*The Polymerization of 3,3-Bis(chloromethyl)oxetane with Boron Trifluoride-Diethyl Etherate in the Presence of Glycidyl Methacrylate**

By Takayuki OTSU, Shuzo AOKI and Minoru IMOTO

(Received July 27, 1963)

Recently Saegusa and his colaborators[1] reported that three-membered cyclic ethers, such as propylene oxide and epichlorohydrin, showed a cocatalytic effect on the polymerization of tetrahydrofuran and 3, 3-bis(chloromethyl)oxetane with Lewis acid catalysts. We also found that glycidyl methacrylate and glycidyl acetate could serve as both cocatalyst and comonomer in the polymerization of tetrahydrofuran catalyzed by boron trifluoride-diethyl etherate.[2] Several copolymers of tetrahydrofuran and 3, 3-bis(chloromethyl)oxetane with some other three-membered cyclic ethers have been prepared.[3] This paper is concerned with the polymerization of 3, 3-bis(chloromethyl)oxetane with boron trifluoride-diethyl etherate in the presence of glycidyl methacrylate.

Experimental

3, 3-Bis(chloromethyl)oxetane, glycidyl methacrylate and boron trifluoride-diethyl etherate were carefully distilled in nitrogen atmosphere under reduced pressure. The middle fraction was collected and used. Methylene chloride was washed with aqueous sodium carbonate and then with distilled water, dried over calcium chloride, and distilled. The polymerization and copolymerization were carried out in a glass-stoppered tube. After a specified time, the polymerization mixture was poured into methanol. The polymer precipitated was filtered off on a glass filter, washed with methanol, and dried under vacuum. The composition of the copolymer was calculated from the results of the chlorine analysis.

Results and Discussion

The effects of the catalyst concentration and of the polymerization temperature on the polymerization rate of 3, 3-bis(chloromethyl)-oxetane in the presence of glycidyl methacrylate and boron trifluoride-diethyl etherate were investigated. The results are shown in Table I. The yield of the polymer increased with the increases in the concentration of

---

* Vinyl Polymerization. LXXXII.

[1] T. Saegusa, H. Imai and J. Furukawa, *Makromol. Chem.*, **54**, 218 (1962); T. Saegusa, H. Imai, S. Hirai and J. Furukawa, *J. Chem. Soc., Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **66**, 474 (1963).

[2] T. Otsu, K. Goto, S. Aoki and M. Imoto, *Makromol. Chem.*, in press.

[3] H. Meerwein, D. Delfs and H. Morschel, *Angew. Chem.*, **72**, 927 (1960); W. J. Murbach and A. Adicoff, *Ind. Eng. Chem.*, **52**, 772 (1960); L. A. Dickinson, *J. Polymer Sci.*, **58**, 857 (1962).

TABLE I. THE EFFECTS OF BORON TRIFLUORIDE-DIETHYL ETHERATE-GLYCIDYL METHACRYLATE CONCENTRATION AND POLYMERIZATION TEMPERATURE ON THE POLYMERIZATION OF 3,3-BIS(CHLOROMETHYL)OXETANE

Run No.	Boron trifluoride-diethyl etherate g.	Glycidyl meth-acrylate g.	3,3-Bis-(chloro-methyl)oxetane g.	CH_2Cl_2 ml.	Temp. °C	Time hr.	Yield g.
B-1	0.4	0	4.0	10	−78	3	0.3
15	0.05	0.05	4.0	10	−78	48	0.4
3	0.1	0.1	4.0	10	−78	48	0.6
16	0.4	0.4	4.0	10	−78	1.5	0.8
17	1.0	1.0	4.0	10	−78	1.5	1.3
3	0.1	0.1	4.0	10	−78	48	0.6
11	0.1	0.1	4.0	10	30	5	0.7
4	0.1	0.5	4.0	10	−78	48	0.1
9	0.1	0.5	4.0	10	0	48	0.3
12	0.1	0.5	4.0	10	30	2	1.8
5	0.1	2.0	4.0	10	−78	48	trace
10	0.1	2.0	4.0	10	0	48	0.1

TABLE II. THE RESULTS OF COPOLYMERIZATION OF 3,3-BIS(CHLOROMETHYL)OXETANE WITH GLYCIDYL METHACRYLATE*

Run No.	Boron trifluoride-diethyl etherate g.	Glycidyl meth-acrylate g.	3,3-Bis-(chloro-methyl)oxetane g.	Temp. °C	Time hr.	Yield g.	Cl (%) in copolymer
3	0.1	0.1	4.0	−78	48	0.6	
4	0.1	0.5	4.0	−78	48	0.1	
5	0.1	2.0	4.0	−78	48	trace	
6	0.1	4.0	4.0	−78	48	trace	
B-2	0.4	0	4.0	0	0.5	2.0	45.67**
18	0.4	0.2	4.0	0	0.37	1.0	45.60
21	0.4	0.5	4.0	0	0.25	0.2	43.37
19	0.4	1.0	4.0	0	3	0.5	39.31
22	0.4	2.0	4.0	0	0.5	0.1	40.75
20	0.4	4.0	4.0	0	4	0.2	33.15

* 10 ml. of CH_2Cl_2 was used as a diluent.

** Calcd. for $C_5H_8OCl_2$: Cl, 45.73%.

boron trifluoride-diethyl etherate-glycidyl methacrylate and in the polymerization temperature; therefore, it was clear that glycidyl methacrylate serves as a cocatalyst for the polymerization of 3,3-bis(chloromethyl)oxetane as well as for that of tetrahydrofuran.[2)]

Table II shows the results of the copolymerization of 3,3-bis(chloromethyl)oxetane with glycidyl methacrylate at −78 and 0°C. As can be seen from Tables I and II, the yield of the polymer decreased as the concentration of glycidyl methacrylate increased relative to the concentration of boron trifluoride-diethyl etherate. These results may be interpreted in terms of the decreased reactivity of the oxonium cation derived from glycidyl methacrylate, since the carbon-carbon double bond in glycidyl methacrylate was quite inert for

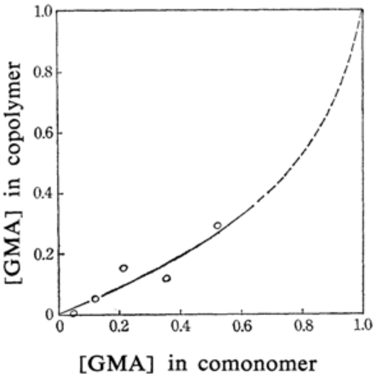

Fig. 1. Monomer-copolymer composition curve for copolymerization of 3,3-bis(chloromethyl)oxetane with glycidyl methacrylate at 0°C.

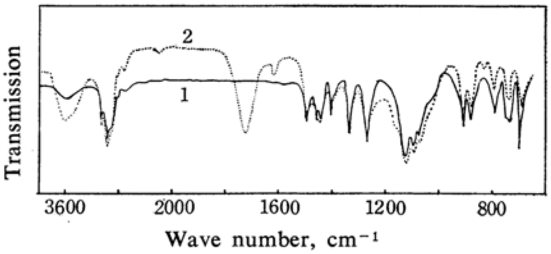

Fig. 2. Infrared spectra of poly-3,3-bis(chloromethyl)oxetane (1) and 3,3-bis(chloromethyl)-oxetane-glycidyl methacrylate copolymer (2) in KBr disk.

the cationic polymerization of tetrahydrofuran, as has been reported in a previous paper.[2)]

From the chlorine contents in the copolymer (Table II), a monomer-copolymer composition curve for this copolymerization at 0°C was drawn (cf. Fig. 1). The apparent monomer reactivity ratios were calculated to be:

r(3,3-bis(chloromethyl)oxetane) = 2.6

r(glycidyl methacrylate) = 0.2

These values are the same as those obtained for the tetrahydrofuran-glycidyl methacrylate copolymerization.[2)]

The infrared spectrum of the copolymer (Fig. 2) shows absorption bands at 1730 and 1640 cm^{-1} due to a carbonyl group and a carbon-carbon double bond respectively, evidently arising from the glycidyl methacrylate unit of the polymer chain. Accordingly, it has been concluded that only the three-membered cyclic ether (epoxy) group in glycidyl methacrylate participated in the copolymerization with the 3,3-bis(chloromethyl)oxetane catalyzed by boron trifluoride-diethyl etherate.

Department of Applied Chemistry
Faculty of Engineering
Osaka City University
Kita-ku, Osaka