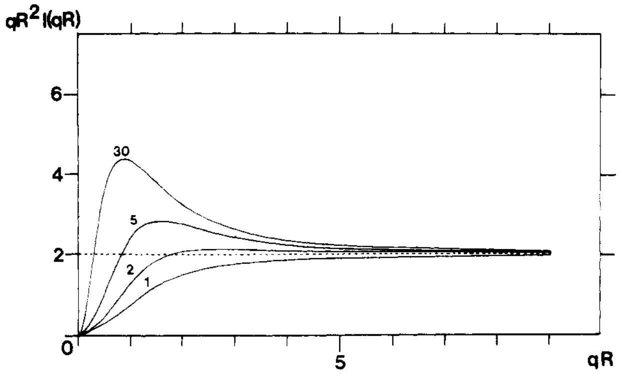

Figure 10. Theoretical Kratky plots computed from relations 17 and 18. The numbers correspond to the clustering number, N_c.

peaks in this kind of cluster using a Kratky representation (Figure 10). Such a result means that in the peak region, when $q^2I(q)$ decreases, exponents higher than $p = 2$ are found. Furthermore, this calculation may be applied to clusters made of rodlike structures by considering the form factor of rod instead of $P_G(q)$. From the above relations, it is obvious that exponents higher than $p = 1$ will be obtained, which corresponds to some results presented in this paper.

A more realistic approach would consist of taking into account a lack of inhomogeneity in the sample. Then $I(q)$ can be expressed

$$I(q) = C^{te}C_DN_{c,w}M_w\int P_{N_c}{}^{c}(q)f(N_c)\,dN_c$$

where $N_{c,w}$ is the weight-average number of chains in the cluster and $f(N_c)$ the distribution function of N_c. However, such an improvement of the model would not change the character of the scattering function described above.

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Structural Studies of Poly(ethylenimine). 1. Structures of Two Hydrates of Poly(ethylenimine): Sesquihydrate and Dihydrate

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ABSTRACT: X-ray structure analysis confirmed that the hygroscopic nature of crystalline linear poly(ethylenimine) is attributable to the formation of crystalline hydrates. There are two distinct hydrates in which "water of crystallization" exists stoichiometrically. One is a hydrate with a mole ratio of ethylenimine unit to water of 1/1.5, i.e., sesquihydrate. The crystals of the sesquihydrate are monoclinic with a = 11.55 Å, b = 9.93 Å, c (fiber axis) = 7.36 Å, and β = 104.5°. The space group is $C2/c$, and the unit cell contains 8 monomeric units and 12 water molecules. The other is a dihydrate; i.e., the mole ratio is 1/2. The crystals of the dihydrate are again monoclinic $C2/c$ with a = 13.26 Å, b = 4.61 Å, c (fiber axis) = 7.36 Å, and β = 101.0°. The unit cell contains 4 monomeric units and 8 water molecules. The theoretical value of water content of the crystal lattice is 38.6 wt % for the sesquihydrate and 45.6 wt % for the dihydrate. The polymer chains are planar zigzag in both hydrates, and the crystals of both hydrates consist of an alternating stack of a layer of polymer chains and a layer of water molecules arranged parallel to the bc plane. In particular, the water network in the dihydrate is the same as that of ordinary ice. Hydrogen bonds of the types N–H···O, O–H···O, and O–H···N play a major role in the stabilization of the crystal lattices. Irrespective of the difference in mole ratio between the two hydrates, all of the NH hydrogen atoms and H_2O hydrogen atoms in both hydrates are able to participate in hydrogen bondings, but an irregularity with respect to the disposition of these hydrogen atoms is proposed. The sesquihydrate transforms into the dihydrate on further absorption of water, retaining the uniaxial orientation, and this feature is explainable in terms of the structures of both hydrates.

Much literature in the industrial, agricultural, and biological fields has appeared for poly(ethylenimine) (PEI) and related compounds. Conventional PEI obtained from ethylenimine (EI) (PEI I) is amorphous because many branches along the polymer chain suppress crystallization.[1-5] In contrast, PEI obtained from 2-oxazoline (PEI II) is highly crystalline owing to its linear structure.[6] However, linear PEI has two characteristics which have

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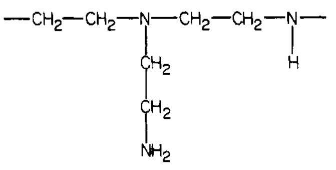
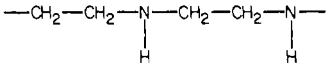


$$-CH_2-CH_2-\underset{\underset{\underset{NH_2}{|}}{\underset{CH_2}{|}}}{\underset{CH_2}{\underset{|}{N}}}-CH_2-CH_2-\underset{\underset{H}{|}}{N}-$$

I



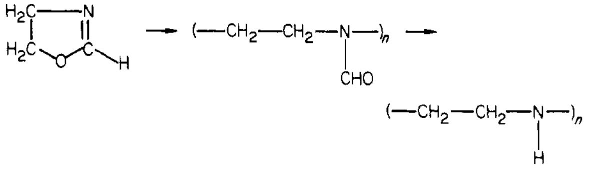
$$-CH_2-CH_2-\underset{\underset{H}{|}}{N}-CH_2-CH_2-\underset{\underset{H}{|}}{N}-$$

II

hindered its structural analysis: (1) linear PEI is characterized by a low molecular weight and (2) it is hygroscopic. The first feature has made it difficult to prepare a uniaxially oriented specimen, and the second feature has presented the problem of whether water is absorbed by the polymer in the amorphous part, the crystalline part, or both. We have not yet succeeded in obtaining a uniaxially oriented specimen, indispensable for X-ray structure analysis of the anhydrous crystalline phase. However, we have obtained some information on the hydration of this polymer. We reported previously the crystalline hydrate of poly(oxacyclobutane), in which the water/monomeric unit mole ratio is 1/1.[7] As for PEI, we found two distinct crystalline hydrates with EI/H_2O mole ratios of 1/1.5, i.e., sesquihydrate, and 1/2, i.e., dihydrate. So far as we are aware, this is the first case of a synthetic polymer for which structures of such crystalline hydrates could be revealed. This paper is concerned with the crystal structures of the two hydrates of PEI and, in particular, with the modes of hydrogen bonding in the two hydrates.

Experimental Section

PEI used in this study was prepared from 2-oxazoline through the alkaline hydrolysis of poly(*N*-formylethylenimine) (reaction 1).[6] The molecular weight of this PEI is about 3000, and the



(1)

NMR spectrum indicates no sign of branching for this polymer. This PEI is remarkably hygroscopic. When a linear PEI sample which had absorbed any amount of water was heated to dryness at 100 °C (above the melting temperature) in vacuo and cooled, the highly crystalline anhydrous phase could indeed be obtained in the unoriented state. However, a uniaxially oriented specimen of the anhydrate has not yet been obtained from the unoriented sample on stretching or rolling, mainly due to the low molecular weight. In addition, successive X-ray diffraction patterns taken for the unoriented anhydrate specimen changed rapidly due to the absorption of moisture in atmospheric air. Consequently, a variety of X-ray diffraction patterns and infrared spectra were obtained, depending on the amount of water absorbed. This implies that there exist multiple crystalline phases. From the many X-ray diffraction patterns, two crystalline phases besides the anhydrate could be discriminated. These two phases will be denoted as phase A and phase B. In order to prepare uniaxially oriented specimens of pure phase A and pure phase B, we expended some efforts. Although it will be necessary to perform an experiment on the dehydration isotherm in order to reveal the detailed nature of the phase change, we report here the methods used for the preparation of uniaxially oriented specimens of phase A and phase B. First, a powdery PEI sample which had already absorbed moisture, exhibiting the X-ray diffraction pattern of phase A (not always necessary to be pure phase A), is melted at 90 °C in atmospheric air to prepare a uniform sheet specimen of 0.8-mm thickness. A uniaxially oriented specimen of phase A is made of such a sheet by rolling along one direction and, if necessary, is allowed to stand for a few hours in a vessel of relative humidity 100% at 18 °C in order to convert it to pure phase A. On being held for 1 day above 20 °C in a vessel of relative humidity 100%, the phase A specimen transforms into phase B, retaining the uniaxial orientation. These procedures are, however, not always reproducible. Each specimen was then checked by X-ray diffraction.

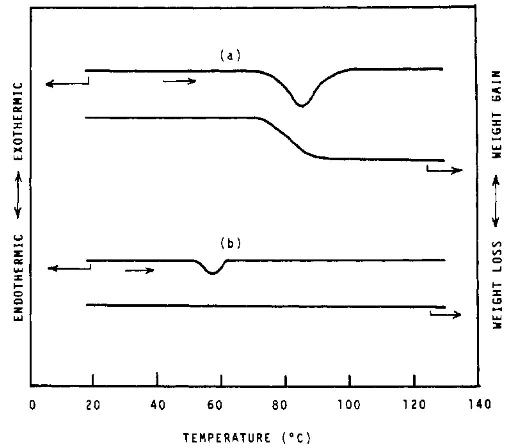


Figure 1. Thermogravimetric diagrams of phase B: (a) first run; (b) second run.

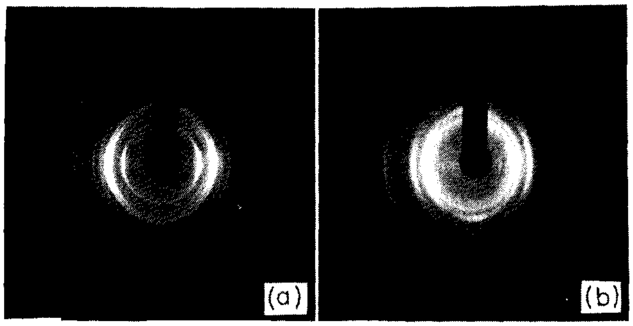


Figure 2. X-ray fiber patterns of two crystalline hydrates of PEI: (a) 1.5-hydrate (phase A); (b) 2-hydrate (phase B).

Figure 1 shows thermogravimetric diagrams for a sample identified by X-ray diffraction as phase B. This sample exhibited a somewhat broad endothermic peak at 83 °C, being accompanied by 45% weight loss due to dehydration; in this experiment a sample pan with a cover having pinholes was used in order to allow dehydration. The second run, taken soon after cooling, exhibited only one endothermic peak at 53 °C, which corresponds to the melting temperature of the anhydrate. In the second run, no additional weight loss was observed. Similarly phase A exhibited about 40% weight loss by dehydration.

These facts strongly indicate that phase A and phase B both are hydrates. Figure 2 shows the X-ray fiber patterns of phases A and B. Although the uniaxial orientation is insufficient, these photographs enabled us to assign each reflection to a certain layer line. As will be confirmed later, phase A is the sesquihydrate, and phase B is the dihydrate. Hereafter phase A and phase B will be denoted as 1.5-hydrate and 2-hydrate, respectively.

The X-ray reflection intensities for such oriented specimens of 0.5-mm width and 0.25-mm thickness were obtained with nickel-filtered copper Kα radiation by the multiple-film method, and the intensities were measured by visual comparison with a standard intensity scale. The reflection intensities for the powder samples were also measured with a diffractometer.

Determination of the Structures of the Two Hydrates

Phase A and phase B both crystallize into the monoclinic system: the cell constants are listed in Table I. The space group was determined from the systematic absences of reflections for both phases (hkl, $h + k = 2n + 1$; $h0l$, $h = 2n + 1$ and $l = 2n + 1$; $0k0$, $k = 2n + 1$) as either $C2/c$ or

Table I
Crystal Data of Two PEI Hydrates

	phase A 1.5-hydrate	phase B 2-hydrate
crystal system	monoclinic	monoclinic
space group	$C2/c$ (C_{2h}^6)	$C2/c$ (C_{2h}^6)
a, Å	11.55	13.26
b, Å	9.93	4.61
c,[a] Å	7.36	7.36
β, deg	104.5	101.0
no. of molecules per unit cell		
-CH_2CH_2NH- unit	8	4
H_2O	12	8
wt % of H_2O in hydrate	38.6	45.5
density, g/cm^3		
obsd	1.13	1.16
calcd	1.14	1.18

[a] Polymer chain axis.

Table II
Plausible Models for Two PEI Hydrates

no. of molecules per unit cell	density, g/cm^3	wt % H_2O
Phase A		
8 EI, 10 H_2O	1.06	34.3
8 EI, 12 H_2O	1.14	38.6
8 EI, 14 H_2O	1.21	42.3
Phase B		
4 EI, 6 H_2O	1.05	38.6
4 EI, 8 H_2O	1.19	45.6
4 EI, 10 H_2O	1.32	51.1

Cc; the former was established finally.

From the observed fiber period of 7.36 Å together with the relatively intense third layer line for both hydrates, the PEI chain could be unequivocally assumed to be zigzag planar; i.e., the structural repeating unit consists of two monomeric units, ignoring the regularity with respect to the disposition of NH hydrogen atoms along with the polymer chain (this problem will be examined later).

To set up the crystal models of phase A and phase B, the following points were taken into account.

(1) The polymer chain is planar zigzag.

(2) If the two phases A and B are hydrates, the NH groups and water molecules must participate in as many hydrogen bondings as possible.

(3) The water content over the whole sample is no indication of the water content of the crystalline part. However, both phase A and phase B are so highly crystalline that there is only faint, if any, X-ray scattering by the amorphous part. Therefore the discrepancy between the observed water content over the whole sample and the water content of the crystalline part does not appear to be great.

(4) The unit cell of the *C*-centered lattice, *C*2/*c* or *Cc*, must contain a certain even number of polymer chains and water molecules.

First, taking into account the *ab* cross section of the unit cell together with the cross section of the planar zigzag PEI chain, we expect that the unit cell contains 4 polymer chains (or 8 monomeric units) in phase A while 2 chains (or 4 monomeric units) in phase B. Next, considering the observed density and water content, we choose the number of water molecules per unit cell from a few restricted even numbers. The plausible models are listed in Table II. Among them the model of 8 monomeric units and 12 water molecules per unit cell of phase A (1.5-hydrate) gives the reasonable density of 1.14 g/cm^3 and water content of 38.6 wt % as compared with the observed values of 1.13 g/cm^3 and about 40 wt %, respectively. Similarly, assuming 4 monomeric units and 8 water molecules per unit cell of

Table III
Atomic Coordinates and Thermal Parameters of Two PEI Hydrates

atom	Wycoff notation	weight in structure factor	x/a	y/b	z/c	B, Å^2
			(a) 1.5-Hydrate			
C	f	1.0	0.210	−0.044	0.163	4.0
C	f	1.0	0.210	−0.044	0.491	4.0
N	f	1.0	0.210	0.041	0.327	4.0
O(1)[a]	f	1.0	0.036	0.374	0.577	4.0
O(3)[a]	e	0.5	0.000	0.218	0.250	4.0
H of CH_2	f	1.0	0.290	−0.107	0.194	5.0
H of CH_2	f	1.0	0.290	−0.107	0.522	5.0
H of CH_2	f	1.0	0.130	−0.107	0.132	5.0
H of CH_2	f	1.0	0.130	−0.107	0.460	5.0
H of NH	f	0.5	0.138	0.098	0.299	5.0
H of NH	f	0.5	0.283	0.098	0.355	5.0
H of H_2O	f	0.5	0.070	0.159	0.273	5.0
H of H_2O	f	0.5	0.013	0.272	0.363	5.0
H of H_2O	f	0.5	0.121	0.402	0.608	5.0
H of H_2O	f	0.5	0.011	0.374	0.695	5.0
H of H_2O	f	0.5	0.011	0.461	0.524	5.0
H of H_2O	f	0.5	0.023	0.319	0.463	5.0
			(b) 2-Hydrate			
C	f	1.0	0.000	−0.095	0.086	3.8
N	e	0.5	0.000	0.086	0.250	3.8
O	f	1.0	0.215	0.276	0.319	3.8
H of CH_2	f	1.0	0.069	−0.231	0.110	5.0
H of CH_2	f	1.0	−0.069	−0.231	0.062	5.0
H of NH	f	0.5	0.062	0.209	0.271	5.0
H of H_2O	f	0.5	0.142	0.211	0.294	5.0
H of H_2O	f	0.5	0.240	0.256	0.453	5.0
H of H_2O	f	0.5	0.239	0.456	0.267	5.0
H of H_2O	f	0.5	0.239	0.098	0.267	5.0

[a] See Figure 5 for numbering.

phase B (dihydrate), the calculated density of 1.18 g/cm^3 and water content of 45.6 wt % are good agreement with the observed values of 1.16 g/cm^3 and about 45 wt %, respectively.

The number of general equivalent points is 8 for the space group $C2/c$ while only 4 for the space group Cc. Therefore it is most likely that 8 monomeric units in phase A or 8 water molecules in phase B occupy the general equivalent points of $C2/c$. In phase A, 12 water molecules should be divided into 8 molecules and 4 molecules located at different symmetry sites. On the other hand, 4 monomeric units in phase B must be disposed at degenerated sites: the planar zigzag PEI chain requires that the main-chain atoms are in the bc plane and that the twofold rotation axes parallel to the b axis pass through the NH nitrogen atoms. Accordingly, the positions of the nonhydrogen atoms in each phase, expressed in terms of Wycoff notation and point symmetry for $C2/c$ in ref 8, are considered as follows:

Phase A (1.5-hydrate)

	Wycoff notation	point symmetry
8 C atoms	f	1
8 C atoms	f	1
8 N atoms	f	1
8 O atoms	f	1
4 O atoms	e	2

Phase B (2-hydrate)

	Wycoff notation	point symmetry
8 C atoms	f	1, where $x = 0$
4 N atoms	e	2
8 O atoms	f	1

The crystal models of both hydrates in which the atomic positions were appropriately given showed good agreement between observed and calculated structure factors. The structures were then refined so as to minimize the R factor, $\sum|I_o^{1/2} - I_c^{1/2}|/\sum I_o^{1/2}$, where $I = \sum mF^2$, by varying the atomic coordinates of the polymer chains and the water molecules. The hydrogen atoms were also included in the calculation of structure factors on the following assumptions: C–H = 1.09 Å, N–H = 0.99 Å, O–H = 0.98 Å, H–C–H = 110°, C–N–H = 109.5°. The final atomic coordinates and thermal parameters are shown in Table III, and the observed and calculated structure factors are listed in Table IV. The simple conformation of the polymer chains enabled us to determine the crystal structures of both hydrates with fairly small R factors, 10% for the 1.5-hydrate and 9% for the 2-hydrate when only observed reflections were taken into account. Figures 3 and 4 show the crystal structures of 1.5-hydrate and 2-hydrate, respectively, including the symmetry symbols of the space group $C2/c$. Figures 5 and 6 illustrate the structures of 1.5-hydrate and 2-hydrate, respectively, and display the modes of hydrogen bond network; in the figures the NH hydrogen atoms and H_2O hydrogen atoms are omitted for simplicity. It should be noted, however, that, as shown in Table III, the NH hydrogen atoms and H_2O hydrogen atoms were assumed to take statistical dispositions. A weight of 0.5 in the column "weight in structure factor", the so-called "occupancy factor", for the NH hydrogen atoms represents that these hydrogen atoms will be able to occupy two positions of the pyramidal structure of the -NH- groups, i.e., the left and right sides about the main-chain plane. In connection with the statistical disposition of the NH hydrogen atoms, two hydrogen atoms of a water molecule were assumed to be disposed statistically on the four tetrahedrally coordinated bonds at the oxygen atom, corresponding to the half-hydrogen model in ice proposed by Pauling[9] and later proven by neutron diffraction.[10] A weight of 0.5 in the structure factor for the H_2O hydrogen atoms is based on this statistical structure. Neutron and X-ray diffraction studies of many hydrates of inorganic and organic compounds give, on the average, an O–H bond length of 0.98 Å and an H–O–H bond angle of 108.0° for water.[11] The precise positions of H_2O hydrogen atoms cannot be determined for such polymer hydrates. In both hydrates, therefore, the H_2O atoms were conventionally disposed on the O···O or O···N lines.

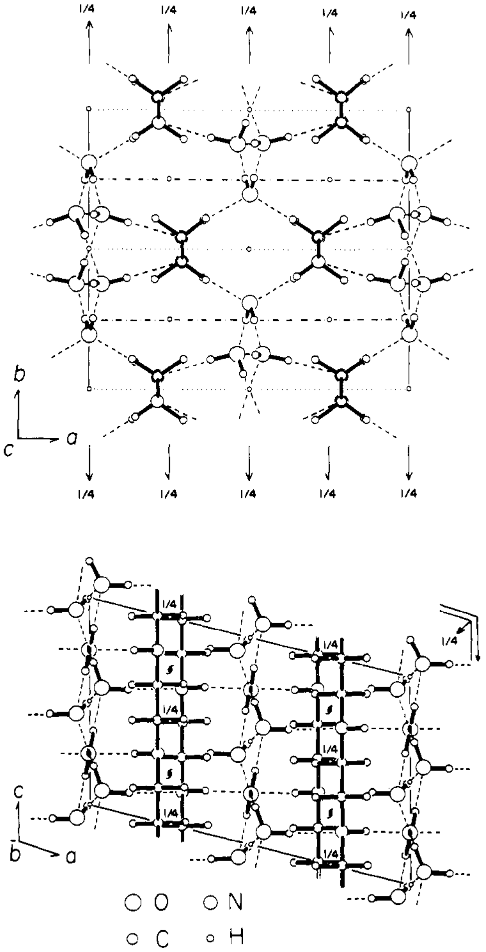


Figure 3. Crystal structure of 1.5-hydrate (phase A): (top) c projection; (bottom) $-b$ projection. Hydrogen bonds are shown by broken lines.

Results and Discussion

Conformation of Polymer Main Chain. The polymer chains in both hydrates are planar zigzag. The bond lengths and bond angles determined are as follows: C–C, 1.53 Å in both hydrates; C–N, 1.47 Å in both hydrates; C–N–C, 110° in the 1.5-hydrate and 111° in the 2-hydrate; N–C–C, 110° in the 1.5-hydrate and 111° in the 2-hydrate. These values are close to those usually accepted.

In the polyether series $[-(CH_2)_m-O-]_n$, poly(ethylene oxide) ($m = 2$) takes a 7/2 helical conformation in the ordinary crystalline form,[12] and the planar zigzag form is able to coexist with the ordinary form only under high tensions;[13] however, no crystalline hydrate has been found in spite of the affinity between water and the polymer in aqueous solutions. Poly(oxacyclobutane) ($m = 3$) is again able to assume the planar zigzag conformation only in the hydrate[7] or under high tensions.[14] The molecular con-

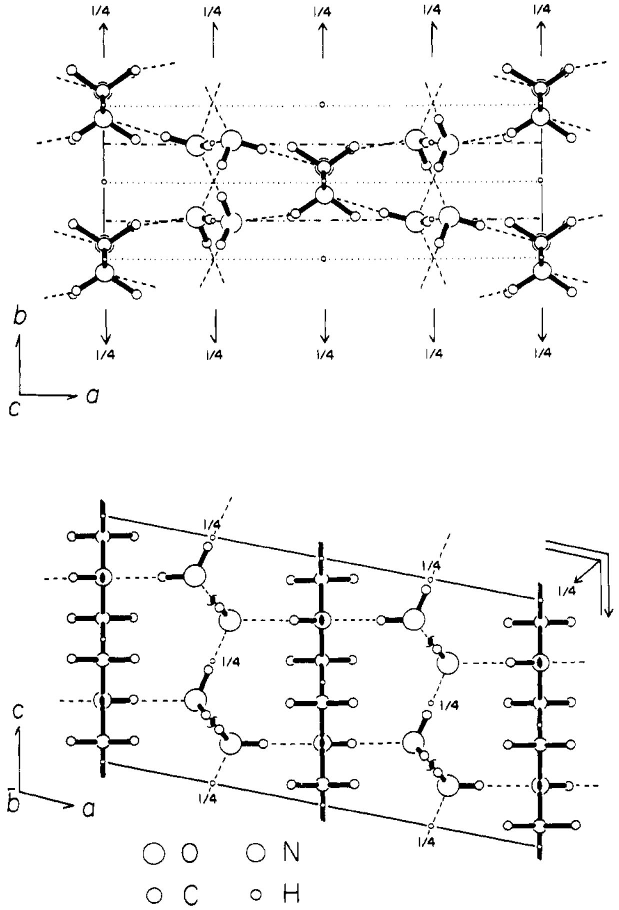


Figure 4. Crystal structure of 2-hydrate (phase B): (top) c projection; (bottom) $-b$ projection.

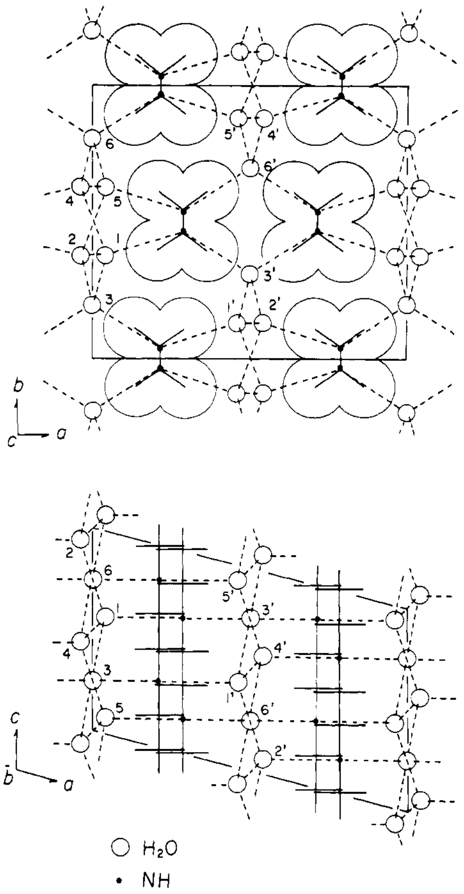


Figure 5. Scheme of hydrogen bondings in 1.5-hydrate.

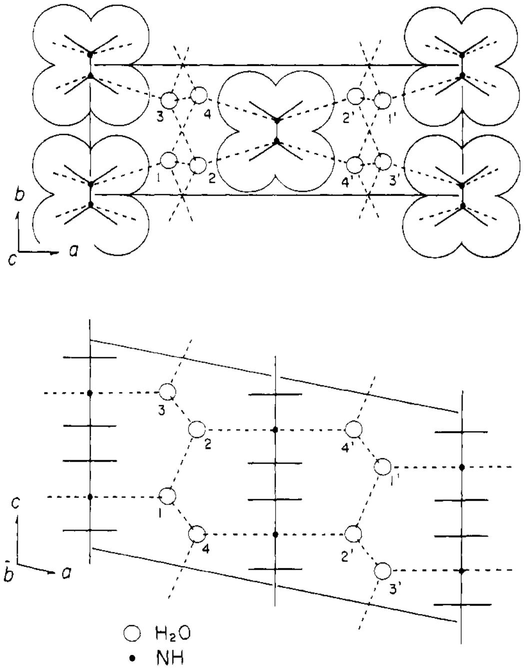


Figure 6. Scheme of hydrogen bondings in 2-hydrate.

formation of PEI in the anhydrate is therefore of much interest and is now under study.

Structure of the -NH-Group. It was impossible to determine by crystal structure analysis alone accurate positions of hydrogen atoms because of the minor contribution of hydrogen atoms to the reflection intensities. However, since it was possible for the NH nitrogen atoms to take a pyramidal structure, the regularity with respect to the disposition of the NH hydrogen atoms along the polymer chain, like the stereoregularity in vinyl polymers, needed to be examined. It should be noted, however, that the disposition of NH hydrogen atoms may not be fixed for a given polymer chain but variable by the nitrogen inversion. Especially in the 2-hydrate, the twofold rotation axes passing through the nitrogen atoms require inevitably the statistical disposition of NH hydrogen atoms, though it is not uniquely decided whether the statistical crystal structure will rise due to any irregular packing of the polymer chains, possessing themselves a certain regular structure or the random disposition of NH hydrogen atoms along the polymer chain itself. It is reasonably inferred, however, that the irregularity with respect to the disposition of NH hydrogen atoms, even if it is so great, does not disrupt the chain packing in both hydrates because of the small spatial occupancy of a hydrogen atom. Examples of similar irregularity are provided by poly(vinyl fluoride)[15] and poly(vinyl alcohol);[16] these two polymers are highly crystalline in spite of the atactic attachment of fluorine atoms or OH groups. In Figures 3 and 4, the NH hydrogen atoms are conventionally disposed as "syndiotactic" (disposed on one side of the main-chain plane) for the 1.5-hydrate, and as "isotactic" (disposed alternately on opposite sides) for the 2-hydrate. Additional details concerning proton exchange and nitrogen inversion, which may be correlated with the disordered structures, of the NH hydrogen atoms and H_2O hydrogen atoms in both hydrates are future problems.

Molecular Packing. In both hydrates the polymer chains are arranged in such a way that the main-chain

Table IV
Observed and Calculated Structure Factors of Two PEI Hydrates

hkl	$(mF_o^2)^{1/2}$	$(mF_c^2)^{1/2}$
(a) 1.5-Hydrate		
110		5
200	39	35
020	83	87
220	141	159
310	116	138
130	54	51
400	97	98
330 420 040	50	44
240	67	64
510	79	69
150	59	48
600 530 440	71	64
620 350	34	31
060		9
710 260	43	52
640 550	44	35
730	45	44
460		4
800 170	39	34
820		27
370		14
$\bar{1}11$	25	20
111		2
021	39	37
$\bar{2}21$ $\bar{3}11$	36	37
221 $\bar{1}31$	55	57
311		8
131	43	42
$\bar{4}21$ $\bar{3}31$		17
041		10
$\bar{5}11$ 331 $\bar{2}41$	52	56
421	52	44
241		15
511		6
$\bar{1}51$ $\bar{5}31$		17
$\bar{4}41$		9
151		19
$\bar{6}21$		14
$\bar{3}51$ 531		25
351 $\bar{7}11$ 621	39	41
061		3
002		0
$\bar{1}12$ $\bar{2}02$	39	43
112		13
020 $\bar{3}12$ $\bar{2}22$	45	40
202		5
$\bar{4}02$		17
$\bar{1}32$ 222	36	34
132 $\bar{4}22$ 312	w	32
$\bar{3}32$	34	40
$\bar{5}12$	w	32
042 $\bar{2}42$ 402	46	53
332		5
$\bar{6}02$		4
422		7
$\bar{1}13$	62	73
$\bar{3}13$		14
$\bar{2}23$ 113		19
023		20
$\bar{1}33$	67	62
$\bar{4}23$		33
$\bar{3}33$ 223 $\bar{5}13$ 133	60	65
313	w	35
$\bar{2}43$		8
043		5
$\bar{5}33$		9
$\bar{6}23$ $\bar{4}43$ 333 243	57	58
423 $\bar{1}53$	w	31
$\bar{7}13$ $\bar{3}53$ 153	57	56
513		14
$\bar{6}43$		23
$\bar{7}33$		7
$\bar{5}53$ $\bar{2}63$ 443 063	47	49
353 533		16
$\bar{8}23$		5
(b) 2-Hydrate		
200	16	15
110	72	72
400	76	84
310	60	66
020 510	46	45
220 600	62	60
420		6
710	38	36
800		18
620	w	23
130		3
$\bar{1}11$	38	34
111	16	13
$\bar{3}11$	42	44
311		9
$\bar{5}11$	38	38
021		7
$\bar{2}21$		8
511 221	w	24
$\bar{4}21$		1
421		6
$\bar{7}11$		22
711		18
$\bar{6}21$		0
$\bar{1}31$		9
002	18	28
$\bar{2}02$		8
202 $\bar{1}12$	29	28
112		8
$\bar{4}02$		2
$\bar{3}12$		11
312 402	30	29
$\bar{5}12$		2
$\bar{6}02$		16
022		14
$\bar{2}22$		8
222	29	25
512		2
$\bar{4}22$		9
$\bar{1}13$	51	60
$\bar{3}13$		8
113		6
$\bar{5}13$ 313	36	43
$\bar{2}23$ 023	35	30
$\bar{4}23$ 223	37	34
$\bar{7}13$		4
513		6
$\bar{6}23$ 423		16
713		4

planes are parallel to the *bc* plane. However, as is seen in the top portions of Figures 5 and 6, the polymer chains do not come into $CH_2\cdots CH_2$ van der Waals contact. On the other hand, the O⋯O and O⋯N distances shown in Table V obviously indicate the formation of hydrogen bonds. The hydrogen bondings therefore play a major role in the stabilization of the crystal lattices. By comparing the hydrogen bond distances between the two hydrates, one notes that the 1.5-hydrate seems to form a more "open structure" than the 2-hydrate.

Water Network. In Figure 7 the water networks of the two hydrates are compared with that in ordinary ice (hexagonal phase Ih).[11] For each crystal three projections of the water network viewed along mutually perpendicular axes are shown. The difference and similarity among their network structures are clearly recognized in these figures. In both hydrates each H_2O oxygen atom is bonded to four hydrogen atoms; two of them are covalently bonded and the remaining two are hydrogen bridged from neighboring water molecules or NH groups. In the 2-hydrate all of the

Table V
Hydrogen Bond Distances (Å) and Angles (Deg) in Two PEI Hydrates

(a) 1.5-Hydrate[a]

Distances

O(1)· · ·O(2)	2.87	O(1)· · ·N(a)	2.96
O(1)· · ·O(3)	2.80	O(3)· · ·N	2.93
O(1)· · ·O(4)	2.79		

Angles

N· · ·O(3)· · ·N(b)	106	O(2)· · ·O(1)· · ·O(4)	104
O(1)· · ·O(3)· · ·O(2)	104	O(2)· · ·O(1)· · ·N(a)	106
O(1)· · ·O(3)· · ·N	103	O(3)· · ·O(1)· · ·N(a)	107
O(3)· · ·O(1)· · ·O(2)	138	O(4)· · ·O(1)· · ·N(a)	91
O(3)· · ·O(1)· · ·O(4)	100		

(b) 2-Hydrate[b]

Distances

O(1)· · ·O(2)	2.66	O(1)· · ·N	2.93
O(1)· · ·O(4)	2.75		

Angles

O(2)· · ·O(1)· · ·O(4)	112	N· · ·O(1)· · ·O(4)	125
O(2)· · ·O(1)· · ·O(4a)	103	N· · ·O(1)· · ·O(4a)	87
O(4)· · ·O(1)· · ·O(4a)	114	N· · ·O(1)· · ·O(2)	105

[a] a: $(^1/_2 - x, ^1/_2 - y, 1 - z)$; b: $(\bar{x}, y, ^1/_2 - z)$. [b] a: $(x, y - 1, z)$.

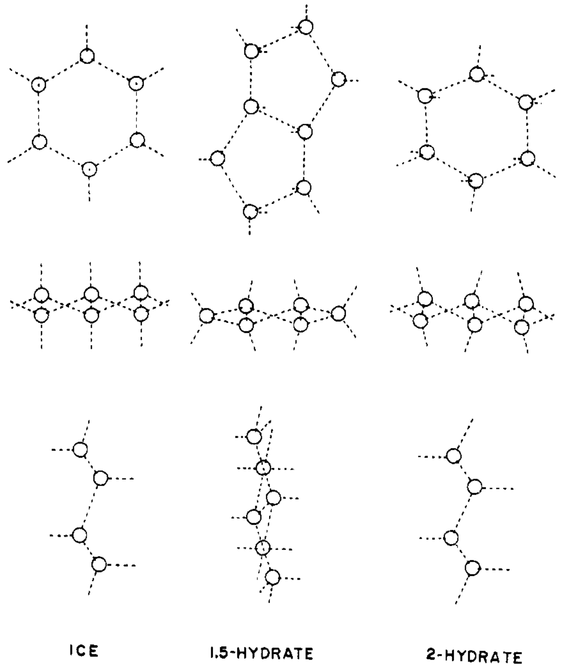


Figure 7. Three projections of water network in ice, 1.5-hydrate, and 2-hydrate viewed along mutually perpendicular axes.

oxygen atoms are equivalent, each oxygen atom being in a tetrahedral environment consisting of three water molecules and one NH group (see also Figure 6). In the 1.5-hydrate there are two kinds of oxygen atoms located at crystallographically nonequivalent sites: Besides 8 oxygen atoms located at the general equivalent sites as in the dihydrate (oxygen atoms 1, 2, 4, 5, 1′, 2′, 4′, and 5′ in Figure 5), there are 4 oxygen atoms that occupy the sites of symmetry C2 (oxygen atoms 3, 6, 3′, and 6′), and they are in a tetrahedral environment consisting of two water molecules and two NH groups. In any event, all of the NH hydrogen atoms and H_2O hydrogen atoms are able to participate in hydrogen bondings in both hydrates. The water network in the 1.5-hydrate is, however, different from that in the ordinary ice. The water network in the 1.5-hydrate consists of the staggered pentagonal rings of water molecules. These pentagonal rings are rather similar to a component of the polyhedral framework of water in gas hydrates and alkylamine hydrates which are clathrate or semiclathrate hydrates,[11,17] although the five oxygen atoms of the pentagonal rings in these clathrates are coplanar or almost coplanar. On the other hand, the 2-hydrate exhibits a water network quite similar to that of ordinary ice, ignoring the slight distortion of the network (see angles of hydrogen bonds in Table V); in other words, the crystal lattice of the 2-hydrate consists of an alternating stack of a layer of the polymer chains and a layer of ice arranged parallel to the *bc* plane.

Transition from 1.5-Hydrate to 2-Hydrate. When the 1.5-hydrate is further exposed to water vapor, it tends to transform into the 2-hydrate. This transition will be performed from a geometrical viewpoint by addition of water molecules near the water molecules 3, 3′, 6, and 6′ in the 1.5-hydrate, changing the mole ratio from 1/1.5 to 1/2 and involving slight shifts of the polymer chains and the water molecules in the *bc* plane and a slight expansion of the unit cell. Accordingly, it is readily understood that the phase change from the 1.5-hydrate to the 2-hydrate takes place with retention of the uniaxial orientation of the crystallites.

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