Crystal structure of poly(ethylenimine)–hydrogen chloride complex

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Linear poly(ethylenimine) was found to form a crystalline complex with hydrogen chloride when poly(ethylenimine) in the state of its anhydrate or hydrates was immersed in concentrated hydrochloric acid or exposed to HCl vapour. The crystal structure of the HCl complex was determined by X-ray diffraction. The crystals are metrically tetragonal with cell constants $a=b=5.06$ Å and c (chain axis) $=7.57$ Å and the unit cell includes one planar zigzag polymer chain (two monomeric units) and two HCl molecules (the molar ratio is 1:1). The space group of the crystals is, however, not of the tetragonal system: the structure determined can be expressed in terms of any of the following crystal systems and space groups: orthorhombic $P222_1$, orthorhombic $Pcm2_1$, orthorhombic $Pc2m$, and monoclinic $P2_1/m$ (c unique). The Cl···N distance of 3.05 Å strongly indicates that every NH and HCl hydrogen atom participates in hydrogen bondings between nitrogen and chlorine atoms. The HCl complex has a fairly high melting temperature of 265°C, which is about 200°C higher than those of the anhydrate and hydrates.

(Keywords: X-ray diffraction; crystal structure; complex formation; poly(ethylenimine); hydrogen chloride; hydrogen bonding; d.s.c.)

INTRODUCTION

In previous studies[1-3] the four kinds of crystalline phase of linear poly(ethylenimine) ($-CH_2CH_2NH-$, PEI) have been subjected to X-ray analysis. These crystalline phases are distinct from each other in their 'water of crystallization' content and accordingly their scheme of hydrogen bond network. Of these phases, the anhydrate is characterized by double-stranded helical polymer chains connected by interchain N–H···N hydrogen bond bridges. However, this hygroscopic polymer transforms readily in the atmosphere from the anhydrate into one of or a mixture of the three kinds of hydrate, hemi-, sesqui- and di-hydrate, depending on the humidity and the temperature. In all of the hydrates, disregarding the difference in the scheme of hydrogen bond network, the planar zigzag polymer chains allow every NH group to participate in hydrogen bondings of the type N–H···O and N···H–O with water molecules: in these hydrates no N–H···N hydrogen bonds exist. Electric conductivities of the order of 10^{-8}–10^{-4} S cm^{-1} in these phases were interpreted in terms of 'proton-transport' through the hydrogen bonds[4].

Besides these hydrates, the NH groups in PEI would enable the polymer to form complexes with inorganic and organic compounds. There is much in the literature on complex formation of conventional PEI with a variety of compounds[5]. However, since conventional PEI possesses several types of branches irregularly, these complexes are inherently amorphous and hence no details on their structures have been provided.

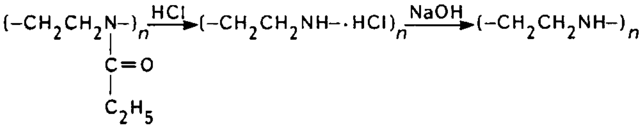
The complex forming ability and electric conductivity of linear PEI–alkali metal salt systems such as NaI[6] and $NaCF_3SO_3$[7] have been investigated. For both salts, the crystalline complexes were found by X-ray diffraction. However, linear PEI has been developed comparatively recently[8,9] and information on this polymer is still scarce compared with other polymers such as polyamides, polyesters and polyethers. This paper presents the crystal structure of a PEI complex with hydrogen chloride and is one of a series of structural studies on linear PEI complexes.

EXPERIMENTAL

Materials

Linear PEI was prepared by hydrolysis of poly(ethyloxazoline) in the presence of hydrochloric acid according to the method of Tanaka *et al.*[10] (*Scheme 1*). Poly(ethyloxazoline) with a weight average molecular weight of 500 000 was supplied by Dow Chemical Japan Ltd.

The PEI–HCl complex was obtained as white precipitates when the reaction mixture was poured into an excess of methanol. The PEI–HCl complex was also obtained by immersing the resulting PEI, irrespective of whether it was in the state of the anhydrate or hydrates, in concentrated hydrochloric acid or by exposing it to HCl vapour from the acid at room temperature. The completion of the conversion from the anhydrate or hydrates to the HCl complex was determined by X-ray diffraction. A day was almost sufficient to complete the conversion. However, the brittle property of the HCl



$$(-CH_2CH_2\underset{\substack{|\\ C=O\\ |\\ C_2H_5}}{N}-)_n \xrightarrow{HCl} (-CH_2CH_2NH\cdot\cdot HCl)_n \xrightarrow{NaOH} (-CH_2CH_2NH-)_n$$

Scheme 1

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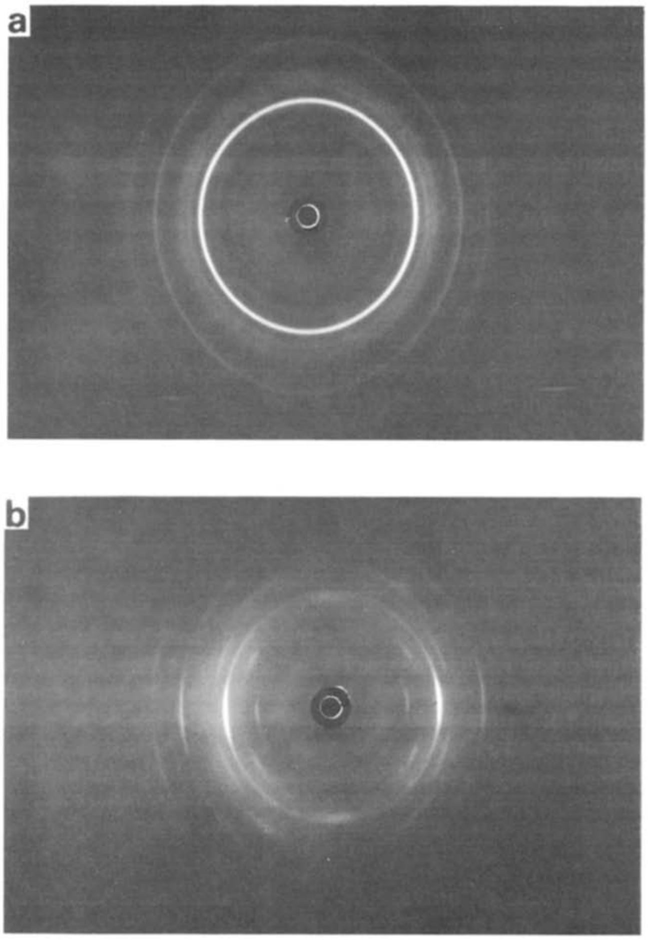

Figure 1 X-ray diffraction photographs of PEI–HCl complex: (a) precipitates; (b) uniaxially oriented specimen obtained by exposing PEI to HCl vapour

complex made it difficult to elongate the unoriented complex. To obtain the oriented specimen, the following treatment was necessary. A PEI specimen was elongated before exposure to HCl vapour. During the exposure, slight loading at the ends of the specimen was needed to keep the orientation, otherwise the original orientation was lost. Even by this method it was difficult to obtain a highly oriented specimen of the complex.

Elementary analyses

Elementary analyses for two specimens thus obtained gave the result that the chemical composition can be expressed in terms of $C_{2.01}H_{5.01}N_{1.00}\cdot 0.98HCl\cdot 0.43H_2O$ and $C_{2.03}H_{5.08}N_{1.00}\cdot 0.99HCl\cdot 0.29H_2O$, respectively.

X-ray measurements

Nickel-filtered copper Kα radiation was used throughout this study. *Figure 1* shows X-ray photographs of the HCl complex obtained as white precipitates and by exposing PEI to HCl vapour. Both diffraction patterns are essentially identical except for the difference in orientation. The *d*-spacings of the reflections were measured with a cylindrical camera of 100 mm diameter and they were corrected with those of NaCl powder. The reflection intensities were measured with a diffractometer for the non-oriented sample (*Figure 2*) and by the multiple-film method for the uniaxially oriented sample. The data from the latter method were used to separate overlapped reflections in the data from the former method. The intensities obtained by the film method were measured visually with a standard intensity scale. Lorentz polarization factors were applied to the observed intensities to obtain the structure factors.

Density measurements

The densities of the samples were determined by a flotation method with the density of the liquid media (carbon tetrachloride + toluene) measured with a pycnometer.

Differential scanning calorimetry measurements

A Rigaku Denki differential scanning calorimeter was employed. Samples were run from room temperature to 300°C at a heating rate of 10°C min^{-1}.

STRUCTURE ANALYSIS

All the observed reflections were indexed on a metrically tetragonal cell with cell constants of $a = b = 5.06$ Å and c (chain axis) = 7.57 Å. The observed fibre repeat of 7.57 Å was straightforwardly interpreted in terms of the planar zigzag conformation of PEI chains, in which the fibre repeat comprises two monomeric units, as in the PEI hydrates[1,3]. The average observed density of 1.32 g cm^{-3} was explained well when one polymer chain (two monomeric units) and two HCl molecules were included in the unit cell (the calculated density is 1.36 g cm^{-3}). The molar ratio EI/HCl of 1:1 based on this assumption is again in accord with the result of the elementary analyses. On the other hand, the variation in water content from sample to sample was attributed to the difference in the water content in the amorphous region.

No systematic absences of reflections were found, except for disappearance of the 001 and 003 reflections, which is indicative of the planar zigzag conformation of the PEI chains. Although the unit cell is metrically tetragonal, no appropriate space groups of the tetragonal system were found for the unit cell which includes only one polymer chain. Therefore the space group was thought to be of the orthorhombic or monoclinic system. On the basis of a geometrical consideration according to the equivalent postulate[11,12], together with structure factor calculations, the structural model was determined with reasonable certainty by trial and error. This

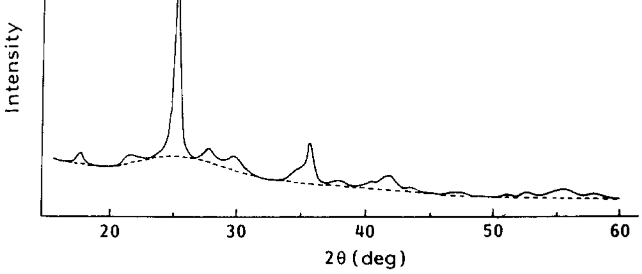

Figure 2 X-ray diffraction curve of PEI–HCl complex (precipitates)

Table 1 Fractional atomic coordinates and thermal parameters

	x	y	z	B(Å^2)
Cl	0.089	0.000	0.250	8.3
C[a]	0.579	0.500	0.085	8.2
N	0.425	0.500	0.250	8.3
H	0.698	0.323	0.085	8.1
H	0.698	0.677	0.085	8.1

[a] The coordinates of another carbon atom are $(-x,\ -y,\ -z)$

Table 2 Observed (F_o) and calculated (F_c) structure factors[a]

hkl	$\lvert F_o\rvert$	$\lvert F_c\rvert$
100, 010	6.6	4.8
110	46.7	42.8
200, 020	32.0	25.6
210, 120	–	0.9
220	10.1	10.4
300, 030	–	1.7
310, 130	12.0	13.0
320, 230	–	1.5
400, 040	6.1	6.2
101	6.8	8.4
111	11.9	12.1
201	10.5	10.4
211, 121	20.0	15.9
221	8.9	8.1
301	6.2	6.7
311, 131	7.1	8.1
321, 231	7.8	8.1
002	14.7	17.3
102, 012	17.8	18.4
112	16.4	16.7
202, 022	8.8	12.2
212, 122	11.5	9.9
222	–	4.0
302, 032	–	4.8
312, 132	5.6	6.3
322, 232	–	2.2
103	15.2	12.0
113	–	0.4
203	–	0.6
213, 123	16.6	17.2
223	–	1.6
303	8.0	7.4
313, 133	–	1.7
323, 233	10.2	9.5

[a] These values are reduced to those for the fibre photograph. $|F(hkl)| = |F(\bar{h}kl)|$

structural model could be expressed in terms of any of the following space groups: orthorhombic $P222_1$, orthorhombic $Pcm2_1$, orthorhombic $Pc2m$, and monoclinic $P2_1/m$ (c unique). In each space group, which has four equivalent points, the two Cl and two N atoms in the unit cell must occupy special positions (e.g. Cl: $x, 0, 1/4$; $\bar{x}, 0, 3/4$, and N: $x, 1/2, 1/4$; $\bar{x}, 1/2, 3/4$). The structural model was then refined by the least-squares method by assuming the space group $P2_1/m$, where the y-coordinates of the main chain atoms were fixed to 1/2. (Other space groups examined must give the same result when the variable parameters are similarly subjected to restrictions obeying the equivalent postulate.) The CH_2 hydrogen atoms were disposed at the tetrahedral positions about the C atom. The NH and HCl hydrogen atoms were ignored in the structure factor calculation. The final discrepancy factor $R\ (=\sum |I_o^{1/2} - I_c^{1/2}|/\sum I_o^{1/2})$ was 11.4% for all the observed reflections. *Table 1* shows the fractional atomic coordinates and thermal parameters. The observed and calculated structure factors are listed in *Table 2*. The crystal structure is shown in *Figure 3*.

RESULTS AND DISCUSSION

The present study revealed that PEI forms a crystalline complex with hydrogen chloride with a stoichiometric molar ratio (EI/HCl) of 1:1. Although the X-ray diffraction patterns did not provide an unequivocal solution of the problem of the crystal system and space group, a situation which we have often encountered with polymer crystals, the structure obtained can be expressed in terms of any of the following space groups: orthorhombic $P222_1$, orthorhombic $Pcm2_1$, orthorhombic $Pc2m$, and monoclinic $P2_1/m$ (c unique). The PEI chains take essentially the planar zigzag conformation, as in the PEI hydrates. The dimensions of the PEI chains are as follows: C–C = 1.53, C–N = 1.47 Å, C–C–N = C–N–C = 116°. These values are not unusual.

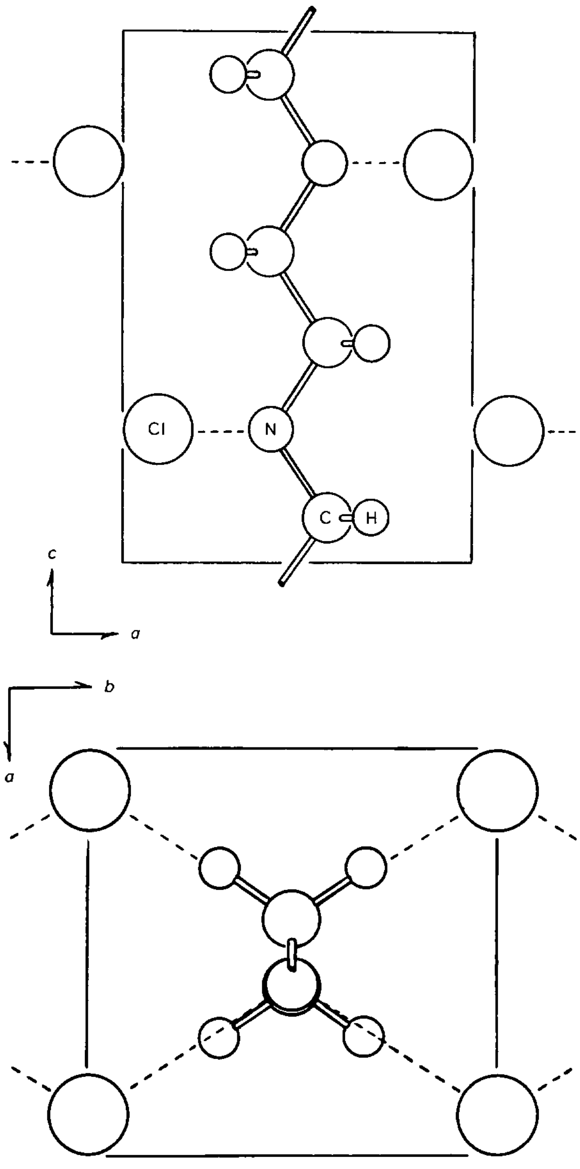

Figure 3 Crystal structure of PEI–HCl complex. Broken lines indicate hydrogen bonds

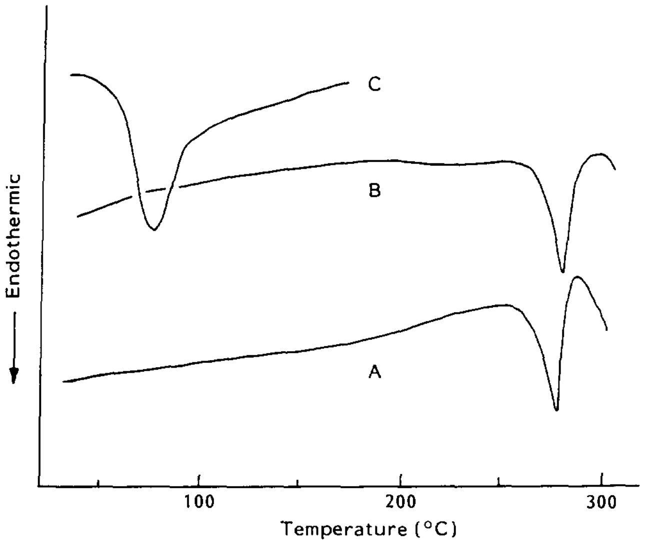

Figure 4 D.s.c. traces of: A, PEI–HCl complex (precipitates); B, PEI–HCl complex obtained by exposing PEI to HCl vapour; C, PEI hemihydrate

The N···Cl distance of 3.05 Å clearly indicates the formation of strong hydrogen bonds between NH and HCl. Hydrogen bonds are generally directional, i.e. X–H···Y atoms tend to lie in line. The result of this study does not allow us to discuss the bond nature of the HCl (ionic or covalent). However, the crystal structure enables the N–H···Cl atoms to lie in line when the NH hydrogen atom is disposed tetrahedrally about N, where the NH hydrogen atom and hence the HCl hydrogen atom can be disposed statistically on the two hydrogen bonds from each N and Cl atom, which are shown by broken lines in *Figure 3*. The hydrogen bonds connect NH and HCl alternately along the *b*-axis so as to enable every HCl and NH group to participate in the hydrogen bondings. The Cl···C and Cl···Cl distances of 3.86 and 3.89 Å, respectively, are again normal.

The crystal lattice does not possess enough large open spaces to accommodate water molecules as 'lattice water'. Therefore, water included in the samples examined may be only in the amorphous regions, although the possibility that a small amount of 'water of crystallization' in the original samples remains unchanged is not always denied.

As already described, in the PEI anhydrate the N–H···N hydrogen bonds, which themselves are relatively weak compared with N–H···O and O–H···O hydrogen bonds, are spent to form the double-stranded helices and the association of these helices is due to rather weak van der Waals interactions. The melting temperature of the anhydrate is therefore rather low (58°C). In the PEI hydrates, the hydrogen bond networks (N–H···O and N···H–O in the hemihydrate and N–H···O, N···H–O and O–H···O in the sesquihydrate and dihydrate) are formed. These hydrates melt at higher temperatures (about 80°C). The HCl complex exhibits an outstandingly high melting temperature of 265°C, as shown in *Figure 4*, in which the onset of decomposition of PEI is also seen at about 290°C. As already mentioned, water in the hydrates is replaced readily by HCl. This feature indicates strong interactions between the NH groups and HCl molecules. In practice, once the HCl complex is formed, the complex is stable for a long time in air.

Other inorganic and organic acids have also been found to form crystalline complexes with PEI. Structural studies on these complexes are now in progress.

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