

Crystal structure of poly(ethylenimine)–acetic acid complex

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Linear poly(ethylenimine) was found to form a highly crystalline complex with acetic acid with a molar ratio of 1:1, $(-\text{CH}_2\text{CH}_2\text{NH}-\text{CH}_3\text{COOH})_n$, when the polymer, irrespective of whether it was in the state of its anhydrate or hydrates, was exposed to acetic acid vapour. The crystal structure of the complex was determined by X-ray diffraction. The crystal system is monoclinic with cell constants $a = 5.76 \text{ \AA}^*$, $b = 6.20 \text{ \AA}$, $c(\text{chain axis}) = 7.39 \text{ \AA}$ and $\gamma = 95^\circ$ (c -unique), and the space group is $P2_1/m$. The unit cell contains two monomeric units (one chain) and two acetic acid molecules. The polymer chains are essentially planar zigzag, the fibre repeat comprising two monomeric units. Planar acetic acid molecules are stacked horizontally along the polymer chain axis at the levels of the two polymer nitrogen atoms. Hydrogen bonds of the types $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{N}$ link the polymer chain and the acetic acid molecule alternately to form an infinite chain structure at the two levels; the scheme of the hydrogen bondings is similar to that in acetic acid crystals. The melting temperature of the complex is $\approx 135^\circ\text{C}$, which is higher than those of the polymer hydrates by about 55°C .

(Keywords: poly(ethylenimine); acetic acid; poly(ethylenimine)–acetic acid complex; crystal structure; hydrogen bondings; X-ray diffraction; d.s.c.)

INTRODUCTION

Linear poly(ethylenimine) ($-\text{CH}_2\text{CH}_2\text{NH}-$, PEI) is usually in the state of its hemihydrate¹, sesquihydrate² or dihydrate² in the atmosphere depending on the temperature and the humidity because of its remarkably hygroscopic nature. Although these hydrates are distinct from one another in their 'water of crystallization' content and molecular packing, infinite hydrogen bond networks which link PEI chains and water molecules stabilize the crystal lattices of these hydrates: the melting temperatures of these hydrates ($80\text{--}85^\circ\text{C}$) are higher than that of the anhydrate (55°C), in which all $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds are spent to form double-stranded helices of the polymer chains³. Besides these hydrates, PEI has a good potential for complex formation with a variety of compounds. In practice X-ray studies on the PEI–NaI system by Davis *et al.*⁴ and the PEI– NaCF_3SO_3 system by Shriver *et al.*⁵ in connection with their ionic conductivity measurements revealed the presence of a crystalline complex. The complex formation in both systems may be ascribed to coordination bondings between the polymer nitrogen atoms and the cations, though no crystal structure has been proposed for these systems. In a previous paper⁶, the complex formation of PEI with an inorganic acid, HCl, and the crystal structure of the HCl complex were reported. In that case, hydrogen bonding between the polymer and the acid does play a role in the complex formation. In this paper, complex formation of PEI with an organic acid, CH_3COOH , and the crystal structure of the CH_3COOH complex will be reported.

EXPERIMENTAL

Linear PEI was prepared by hydrolysis of poly(ethyl-oxazoline) ($M_w = 500\,000$) supplied by Dow Chemical Japan Ltd. The method of preparation of PEI has been described previously⁶.

PEI anhydrate or hydrates were converted into crystalline PEI– CH_3COOH complex when they were exposed to vapour from liquid acetic acid or from a mixture of acetic acid and carbon tetrachloride at room temperature. Although the process of the conversion varied depending on the crystal form of the original PEI specimen, the temperature and the humidity, two or three days were sufficient to obtain the highly crystalline CH_3COOH complex; completion of the conversion was checked by disappearance of the X-ray diffraction pattern of any PEI crystal form.

PEI– CH_3COOH complex was also obtained when PEI was cast from acetic acid solutions. If PEI crystals coexisted in the specimen thus obtained, the specimen was exposed to acetic acid vapour. No polymorphism was observed for the PEI– CH_3COOH system, irrespective of the preparation methods and conditions. However, the brittle property of the complex made it difficult to elongate the unoriented specimens. Therefore, a uniaxially oriented specimen indispensable to the X-ray structure analysis was prepared by using the same technique as for the PEI–HCl complex⁶.

X-ray measurements

Nickel-filtered copper $K\alpha$ radiation was used throughout this study. Figure 1 shows an X-ray fibre photograph of the CH_3COOH complex obtained by exposing PEI to CH_3COOH vapour. The d -spacings of the reflections

* $1 \text{ \AA} = 10^{-1} \text{ nm}$

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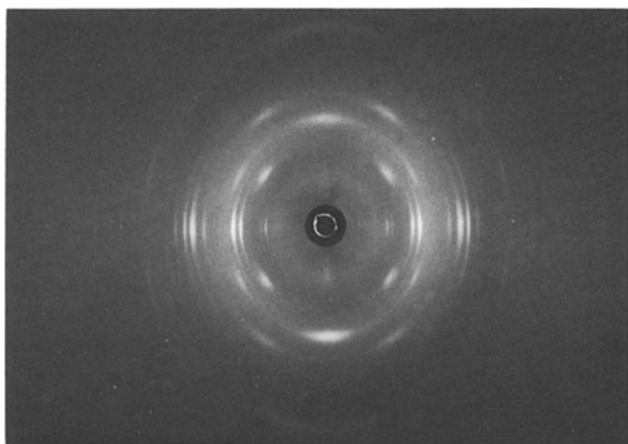


Figure 1 X-ray fibre photograph of PEI-CH₃COOH complex

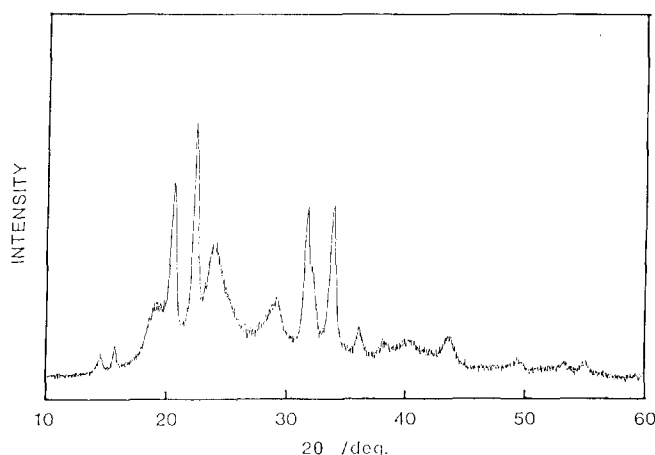


Figure 2 X-ray diffraction curve of PEI-CH₃COOH complex

were measured with a cylindrical camera of 100 mm diameter and corrected with those of NaCl powder. The reflection intensities were obtained by the multiple film method for the uniaxially oriented specimen, and measured visually with a standard intensity scale. The reflection intensities from the non-oriented cast-film were obtained with a diffractometer (Figure 2). Both data were corrected by individual Lorentz-polarization factors to obtain the structure factors.

Density measurements

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

Differential scanning calorimetry measurements

A Rigaku Denki differential scanning calorimeter was employed. The samples were run from room temperature to 200°C at a heating rate of 10°C min⁻¹.

STRUCTURE ANALYSIS

All the observed reflections could be indexed unequivocally in terms of a monoclinic cell with comparatively small cell constants $a = 5.76$, $b = 6.20$, c (chain axis) = 7.39 Å and $\gamma = 95^\circ$ (c -unique). The observed fibre period of 7.39 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 PEI hydrates and PEI-HCl complex. Therefore, the unit cell must contain at least two monomeric units (one chain). If the unit cell contains two monomeric units and two CH₃COOH molecules (the molar ratio is 1:1), the crystal density is calculated to be 1.30 g cm⁻³, while if it contains two monomeric units and one CH₃COOH molecule the density is calculated to be 0.92 g cm⁻³. The molar ratio 1:1 appears to be reasonable compared with the observed density of 1.22 g cm⁻³.

No systematic absences of reflections were found, except for disappearance of the meridional 001 and 003 reflections, which was confirmed by a Weissenberg photograph taken by oscillating the uniaxially oriented specimen around the vertical direction to the chain axis. The space group was therefore determined to be either P2₁ or P2₁/m, the number of general equivalent points being two or four, respectively.

The extremely strong 002 reflection definitely suggests that the CH₃COOH molecules are stacked horizontally along the polymer chain axis at an interval of $c/2$. An approximate structure model, in which the chain axis coincides with a twofold screw axis of the unit cell and the main chain plane of PEI is almost parallel to the b -axis (the setting angle is nearly 0°), was obtained by trial and error and was refined by the diagonal least squares method under an assumption of P2₁/m. In this case, all the acetic acid atoms and the nitrogen atoms of PEI were disposed in special positions in mirror planes at $z = \frac{1}{4}$ and $\frac{3}{4}$. The NH and CH₃COOH hydrogen atoms were ignored in the structure factor calculation, but the CH₂ hydrogen atoms of PEI were included in the final stage by assuming the normal bond length and the bond angle. The discrepancy factor R dropped to 13.6% for all the observed reflections ($R = \sum |I_o^{1/2} - I_c^{1/2}| / \sum I_o^{1/2}$, where $I = \sum mF^2$, m being the multiplicity of a reflection superimposed on one diffraction spot in the fibre photograph).

Another model, in which the main chain plane of PEI is almost parallel to the a -axis (the setting angle is nearly 90°) and the space group is again P2₁/m, was also examined by the same procedure. The R factor, however, did not drop below 22%.

The third model, in which the setting angle is the same as in the first model and the CH₃COOH molecular plane is not horizontal to the chain axis, was examined for both P2₁ and P2₁/m. In the latter space group, the model must be a statistical structure with respect to the orientation of the CH₃COOH molecular plane. The R -factors for both models never dropped below that for the first model.

Therefore, the first model was concluded to be the structure of PEI-CH₃COOH complex. The fractional atomic coordinates and thermal parameters are listed in Table 1. The observed and calculated structure factors are shown in Table 2. The crystal structure is shown in Figure 3.

RESULTS AND DISCUSSION

Stoichiometry of PEI-CH₃COOH complex

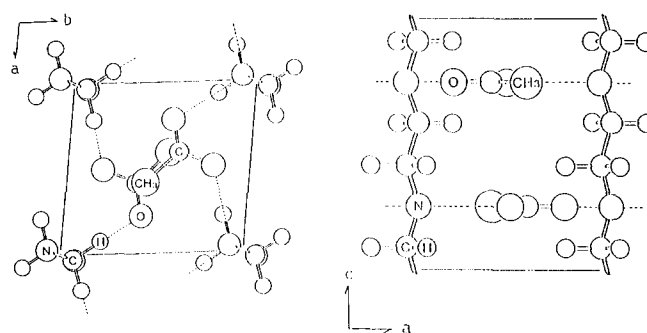
This study revealed that the crystalline complex in the PEI-CH₃COOH system is a stoichiometric compound with a molar ratio of 1:1. This molar ratio is, as shown later, surely one of the proper molar ratios which satisfy the condition that every hydrogen atom of NH groups

Table 1 Fractional atomic coordinates and thermal parameters

	Weight in structure factor	x	y	z	B(Å ²)
C ^a	1.0	-0.044	-0.058	0.088	8.7
N ^a	0.5	0.018	0.067	0.250	8.7
O(1) ^b	0.5	0.505	0.178	0.250	8.4
O(2) ^b	0.5	0.785	0.430	0.250	8.6
C ^b	0.5	0.571	0.383	0.250	8.7
C ^b	0.5	0.400	0.561	0.250	8.2
H of CH ₂ ^a	1.0	-0.208	-0.133	0.088	8.2
H of CH ₂ ^a	1.0	0.095	-0.206	0.088	8.2

^a PEI^b CH₃COOH**Table 2** Observed (F_o) and calculated (F_c) structure factors^a

hkl	F_o	F_c
010	6.9	9.6
100	5.3	6.5
$\bar{1}10$	26.5	23.8
110	30.2	36.6
020	18.4	19.2
200	23.0	23.9
$\bar{1}20$	25.1	30.9
$\bar{2}10, 120$	25.4	27.3
210	16.6	14.3
$\bar{2}20$	-	2.1
030	-	3.4
220	-	1.1
$\bar{1}30$	-	2.9
300	-	0.6
130, $\bar{3}10$	10.2	13.9
$\bar{2}30, 310$	8.9	9.4
$\bar{3}20$	12.9	9.7
230, $\bar{3}20$	7.4	4.7
040	-	3.2
$\bar{1}40$	7.7	7.9
$\bar{3}30$	-	6.6
140	-	2.9
400, $\bar{2}40, \bar{4}10$	10.3	9.2
011	18.7	18.5
101	15.9	13.4
$\bar{1}11$	17.8	18.5
111	-	5.1
021	-	1.6
201	-	5.3
$\bar{1}21$	-	1.6
$\bar{2}11$	-	3.4
211, $\bar{1}21$	11.9	13.1
$\bar{2}21$	18.3	15.0
031	-	4.8
221	-	3.4
$\bar{1}31$	-	3.9
301	-	3.0
131	-	2.9
$\bar{3}11$	-	0.4
311	15.0	9.1
002	38.5	39.2
102, 012	19.4	23.4
$\bar{1}12$	-	3.0
112	9.9	11.5
022	-	5.4
202, $\bar{1}22$	12.1	13.7
103, 013	19.0	18.4
113	9.7	6.8
023	6.3	7.8
203	-	1.4
$\bar{1}23$	-	3.3
$\bar{2}13$	-	0.2
123	-	3.2
213	7.0	11.9
223, $\bar{1}33, 033$	12.3	13.1

^a Values reduced to those for the fibre photograph**Figure 3** Crystal structure of PEI-CH₃COOH complex. ---, Hydrogen bonds

and of COOH groups of the acid is able to participate in hydrogen bonding. As for the PEI-CH₃COOH system, no other crystalline forms were found throughout this study.

Molecular dimensions

The PEI chains are essentially planar zigzag, as in PEI hydrates and PEI-HCl complex. The bond lengths and bond angles are as follows: C-C = 1.55 Å, C-N = 1.46 Å, C-N-C = 110.7°, N-C-C = 112.6° for PEI; C-C = 1.54 Å, C-O(1) = 1.29 Å, C-O(2) = 1.24 Å, C-C-O(1) = 123.6°, C-C-O(2) = 121.1° for CH₃COOH. These values are not unusual.

Hydrogen bonds

Hydrogen bonded N...O distances found so far for many low molecular weight compounds range between 2.73 and 3.22 Å and are averaged as 2.88 Å (Reference 7). In addition, hydrogen bonds are generally directional, i.e. X-H...Y atoms tend to lie in line. Since the scattering power of hydrogen for X-rays is extremely low, no direct X-ray evidence was obtained regarding the NH and COOH hydrogen positions. However, the N...O distances of 2.72 and 2.83 Å found in PEI-CH₃COOH complex obviously indicate formation of hydrogen bonds between the PEI chain and the acid: the crystal structure enables the N-H...O and O-H...N atoms to lie in line when the NH hydrogen atoms are disposed tetrahedrally about N. The hydrogen bonds are shown by broken lines in Figure 3.

The modes of the molecular packings in fatty acid crystals are classified, in terms of the scheme of hydrogen bonding, into dimer-type and chain-type; formic acid⁸ and acetic acid⁹ belong to the latter type. Again, in PEI-CH₃COOH complex, the infinite hydrogen bond chains do lie in planes at $z = \frac{1}{4}$ and $\frac{3}{4}$ with an interval of 3.70 Å. Similarity between the chain structure of the hydrogen bonds in acetic acid and that in the complex can be seen in Figure 4.

The hydrogen bonds between the PEI chain and the acetic acid molecule surely govern the crystal structure of the complex, but they do not bring about an open structure like ice, i.e. other intermolecular (van der Waals) distances are also not unusual: the closest intermolecular distances are 3.83 Å for C(PEI)...C(CH₃), 3.31 Å for C(PEI)...O and 3.71 Å for C(COO)...C(CH₃).

Melting temperature

The differential scanning calorimetry curve for the

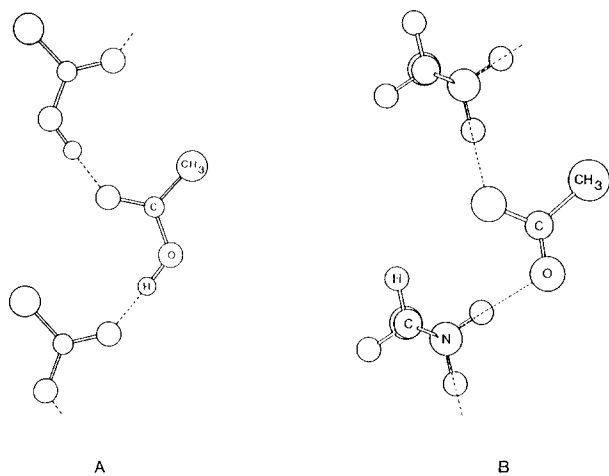


Figure 4 Schemes of hydrogen bondings in: (A) CH_3COOH crystal; (B) PEI- CH_3COOH complex

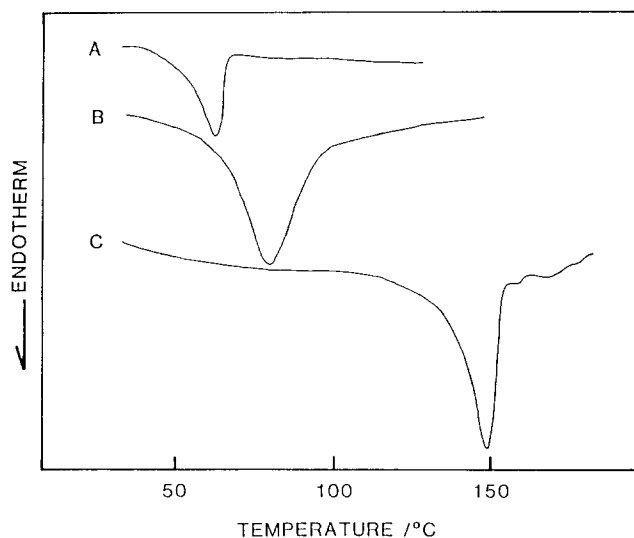


Figure 5 D.s.c. curves of: A, PEI anhydrate; B, PEI hemihydrate; C, PEI- CH_3COOH complex

CH_3COOH complex (Figure 5, curve C) indicates that the melting temperature of the complex is $\approx 135^\circ\text{C}$, which is higher than the melting temperatures of PEI hydrates by $\approx 55^\circ\text{C}$, although it is considerably lower than that of PEI-HCl complex (265°C).

Other PEI complexes

Except for PEI anhydrate, all PEI hydrates, PEI-HCl and PEI- CH_3COOH complexes examined so far comprise zigzag planar PEI chains with the guest molecules linked to the PEI chains by hydrogen bonds. However, preliminary studies on other PEI complexes, for example with HBr and HCOOH, revealed that these systems exhibit polymorphism and, unlike the above complexes, the PEI chains do not take the planar zigzag conformation. Structural studies on these systems are now in progress.

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