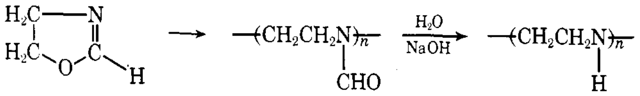
Crystalline Polyethylenimine

It is well known that polyethylenimine produced by the ring-opening cationic polymerization of ethylenimine (EI) has a highly branched structure.[1–4] Owing to the labile hydrogens of secondary amine groups in the main chain of the product polymer, the preparation of a linear poly(EI) from EI has not been accomplished as yet.

In this paper we wish to report a linear and crystalline poly(EI). It is prepared by the alkaline hydrolysis of poly(*N*-formylethylenimine) which is obtained by the isomerization polymerization of unsubstituted 2-oxazoline initiated by $BF_3 \cdot OEt_2$ in dimethylformamide at 80°.[5]



To a solution of 0.606 g of poly(*N*-formylethylenimine)[5] (mol wt 2800 by vapor pressure osmometry) in 7 ml of water was added 0.612 g of NaOH. The homogeneous reaction mixture was stirred at 98° for 3 hr. When the solution was then cooled to room temperature, a white precipitate was formed. The solid was washed thoroughly with water until the washings became neutral. The precipitate was recrystallized twice from water, and the melted polymer was dried at 90° *in vacuo* giving 0.313 g (85%) of poly(EI). *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.

Poly(EI) thus obtained was shown to be crystalline by X-ray diffraction (Figure 1). As shown in Figure 1, three crystalline peaks were observed, at 2θ = 11.8, 20.5, and 23.8°. By DSC analysis the melting point of this polymer, T_m, was shown to be 58.5°, and the glass transition point was −23.5°. This crystalline polymer is insoluble in water at room temperature and soluble only in hot water. This solubility behavior is quite different from that of the conventional poly(EI) which is readily soluble in cold water.

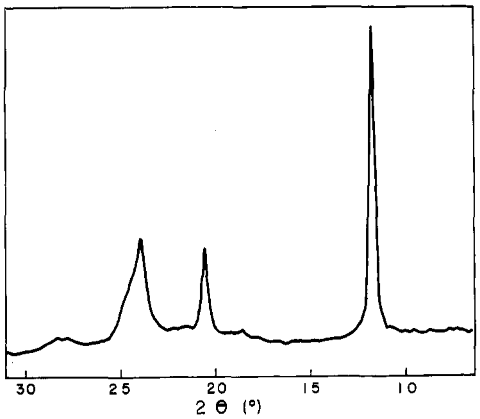


Figure 1. The X-ray diffraction diagram of crystalline polyethylenimine.

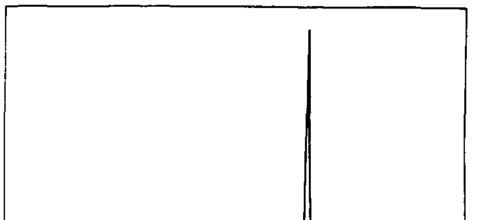


Figure 2. The nmr spectrum of crystalline polyethylenimine ($CDCl_3$).

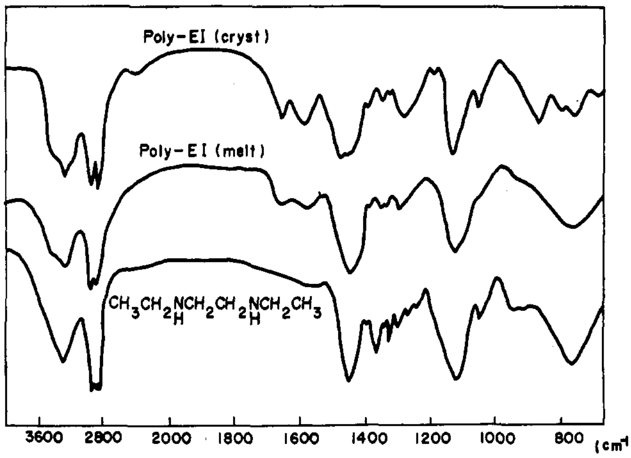


Figure 3. The ir spectra of ethylenimine polymers and *N*,*N*′-diethylethylenediamine (KBr).

The linear structure of poly(EI) prepared by the alkaline hydrolysis of poly(*N*-formylethylenimine) from 2-oxazoline has been supported by nmr (Figure 2) and ir (Figure 3) spectra. In the nmr spectrum of poly(EI) (Figure 2), only two singlets, at δ 2.70 (4 H) and 1.57 ppm (1 H), were observed. The latter peak almost disappeared after D_2O treatment. In Figure 3, the ir spectra of the solid crystalline sample and the melt of poly(EI) are compared with the spectrum of a model compound of *N*,*N*′-diethylethylenediamine. The characteristic bands of the poly(EI) at 3260, 1565, 1470, and 1137 cm^{-1} are ascribed to ν_{NH}, δ_{NH}, δ_{CH_2}, and ν_{C-N} modes, respectively. The bands at 1137, 1045, and 875 cm^{-1} of the solid sample may be assigned to the crystalline bands, since these bands disappear or diminish in the spectrum of the melted sample. The similarity of the spectrum of the melted sample to that of *N*,*N*′-diethylethylenediamine is taken as a support for the linear structure of poly(EI).

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(1) G. D. Jones, A. N. Langsjoen, M. M. C. Neuman, and J. L. Zomlefer, *J. Org. Chem.*, **9**, 125 (1944).

(2) W. G. Barb, *J. Chem. Soc.*, 2564, 2577 (1955).

(3) G. D. Jones, D. C. MacWilliams, and N. A. Braxtor, *J. Org. Chem.*, **30**, 1994 (1965).

(4) C. R. Dick and G. E. Ham, *J. Macromol. Sci., Chem.*, **4**, 1301 (1970).

(5) T. Saegusa, H. Ikeda, and H. Fujii, *Polym. J.*, **3**, No. 1 (1972).