

Isomerization Polymerization of 2-Oxazoline. I. Preparation of Unsubstituted 2-Oxazoline Polymer

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ABSTRACT: Pure unsubstituted 2-oxazoline (OXZ) was first prepared in good yields by modifying Wenker's method.¹ OXZ was found to polymerize by cationic catalyst in an aprotic polar solvent to give a solid polymer. The polymerization of OXZ in less-polar solvents gave polymer in much decreased yields. Lewis acids such as BF_3OEt_2 and SbF_5 , sulfonates, sulfate esters, mineral acids, and alkyl iodide were effective as the polymerization catalyst. But metal chlorides such as SnCl_4 and SbCl_5 were ineffective. The polymer was a white powder, which was soluble in water and insoluble in most organic solvents. The polymer was shown to be crystalline by X-ray diffraction diagram (mp ca. 210°C). The molecular structure of the polymer proved to be poly(*N*-formylethyleneimine) by NMR and IR spectra. Alkaline hydrolysis of poly-OXZ gave crystalline polyethyleneimine (mp 58.5°C).

KEY WORDS 2-Oxazoline / Isomerization Polymerization / Cationic Polymerization / Poly(*N*-formylethyleneimine) / Crystal Polyethyleneimine /

Several 2-substituted-2-oxazolines have been polymerized at elevated temperatures by cationic catalysts to solid polymers having the structures of poly(*N*-acylethyleneimine).²⁻⁵ So far as we know, there has been no study on the polymerization of unsubstituted 2-oxazoline (OXZ). OXZ itself was synthesized for the first time by Wenker¹ only in poor yields. In addition, the purity of OXZ was not high. We have improved the Wenker procedure and prepared OXZ in higher yields. Interestingly pure OXZ was successfully polymerized to solid polymer at lower temperatures than those of 2-substituted monomers.

EXPERIMENTAL

Reagents

Monoethanolamine, methyl formate, and thionyl chloride were commercial reagents and used without further purification. All solvents except for di-*n*-butyl ether were purified by distillation under nitrogen atmosphere and dried on molecular sieves 4A. Di-*n*-butyl ether was dried on metallic sodium and distilled. BF_3OEt_2 , SnCl_4 , SbCl_5 , TiCl_4 , methyl tosylate, dimethyl sulfate, and methyl iodide were purified by distillation.

Commercial *p*-toluenesulfonic acid and AlCl_3 were dried *in vacuo* at 50°C prior to use. Commercial reagents of concd sulfuric acid and SbF_5 were used without further purification.

Preparation of 2-Oxazoline (OXZ)

N-(β -Chloroethyl)formamide 2

Fifty grams (0.42 mol) of thionyl chloride were added dropwise under cooling to a stirred solution of 37.4 g (0.42 mol) of *N*-(β -hydroxyethyl)formamide 1⁶ in 40 ml of DMF. The mixture was then heated at 40—45°C under reduced pressure with nitrogen bubbling for 30 min, and subjected to distillation under reduced pressure. Compound 2 was obtained as a colorless liquid (30.3 g, 67%): bp 104—105°C (3 mm); NMR (CDCl_3) τ 1.80 (s, 1, CHO), 2.70 (s, 1, NH), and 6.35 (m, 4, CH_2). *Anal.* Calcd for $\text{C}_3\text{H}_5\text{ClNO}$: C, 33.51; H, 5.62; Cl, 32.97; N, 13.02; O, 14.88. Found: C, 33.49; H, 5.70; Cl, 32.88; N, 12.99; O, 14.60.

OXZ

To 600 g of 50-% aqueous solution of KOH was added 183 g (1.7 mol) of 2 at 10°C with stirring. The mixture was kept at 15—18°C for about 5 min and the crude OXZ was collected

in a cold trap under 10 mmHg. To the distillate (150 g), 85 g of KOH pellets were added under cooling with ice. The dried OXZ was distilled *in vacuo*. The treatment with KOH pellets was repeated to give 80 g of OXZ, which was then treated with molecular sieves 4A followed by distillation *in vacuo*. The yield was 76 g (63%), and the purity was examined by GLPC (No detectable impurity was observed). *Anal.* Calcd for C_3H_5NO : C, 50.69; H, 7.09; N, 19.71. Found: C, 50.42; H, 7.18; N, 19.74.

Polymerization of OXZ

Polymerization was carried out in a sealed tube at 80°C for 5 hr. As the polymerization progressed, the polymer precipitated as a white powder. After polymerization, an excess amount of methanol was added to the reaction mixture and the polymer was filtered and dried *in vacuo*. *Anal.* Calcd for $(C_3H_5NO)_n$: C, 50.69; H, 7.09; N, 19.71; O, 22.51. Found: C, 50.98; H, 7.16; N, 19.07; O, 22.97.

Alkaline Hydrolysis of Polymer

To a solution of 0.606 g of the polymer in 7 ml of water was added 0.61 g of NaOH. The homogeneous solution was stirred at 98°C for 3 hr. When the solution was cooled to room temperature, white solid precipitated, which was crushed after the addition of 30 ml of water. The material was washed thoroughly with water until the washings became neutral. The precipitate was recrystallized twice from water and dried *in vacuo* for 48 hr to give 0.313 g (85%) of white powder: mp 58.5°C; NMR (CD_3OD) τ 7.25 (s, 1, $\underline{CH_2NCH_2}$). *Anal.* Calcd for $(C_2H_5N)_n$: C, 55.77; H, 11.70; N, 32.53. Found: C, 56.0; H, 11.8; N, 32.2.

The NMR Spectra

NMR spectra were taken on a Varian T-60 instrument using tetramethylsilane (for $CDCl_3$) or 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (for D_2O) as an internal standard.

X-Ray Diffraction

X-ray diffraction diagrams of the powdery polymer were taken by using Rigaku Denki Model SG-7.

Molecular Weight and Viscosity

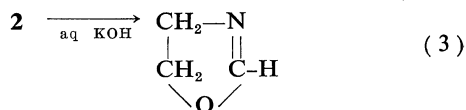
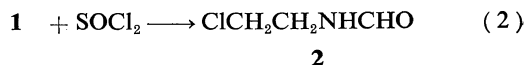
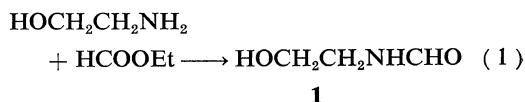
The molecular weight of the polymer was measured by a vapor pressure osmometer (Hitachi-Perkin-Elmer model 115) in water at 59°C. The

solution viscosity of the polymer was measured in water at 30°C, the concentration being 1 g/dl.

RESULTS AND DISCUSSION

Preparation of OXZ

OXZ was synthesized according to Wenker's route.¹



It has been reported, however, that 2 was obtained only in impure form, because of the decomposition during the distillation of the chlorinated mixture of reaction 2. We found that reaction of 2 carried out in tertiary amine or in amide gave improved results to give pure 2 in good yields without any trouble mentioned above. Especially DMF gave the best result (67%). Pure 2 led to the isolation of pure OXZ in the subsequent dehydrochlorination reaction 3 (63%). High purity of the monomer is essential for the polymerization. The monomer sample which had been dried only by KOH gave a very small amount of liquid product. The high polymer was successfully obtained by using the monomer dried on molecular sieves 4A.

The IR and NMR spectra of OXZ are shown in Figures 1 and 2, respectively. The IR spectrum shows bands at 1631 cm^{-1} ($>C=N-$), 1093 cm^{-1} ($C-O-C$), and 975 , 923 , and 868 cm^{-1} (ring skeletal), which are at lower frequencies in comparison with those of 2-substituted-2-oxazolines.³ The NMR spectrum possesses a formyl proton (singlet at τ 3.16 1H), *O*-methylene protons (multiplet centered at τ 5.75 2H), and *N*-methylene protons (multiplet centered at τ 6.21 2H), respectively. The chemical shifts of methylene protons are in the same region as those of 2-substituted-2-oxazolines.⁵

Polymerization of OXZ

The polymerization of OXZ was carried out

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at 80°C in DMF using various cationic catalysts. The results are shown in Table I. Lewis acids such as BF_3OEt_2 and SbF_5 , sulfonate, and sulfate ester, mineral acid, and alkyl iodide were effective and gave white powdery polymers. But metal chloride such as SnCl_4 and SbCl_5 which have been known to initiate the polymerization of 2-substituted-2-oxazolines were ineffective in the OXZ polymerization. Rapid termination which was estimated from the NMR spectra of the polymerization products with these chloride

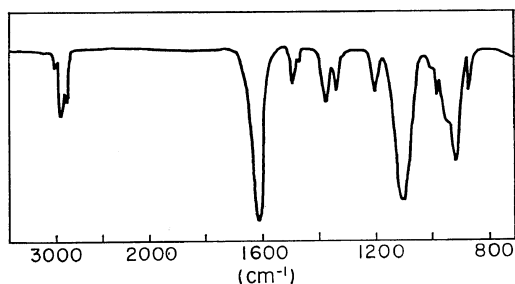


Fig. 1. IR spectrum of 2-oxazoline (neat).

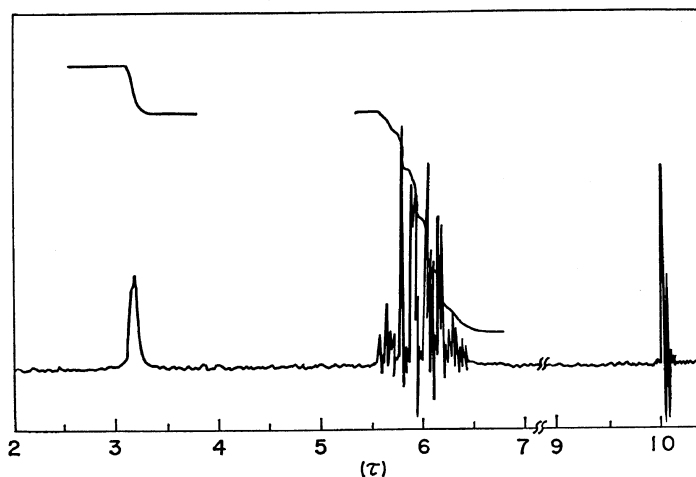


Fig. 2. NMR spectrum of 2-oxazoline (in CDCl_3).

catalysts may be responsible for the failure of polymerization. As shown in Table II, the polymer yield was much affected by the nature of the solvent used. The polymerization in aprotic polar solvents with high dielectric constants such as DMF and acetonitrile resulted in the highest yields of polymer. Nonpolar solvents such as toluene and heptane, on the other hand, gave only a small amount of polymer. A strong base such as pyridine inhibited the polymerization. The polymerization in dimethylsulfoxide gave a large amount of liquid product with lower molecular weights in addition to a small amount of solid polymer.

Characterization of Polymer

The product polymer of OXZ was a white powder melting at *ca.* 210°C and was shown to be crystalline by its X-ray diffraction diagram with a crystalline peak at $2\theta=17.3^\circ$ (Figure 3).

The polymer was soluble only in water and insoluble in most organic solvents. The structure of the new polymer was established on the basis

Table I. Polymerization of 2-oxazoline (Effect of catalysts)^a

Catalyst ^b	Solid polymer yield, %	η_{sp}/c^c	mp, °C
BF_3OEt_2	68	0.20	207—209
SbF_5	73	0.25	200—202
$(\text{CH}_3\text{O})_2\text{SO}_2$	73	0.23	210—212
<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{OCH}_3$	83	0.22	208—210
H_2SO_4	51	0.13	203—209
<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$	32	0.14	200—202
CH_3I	10	0.08	193—197

^a Oxazoline, 7.5—20 mmol; Catalyst, 0.01 mol/mol-OXZ; DMF, 4 ml/ml-OXZ; at 80°C, for 5 hr.

^b SnCl_4 , SbCl_5 , AlCl_3 , and TiCl_4 gave no polymer.

^c In water at 30°C (1 g/dl).

Table II. Polymerization of 2-oxazoline
(Effect of solvents)^a

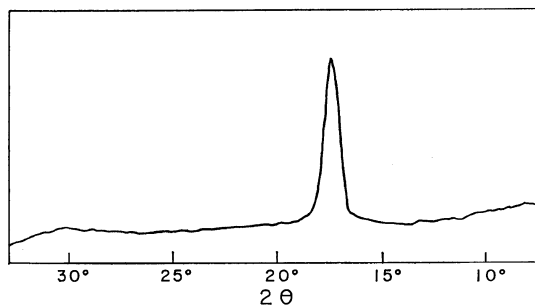
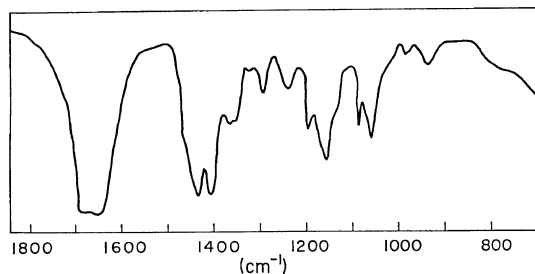
Solvent	Solid polymer yield, %	η_{sp}/c^b	mp, °C
(CH ₃) ₂ NCHO	68.4	0.20	207—209
CH ₃ CN	67.2	0.32 ^c	212—214
C ₆ H ₅ NO ₂	32.6	0.15	214—216
(CH ₃) ₂ SO	16.2 ^d	0.08	183—187
C ₂ H ₄ Cl ₂	13.2	0.10	205—207
(<i>n</i> -C ₄ H ₉) ₂ O	9.3	0.13	213—216
C ₆ H ₅ CH ₃	5.4	0.10	213—214
<i>n</i> -C ₇ H ₁₆	4.3	0.12	213—215
C ₅ H ₅ N	0	—	—

^a 2-Oxazoline, 15 mmol; BF₃OEt₂, 0.15 mmol; Solvent, 4 ml; at 80°C, for 5 hr.

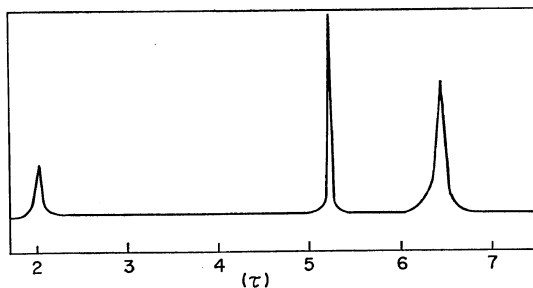
^b In water at 30°C (1 g/dl).

^c The molecular weight measured by vapor pressure osmometry was 2800 (in H₂O, at 59°C).

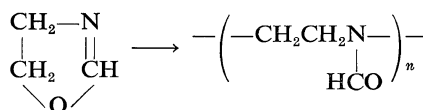
^d A large amount of liq oligomer was also formed.

**Fig. 3.** X-ray diffraction diagram of 2-oxazoline polymer.**Fig. 4.** IR spectrum of 2-oxazoline polymer (KBr).

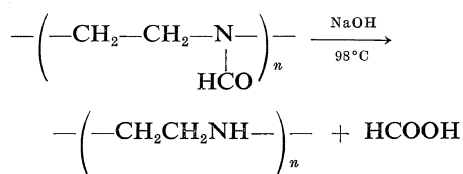
of its NMR and IR spectra. The IR spectrum of the polymer (Figure 4) has a characteristic absorption band of tertiary amide at 1660 cm⁻¹, and its NMR spectrum (Figure 5) shows two

**Fig. 5.** NMR spectrum of 2-oxazoline polymer (in D₂O).

singlets at τ 2.02 (1H) and τ 6.45 (4H), which are reasonably assigned, respectively, to the formyl proton and *N*-methylene protons. Thus, the structure of poly(*N*-formylethyleneimine) has reasonably been proposed. The formation of this type of polymer indicates that OXZ undergoes the cationic ring-cleavage at the 1—5 bond followed by isomerization to amide. Moreover,



the alkaline hydrolysis of the polymer provides additional evidence for proposed structure. Poly-OXZ was easily hydrolyzed by NaOH at 98°C to give a linear polyethyleneimine which proved to be crystalline (mp 58.5°C). This is the first report on crystalline polyethyleneimine. Conventional polyethyleneimines are produced by



the cationic polymerization of ethyleneimine, which are amorphous probably due to highly branched structure.⁷ Later, the details will be published elsewhere.

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