. Apparently some crosslinking occurred through opening of the dioxolane ring. The polymer was not hard solids at high temperatures, but a gummy material. Probably the crosslinking was not so extensive.

When the polymer was mixed in acetone with about 45 weight percent of boron trifluoride etherate and the mixture was evaporated under reduced pressure, the polymer became light brown in 1 hr at room temperature, and became reddish brown in 3 hr. The brown polymer was insoluble in acetone, and when heated up to 160°C it became black hard solids.

Cationic Polymerization of DA. When a mixture of 1 g of DA and 0.15 m*l* of boron trifluoride etherate was allowed to stand in a test tube protected by a calcium chloride tube at room temperature for 67 hr, a hard brown solid polymer was obtained. The polymer was not soluble in acetone, and when heated up to 180°C it was hard black solids.

Results and Discussion

(1,3-Dioxolan-4-yl)methyl acrylate (DA) was prepared from acrylic acid and a mixture of 1,2- and 1,3-methyleneglycerol. The assignment of the structure was supported by correct elemental analyses, formaldehyde determinations, infrared and NMR spectra. The NMR spectrum showed chemical shifts at 6.45 ppm(2H; H_A), 6.1 ppm (1H; H_B), 5.0 ppm (2H; H_C), 4.29 ppm (2H; H_D), 4.0 ppm (2H; H_E) and 3.8 ppm (1H; H_F).



When DA was polymerized in toluene or benzene by azoisobutyronitrile at 80°C, white solid polymer was obtained. The polymer was soluble in acetone or chloroform, and its NMR spectrum showed that vinyl hydrogens (6.45 ppm and 6.1 ppm) were completely converted into aliphatic hydrogens. The evidence suggests that this polymer was formed through the polymerization of carbon-carbon double bonds without participation of dioxolane rings. When the poly DA was heated with *p*-toluenesulfonic acid or was allowed to stand at room temperature with boron trifluoride etherate, some crosslinking occurred and the polymer became insoluble in acetone.

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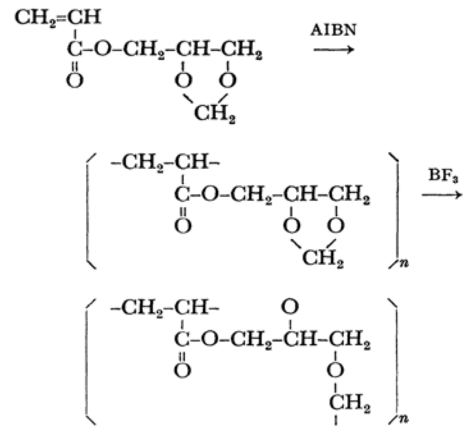
[7] H. Ito, S. Shimizu and S. Suzuki, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **59**, 930 (1956).

[8] H. Sumitomo and Y. Hachihama, *Kobunshikagaku*, **10**, 544 (1953).



When the poly DA was heated alone to 270°C and then cooled, the polymer was insoluble in acetone. Apparently some crosslinking occurred, but much less extensively than the case with boron trifluoride, since the acetone-insoluble polymer was soft at high temperatures.

When the DA monomer was treated with boron trifluoride etherate at room temperature, a reddish brown solid polymer was obtained. It was insoluble in acetone. Its infrared spectrum resembled to that of the polymer prepared by the second-stage cationic polymerization of the poly DA obtained by azoisobutyronitrile. Therefore, it appears that the treatment of DA with boron trifluoride polymerizes not only the dioxolane rings but also vinyl bonds.