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Syntheses and Reactions of Functional Polymers. XLV. Synthesis and Properties of Poly(*N*-glycidyl-2-oxazolidone)

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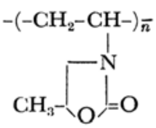
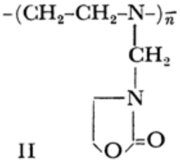
N-Glycidyl-2-oxazolidone was synthesized by the reaction of *N*-sodium-2-oxazolidone with epichlorohydrin. *N*-Glycidyl-2-oxazolidone was polymerized with such Lewis acids as boron trifluoride etherate and aluminum chloride to give a white powder. These polymers adsorbed phenol and methyl bromide effectively. In addition, the copolymerization of *N*-glycidyl-2-oxazolidone with styrene was carried out, and the amount of the adsorption of methyl bromide on the copolymers was measured. The amount of the adsorption of methyl bromide increased in the copolymers as the content of 2-oxazolidone moiety increased. A 1 : 1 molar complex of stannic chloride with *N*-glycidyl-2-oxazolidone was isolated; when the complex was heated, poly(*N*-glycidyl-2-oxazolidone) was obtained quantitatively.

It has been previously reported that poly(*N*-vinyl-5-methyl-2-oxazolidone) I formed complexes with phenol, halogen alkyls, and halogens.[1]

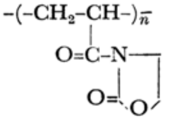


I

Further, we have reported that polyethyleneimine II[2] containing 2-oxazolidone moiety in the side chain and poly(*N*-acrylyl-2-oxazolidone)[3] III formed complexes with phenols and methyl bromide.

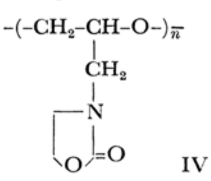


II



III

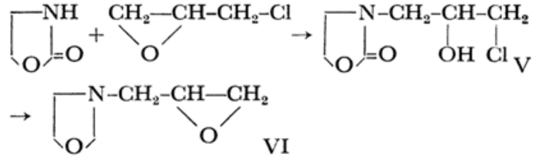
In the present investigation, we attempted to prepare a new type of polymer, poly (*N*-glycidyl-2-oxazolidone) IV, and to investigate its ability to form complexes with phenol and methyl bromide.



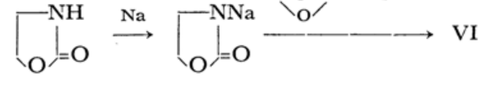
IV

Results and Discussion

Preparation of *N*-Glycidyl-2-oxazolidone (VI). The reactions of active hydrogen compounds with epichlorohydrin using a base[4] or an acid[5] as a catalyst have been reported. Here we tried to synthesize V by the reaction of 2-oxazolidone with epichlorohydrin in the presence of triethylamine, trimethylbenzylammonium chloride, or boron trifluoride etherate, and to prepare VI by treating V with a base. Neither V nor VI could be obtained by these procedures.



On the other hand, by the reaction of *N*-sodium-2-oxazolidone with epichlorohydrin, VI was obtained in a 41% yield. In this reaction, much residue was obtained, probably due to the polymerization during distillation.



The residue was purified by the reprecipitation (adding benzene to a dimethylformamide (DMF) solution) and identified as poly(*N*-glycidyl-2-oxazolidone) by means of its IR spectrum. The

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[1] *Ind. & Eng. Chem.*, **52** No. 12 34A (1960); W. E. Walles and W. F. Tousignant, U. S. Pat. 2872321 (1959).

[2] T. Endo and M. Okawara, *Makromol. Chem.*, **112**, 49 (1968).

[3] T. Endo and M. Okawara Submitted.

[4] N. B. Chapman, N. S. Isaacs and R. E. Parker, *J. Chem. Soc.*, **1959**, 1925.

[5] L. Shechter, J. Wynstra and R. E. Kurkjy, *Ind. & Eng. Chem.*, **48**, 94 (1956); **49**, 1107 (1957).

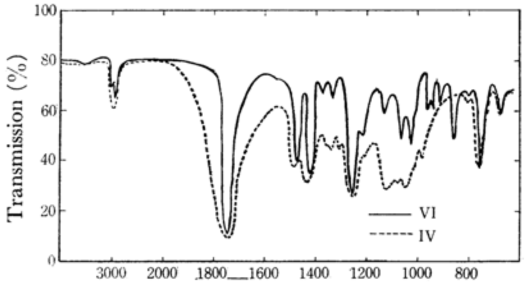


Fig. 1. IR spectra of *N*-glycidyl-2-oxazolidone (VI) and poly (*N*-glycidyl-2-oxazolidone) (IV).

conversion of 2-oxazolidone to VI amounted to 90%, when the polymer produced during distillation was added. VI was identified by an elementary analysis and by means of its IR spectrum. The IR spectrum of VI is shown in Fig. 1. The absorptions of the carbonyl group of cyclic urethane (1745 cm^{-1}) and epoxy ring (910, 850 cm^{-1}) were observed. The results of elementary analysis were in good agreement with the theoretical values.

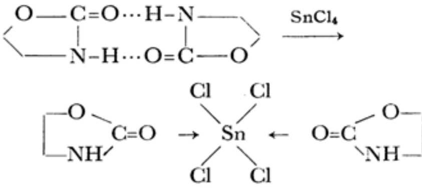
Polymerization of *N*-Glycidyl-2-oxazolidone (VI). As indicated in Table 1, *N*-glycidyl-2-oxazolidone VI was polymerized at 70°C by such Lewis acids as boron trifluoride etherate and aluminum chloride to give a white powder. At low temperatures, however, VI formed stable complexes with Lewis acids and the polymerization did not proceed appreciably. Anionic catalysts, such as triethylamine and sodium methoxide, were also useless in polymerizing VI. The IR spectrum of IV showed the characteristic C=O absorption band at 1745 cm^{-1} and the absorption attributable to ether linkage (1070 cm^{-1}), as is shown in Fig. 1. On the other hand, the epoxy bands at 910 and 850 cm^{-1} in VI disappeared in the IV polymer. Furthermore, the results of the elementary analysis of IV were in good agreement with the theoretical values. IV was soluble in DMF, dimethyl sulfoxide (DMSO), and formic acid, but it was insoluble in common organic solvents, such as alcohols, ketones, and hydrocarbons. However, the IV polymer of a low molecular weight which was polymerized during distillation was soluble in alcohols and water.

TABLE 1. POLYMERIZATION OF *N*-GLYCIDYL-2-OXAZOLIDONE (VI)
(VI 1.5 g; solvent, dioxane 15 m*l*; temp., 70°C)

No.	Catalyst[1]	Time (hr)	Yield (%)	$[\eta]$[3]
1	BF_3OEt_2	14	9	0.44
2	BF_3OEt_2	46	33	0.50
3	$AlCl_3$	39	13	0.46
4	Et_3N[2]	46	0	
5	CH_3ONa	46	0	

1) 2 mol% for VI.
2) Triethylamine.
3) Intrinsic viscosity, measured at 30°C in DMF.

Preparation of the Complexes of 2-Oxazolidone-$SnCl_4$ and *N*-Glycidyl-2-oxazolidone (VI)-$SnCl_4$. When stannic chloride was added, drop by drop to a chloroform or methylene chloride solution of 2-oxazolidone at 0°C, a white precipitate was isolated. The structure of the precipitate was determined by means of a study of the IR spectrum and elementary analysis. The carbonyl absorption (1740 cm^{-1}) of 2-oxazolidone shifted to a lower energy region (1710 cm^{-1}). On the contrary, the absorption band due to the N–H linkage (3275 cm^{-1}) of 2-oxazolidone shifted to a high wave number (3420 cm^{-1}). These observations can be interpreted by assuming that the associated 2-oxazolidone changes to the monomeric structure as a result of the formation of a complex with stannic chloride:



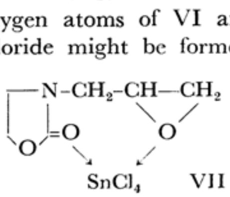
In a similar way, the VI-stannic chloride complex was isolated. The results of the elementary analysis and the IR spectral data of the complex of VI with stannic chloride are summarized in Table 2. The absorption bands due to both C=O and the epoxy ring shifted to lower wave numbers in the complex. From these data, it was concluded that a 1 : 1 molar complex VII of stannic chloride and VI in which two oxygen atoms of VI are coordinated to stannic chloride might be formed as is shown

TABLE 2. THE ELEMENTARY ANALYSES AND IR SPECTRA OF *N*-GLYCIDYL-2-OXAZOLIDONE (VI)-STANNIC CHLORIDE COMPLEX (VII)

	Elementary analyses (%) of VII			
	C	H	N	Cl
Calcd[1]	17.84	2.23	3.47	35.17
Found	17.75	2.30	3.50	35.59

	IR spectral changes (cm^{-1})	
	VI	Complex (XVII)
C=O	1745	1720
epoxy group	850	835

1) Calculated assumig 1 : 1 moar complex of stannic chloride with VI.



VII

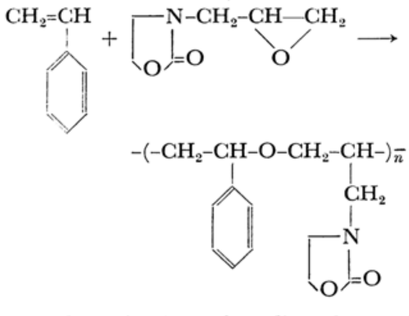
below. When this complex was heated at 60°C for 2 hr, a viscous polymer, IV, was obtained as had been expected.

Copolymerization of *N*-Glycidyl-2-oxazolidone (VI) with Styrene. The copolymerization of *N*-glycidyl-2-oxazolidone with styrene was carried out in dioxane at 70°C using boron trifluoride etherate. The experimental date obtained are summarized in Table 3. The polymers obtained consisted of a white powder. The copolymer composition was determined from the nitrogen content. In the IR spectrum of copolymer, the absorptions of the carbonyl group of the 2-oxazolidone moiety (1745 cm^{-1}), the ether linkage (1070 cm^{-1}) and the phenyl group (1600 and 1490 cm^{-1}) were observed.

TABLE 3. COPOLYMERIZATION OF *N*-GLYCIDYL-2-OXAZOLIDONE (M_1) WITH STYRENE (M_2)
(cat., BF_3OEt_2 2 mol%; temp., 80°C)

No.	$\frac{M_1}{M_1+M_2}\times 100$ 1)	Time (hr)	Conversion(%)	N(%) in copolymer	$\frac{m_1}{m_1+m_2}\times 100$ 2)
1	17	3.5	3.0	0.41	4.1
2	25	6.0	3.6	1.20	11.7
3	50	8.0	5.6	1.61	16.4
4	75	8.0	6.1	2.85	31.6
5	83	8.0	10.5	6.68	68.1

1) M_1, M_2=initial concentrations of the two monomers (mol).
2) m_1, m_2=concentrations of monomers in the copolymer (mol).



The copolymerization of cyclic ethers with vinyl compounds has been reported.[6]

Complex Formation of Poly(*N*-glydicyl-2-oxazolidone) IV with Phenol and Methyl Bromide. When an aqueous solution of IV with a low viscosity ([η]=0.25) was added to a phenolic aqueous solution, the complex of IV with phenol was precipitated as a white viscous form; it was then dried under reduced pressure. The amount of phenol in the complex, as determined by the bromide-bromate method, was 19.6 mol%. In the case of IV of a high viscosity ([η]=0.44,) which was insoluble in water, the polymer was suspended in a phenolic aqueous solution; the solution was then stirred at room temperature for 3 hr. The amount of phenol in the complex, as determined from the amount of decreased phenol in the solution, was 74 mol%. The carbonyl absorption (1745 cm^{-1}) of IV shifted to a lower wave number (1735 cm^{-1}) as a result of the formation of the complex with phenol. Therefore, the bonding force in the IV-phenol complex might be attributable to the hydrogen bonding between the C=O group of the 2-oxazolidone moiety and the hydrogen atom of phenol, as has been discussed before.[3]

In a previous paper,[3] it has been reported that the amount of the adsorption of methyl bromide on the copolymers of *N*-acrylyl-2-oxazolidone and styrene was measured, and that the amount of the adsorption of methyl bromide in the copolymers increased as the content of the 2-oxazolidone group increased. Further, it was suggested the bonding force of the complex formation of the polymers containing a 2-oxazolidone moiety with methyl bromide was the dipole-dipole interaction.

In the present paper, the amount of the adsorption of methyl bromide on the copolymers of *N*-glycidyl-2-oxazolidone VI and styrene was measured at room temperature and 1 atm. The amount of the adsorption of methyl bromide increased as the content of the 2-oxazolidone moiety in the copolymer increased, as is shown in Table 4. Therefore, it was apparent that 2-oxazolidone ring played an important role in the adsorption of methyl bromide on the copolymer.

TABLE 4. ADSORPTION OF METHYL BROMIDE ON THE COPOLYMER OF *N*-GLYCIDYL-2-OXAZOLIDONE (M_1) WITH STYRENE (M_2) (MEASURED AT ROOM TEMP. AND 1 ATM)

No.	Copolymer (g)	$\frac{m_1}{m_1+m_2}\times 100$ 1)	Values of adsorption Experimental (10^{-5} mol)	Values of adsorption Theoretical (10^{-4} mol)
1	0.1	0	0	0
2	0.1	4.1	0.2	0.30
3	0.1	11.7	0.60	0.89
4	0.1	16.7	0.70	1.15
5	0.1	31.7	1.30	1.27
6	0.1	68.1	1.70	4.76
7	0.1	100	2.70	6.45

1) m_1, m_2=concentrations of monomers in the copolymer (mol).
2) Calculated assuming one mole methyl bromide combined with 2-oxazolidone unit mole.

Experimental

Materials. 2-Oxazolidone was prepared by a method reported previously.[3] The sodium dispersion

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[6] M. Mitoh and Y. Minoura, *Makromol. Chem.*, **110**, 197 (1967).

(content 40%; medium, toluene) was a commercial product (Kawaken Fine Chemicals Co.). The epichlorohydrin was dried on calcium hydride and distilled; bp 116—117°C. BF_3OEt_2, $SnCl_4$ and $AlCl_3$ of a reagent grade were used.

Measurements. The IR spectra and refractive indices were measured on Hitachi infrared EPI-S2 and Erma Abbe-refractometers, respectively.

Synthesis of *N*-Glycidyl-2-oxazolidone (VI). The sodium dispersion (20 g, 0.3 g atom) was stirred drop by drop, into a solution containing 22 g (0.25 mol) of 2-oxazolidone in 50 m*l* of benzene at room temperature. After the stirring had been continued for 5 hr at 40°C, epichlorohydrin (46.3 g 0.5 mol) in 50 m*l* of tetrahydrofuran was stirred drop by drop into this solution at 3—5°C. After the stirring had been continued for 5 hr at 60°C the solvents and the unreacted epichlorohydrin were evaporated and the residue was distilled under reduced pressure to obtain 14.6 g (41%) of VI. The VI was redistilled and analyzed bp 107—108°C/0.1 mmHg n_D^{21} 1.4478. Found: C, 49.82; H, 6.38; N, 9.72%. Calcd. for $C_6H_9O_3N$: C, 50.34; H, 6.34; N, 9.72%. The sizable residue obtained on distillation was dissolved in DMF and poured into benzene. The intrinsic viscosity of the polymer thus obtained was 0.25 in water at 30°C.

Polymerization of *N*-Glycidyl-2-oxazolidone (VI). The polymerization was carried out in sealed tubes at 80°C, using BF_3OEt_2 as the catalyst. After polymerization, the polymer was isolated by pouring the reaction mixture into an agitated acetone-water mixture (20 : 1) and the polymer thus precipitated was dried under reduced pressure.

Found: C, 49.70; H, 6.50; N, 9.70%. Calcd for $C_6H_9O_3N$: C, 50.34; H, 6.34; N, 9.79%. The intrinsic viscosity was measured at 30°C in DMF.

Copolymerization of *N*-Glycidyl-2-oxazolidone (VI) with Styrene. The copolymerization of *N*-glycidyl-2-oxazolidone with styrene was carried out in sealed tubes at 70°C, using BF_3OEt_2 as the catalyst. The copolymer was isolated by pouring the reaction mixture into a methanol-acetone mixture (4 : 1) containing a small amount of water. The white polymer thus precipitated was filtered and dried under reduced pressure. The copolymer compositions were determined by nitrogen analysis.

Preparation of 2-Oxazolidone-Stannic Chloride and *N*-Glycidyl-2-oxazolidone (VI)-Stannic Chloride Complexes. Stannic chloride (13 g, 0.05 mol) in 50 m*l* of chloroform was stirred, drop by drop, into a solution containing 3.5 g (0.04 mol) of 2-oxazolidone in 30 m*l* of chloroform at 0°C. The stirring was then continued for 30 min at 0°C. A white crystalline precipitate was isolated from the solution. After having been washed with chloroform five times, the precipitate was dried under reduced pressure to produce 13 g (93%) of the complex of 2-oxazolidone-stannic chloride, mp 145—146°C.

Found: C, 16.49; H, 2.35; N, 6.42; Cl, 31.53%. Calcd for $C_6H_{10}O_4N_2\ SnCl_4$: C, 16.75; H, 2.30; N, 6.44; Cl, 32.68%.

The VI-stannic chloride complex was prepared in a similar way. Stannic chloride (23.3 g, 0.84 mol) in 50 m*l* of chloroform was stirred drop by drop, into a solution containing 2 g (0.014 mol) of VI in 50 m*l* of chloroform at 0°C. The stirring had been continued for 30 min at 0°C, a white crystalline complex was isolated from the solution. After having been washed with chloroform five times, the complex was dried under reduced pressure to obtaine 5.1 g (90%) of VI-stannic chloride. The complex was heated for 2 hr at 65°C and then extracted with chloroform. After the chloroform had been evaporated, IV was obtained quantitatively. The polymer was dried *in vacuo*. The intrinsic viscosity of the polymer was 0.27 at 30°C in water.

Complex Formation of Poly(*N*-glycidyl-2-oxazolidone) (IV) with Phenol and Methyl Bromide. A solution containing 0.874 g of phenol in 20 m*l* of water was added, drop by drop, to a solution containing 0.05 g of IV ($[\eta]=0.25$) in 10 m*l* of water. A viscous precipitate was then isolated from the solution and dried under reduced pressure. The amount of phenol in the complex was determined by the bromide-bromate method. For a heterogeneous system, 0.1 g of IV ($[\eta]=0.44$) was suspended in a solution containing 0.437 g of phenol in 10 m*l* of water. The solution was then stirred for 3 hr at room temperature.

The amount of phenol in the complex was determined from the decrease in the amount of phenol in the solution.