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Structure and Conformation of Poly(ethylene oxide), PEO, in the Trigonal Form of the PEO-Urea Complex at 173 K

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ABSTRACT: The formation of addition complexes between poly(ethylene oxide) (PEO) and urea has been investigated for PEO of various molecular weights. Scanning electron micrographs show the crystals to be made up of "pseudohexagonal" prisms. These in turn consist in stacks of thick prisms that become platelets as $\bar{M}_w$ increases. The evolution of the unit-cell dimensions of these adducts as a function of the molecular weight is reported. A single crystal of the PEO-urea complex was obtained, and its crystal structure established by using standard X-ray diffraction techniques with intensity data measured at 173 K. The crystal belongs to the trigonal system, $P3_121$ space group, and has a unit cell of dimensions $a = b = 10.540$ (2) Å, $c = 9.094$ (2) Å, $\gamma = 120°$. The crystal structure was established by direct methods. The refinement of the atomic coordinates and the temperature factors converged to the value of 0.052 for the agreement index R. The stoichiometry of the adduct is $(-CH_2CH_2O-)_4 \cdot (\text{urea})_9$. In this crystal, one finds that the urea molecules form pseudohexagonal channels in a honeycomblike pattern. The walls of the channels are built by the hydrogen-bonded urea molecules (2/3). The channels are filled with the poly(ethylene oxide) chains and extra urea molecules (1/3). The extra urea molecules within the channels are hydrogen bonded to the poly(ethylene oxide) chain as well as to the channel urea molecules. The poly(ethylene oxide) chain in a given channel may have one of six possible orientations. In the asymmetric unit, poly(ethylene oxide) has the $(ttg)_n$ conformation. It can also be described as having an approximate 4_1 helix. This helix is slightly more squashed than it is in pure PEO. There the advance per chemical unit measured along the chain axis is 2.770 Å, whereas in the PEO-urea complex the advance per chemical unit is only 2.313 Å.

Introduction

Urea is well-known for its ability to form complexes with linear aliphatic chains.[1-3] Angla[2] was able to prepare and characterize a long series of such complexes with hydrocarbons from C_5 to C_{42}. In his crystallographic study of such a complex, Smith[4] showed that the adducts are constituted of hexagonal channels made of the hydrogen-bonded urea molecules, and the linear molecules find their place within these channels. Urea adducts have also been obtained with poly(ethylene glycols) of low molecular weights[5] as well as with poly(ethylene oxide).[6,7] More recently, molecular complexes between urea and $[-(CH_2)_mO-]_n$ (m = 2-4, 6, 8-10), were prepared and characterized.[8] The authors found that for $m \geq 3$, the adducts are similar to those obtained with the normal alkanes. However, in the case of poly(ethylene oxide) (m = 2), the complex adopted a different crystal structure. It is the crystal structure of this adduct that we report in the present paper.

Experimental Section

Preparation. Small quantitites (40 mg) of poly(ethylene glycols) of various molecular weights were added, at room temperature, to a saturated solution of urea in methanol (10 mL). The PEO-urea adducts were formed after a few hours of contact. The solid complexes were extracted from their solutions and then air dried. PEO with an average molecular weight of 100 000 was obtained from the Aldrich Chemical Co.; poly(ethylene glycols) with $\bar{M}_w$ = 950-1050, 2700-3300, 6000-7500, 8500-11 500, and ~35 000 were purchased from Fluka, AG of Switzerland. The lower molecular weight samples ($\bar{M}_w$ = 300, 400) came from J. T. Baker Chemicals of Phillipsburg, NJ. Urea and methanol were grade reagents of Anachemia Chemicals Ltd. of Montreal.

The polydispersity index, $\bar{M}_w/\bar{M}_n$, for all the PEO samples used in this work was verified by gel permeation chromatography (GPC) with the equipment provided by the Waters Co. The three ultrastyragel columns, mounted in series, have a minimum porosity of 10^3, 10^4, and 10^5 Å, respectively. Their temperature is maintained at 30 °C, and that of the refractometer, Waters Model R401, is kept at 33 °C. The experimental value of the density is obtained by pycnometry in a mixture of benzene and chloroform.

Table I
Crystal Data of Interest for the PEO-Urea Complex $(CH_2CH_2O)_4 \cdot (CH_4N_2O)_9$

$C_{17}H_{52}N_{18}O_{13}$	FW = 716.713 uma	$F(000)$ = 384 e
$a = b = 10.540$ (2) Å	$c = 9.094$ (2) Å	$V = 875$ (1) Å^3
trigonal	$P3_121$ (No. 152)	$Z = 1$
$d_0 = 1.33$ g cm^{-3} (room temp)	$d_c = 1.360$ g cm^{-3}	μ(Cu Kα) = 9.45 cm^{-1}
λ(Cu Kα) = 1.54178 Å	T = 173 K	

X-ray Diffraction. Well-formed single crystals of the adduct were obtained from the methanolic solution slightly heated and then left standing at room temperature for a week. Crystals were thus obtained for all the samples of PEO, i.e., $\bar{M}_w$ = 300-100 000. A single crystal of the adduct ($\bar{M}_w$ = 1000) was mounted on a Enraf-Nonius CAD4 diffractometer. The chosen crystal was in the shape of an hexagonal prism bounded by {100}, {010}, {1$\bar{1}$0}, {101} whose dimensions were 0.20 × 0.28 × 0.26 × 0.57 mm. The unit-cell dimensions (see Table I) and the orientation matrix were computed by a least-squares refinement of the angular settings of 25 well-centered reflections in the range $40 \leq 2\theta \leq 50°$. X-ray diffraction photographs were also recorded to ascertain the choice of the space group. The data collection was performed by the ω scan method with a scan width $\Delta\omega = (1.00 + 0.14 \tan \theta)°$ using the Cu Kα graphite-monochromatized radiation. The orientation and stability of the crystal were monitored by using seven standard reflections whose intensities were measured every hour and orientations checked every 100 measurements. The intensities of reflections were measured within the sphere of reflection limited by $2\theta_{max} = 140°$ and $-12 \leq h \leq 12$, $-12 \leq k \leq 12$, $-11 \leq l \leq 9$. To minimize the amplitude of the molecular motion, the X-ray data were collected at low temperature. The unit-cell dimensions and the X-ray intensity data were measured at 173 ± 3 K by using a modified Nonius low-temperature attachment. The largest fluctuation of the intensities of the reference reflections was 2.6%. After the data were reduced to a unique set of measurements, 639 reflections were considered observed with the criterion $I \geq 3.0\sigma(I)$; $\sigma(I)$ was derived from the counting statistics. The combining of symmetry-equivalent sets of data resulted in an agreement index of 0.035. The diffracted intensities were corrected for Lorentz and polarization effects as well as for absorption. (The programs

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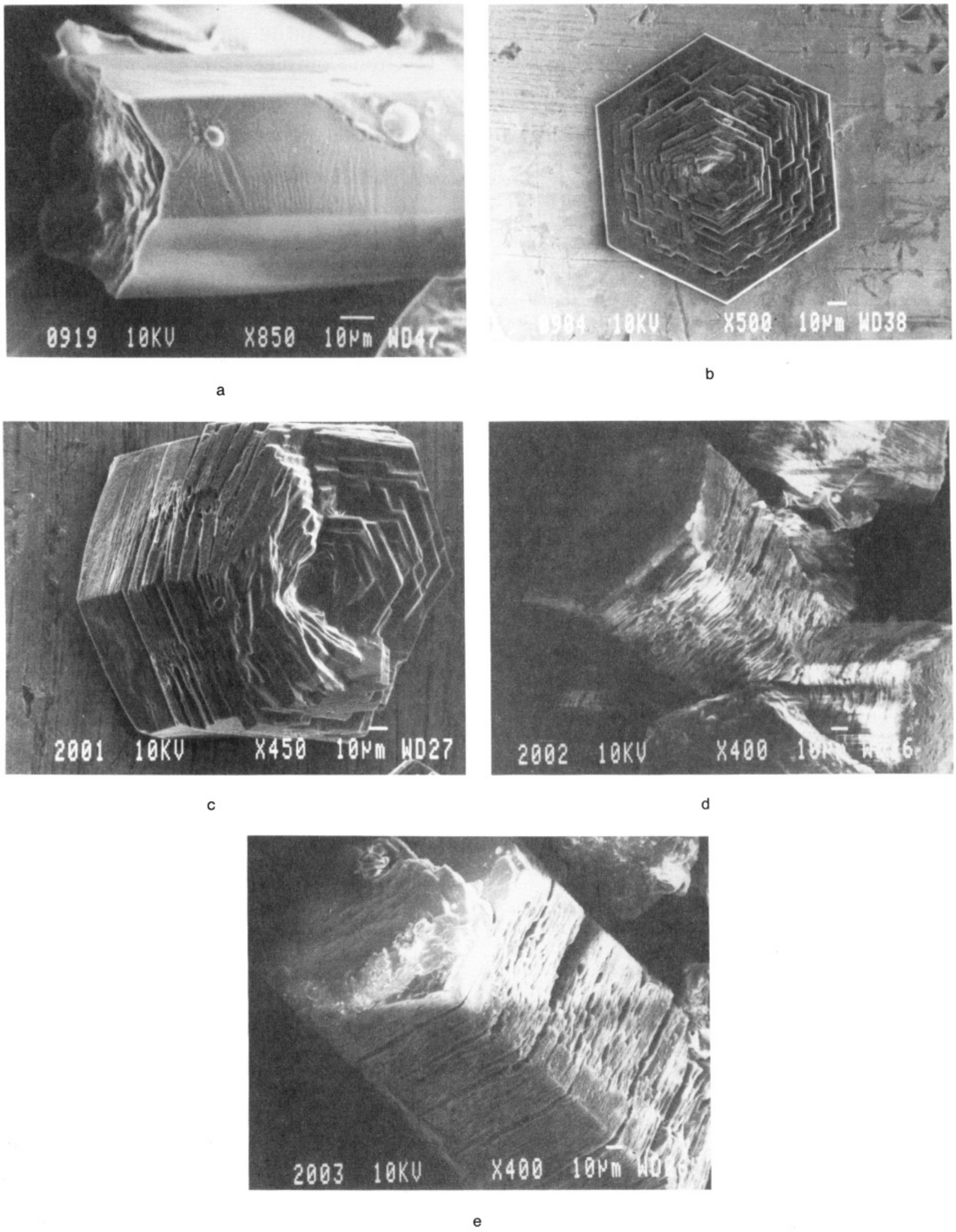

Figure 1. Scanning electron micrographs of crystals of the PEO–urea adducts obtained with PEO of various average molecular weights: (a) side view of a crystal of the PEO(1000)–urea adduct; (b) end-on view revealing the pseudohexagonal cross section; (c) crystal PEO(6000)–urea (the sides are no longer smooth); (d) crystal of PEO(35 000)–urea; (e) crystal of PEO(100 000)–urea.

used are modified versions of NRC-2, data reduction; NRC-10, bond distances and angles; NRC-22, mean planes, SHELX, structure determination and refinement; ORTEP, stereo drawings.[9–11]) The extreme values of the transmission factor are 0.63 and 0.86.

The structure was solved by direct methods using the SHELX program. At first only the urea molecules forming the channels were located. Following the refinement of their atomic coordinates and isotropic thermal parameters (R converged to 0.15), a series of difference Fourier syntheses and refinements revealed first that there are some extra urea molecules within the channels, and then the poly(ethylene oxide) chain was identified. After a few cycles of refinement the H-atom coordinates of the PEO chain were computed and kept at their fixed positions and orientations (d(C–H) = 0.95 Å, θ(C–C–H) = 109°) riding on the

Table II
Fractional Atomic Coordinates and Esd's for the PEO–Urea Complex ($\times10^4$) and U_{eq} (Å^2, $\times10^3$)[a]

atom	x	y	z	U_{eq}
O(11)	6194 (2)	0	3333	35
C(11)	7386 (3)	0	3333	34
N(11)	7525 (2)	−1054 (2)	3998 (2)	47
O(21)	3190 (2)	−1818 (2)	−884 (2)	35
C(21)	4018 (2)	−1249 (2)	206 (2)	33
N(21)	3966 (2)	−2043 (2)	1372 (2)	44
N(22)	4998 (2)	189 (2)	247 (2)	42
O(1)	−833 (6)	−833 (6)	0	69
C(2)	−1089 (7)	−2093 (5)	808 (8)	84
C(3)	249 (8)	−1764 (6)	1676 (8)	85
O(4)	531 (6)	−537 (6)	2555 (6)	69
C(5)	1836 (6)	−122 (8)	3372 (9)	93
C(6)	2256 (7)	1239 (8)	4244 (9)	113
O(7)	953 (8)	953 (8)	5000	82

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a^*_i a^*_j a_i a_j$.

Table III
Unit-Cell Dimensions of the Trigonal Form of the PEO–Urea Complex Obtained from Single Crystals Formed with PEO of Various Average Molecular Weights $\bar{M}_w$

$\bar{M}_w$	a, Å	c, Å	V, Å^3	d_{cal}, g cm^{-3}	T, K
300	10.595 (4)	9.242 (6)	898 (1)	1.325	298
400	10.595 (5)	9.225 (1)	897 (1)	1.327	298
1 000	10.562 (5)	9.252 (5)	894 (1)	1.331	298
	10.540 (6)	9.094 (2)	875 (1)	1.360	173
35 000	10.496 (6)	9.300 (5)	887 (2)	1.341	298
100 000	10.521 (6)	9.259 (6)	888 (2)	1.341	298

Table IV
Comparison of the Bond Distances (Å) and Bond Angles (deg) in Pure Urea, H_2O_2–Urea, and PEO–Urea Combinations

	PEO–urea this work, 173 K		urea		H_2O_2–urea
	$x = 1$	$x = 2$	ref 17, 123 K	ref 18, 295 K	ref 19, 81 K
C(x1)–O(x1)	1.256 (4)	1.257 (3)	1.258 (1)	1.260 (3)	1.266 (1)
C(x1)–N(x1)	1.336 (3)	1.335 (3)	1.341 (1)	1.352 (2)	1.346 (1)
C(21)–N(22)		1.342 (3)			
O(x1)–C(x1)–N(x1)	121.7 (2)	121.8 (2)	121.5 (1)	121.7 (1)	121.0 (1)
O(21)–C(21)–N(22)		121.3 (2)			
N(x1)–C(x1)–N(x2)	116.6 (2)	116.9 (2)	117.0 (1)	116.6 (1)	118.0 (1)

Table V
Geometrical Characteristics of the Hydrogen Bonds between the Urea Molecules Forming the Pseudohexagonal Channels and Also between the Urea Molecule and the PEO Chain within a Channel

		dist, Å			
		PEO–urea this work	urea at 123 K ref 17	H_2O_2–urea at 81 K ref 19	18C6–urea ref 20
N(11)···O(21)	(100,3)[a]	2.970 (3)	2.998 (1)	2.986 (1)	
N(21)···O(11)	(000,1)	2.877 (3)	2.960 (1)	2.935 (1)	
N(21)···O(11)	(000,6)	2.877 (3)			
N(21)···O(21)	(0-10,2)	2.951 (3)			
N(22)···O(21)	(00-1,6)	2.990 (3)			
N(22)···O(11)	(000,1)	3.123 (3)			
N(22)···O(11)	(000,6)	3.123 (3)			
N(11)···O(1)	(100,2)	3.144 (3)			2.848 (3)
N(11)···O(4)	(100,6)	3.241 (6)			2.893 (3)
N(11)···O(4)	(100,1)	3.214 (6)			3.214 (3)
N(11)···O(7)	(100,1)	3.274 (8)			3.282 (3)

[a] Symmetry code: 1, x,y,z; 2, $-y,x-y,z+{}^1/_3$; 3, $-x+y$, $-x,z+{}^2/_3$; 6, $x-y,-y,{}^2/_3-z$.

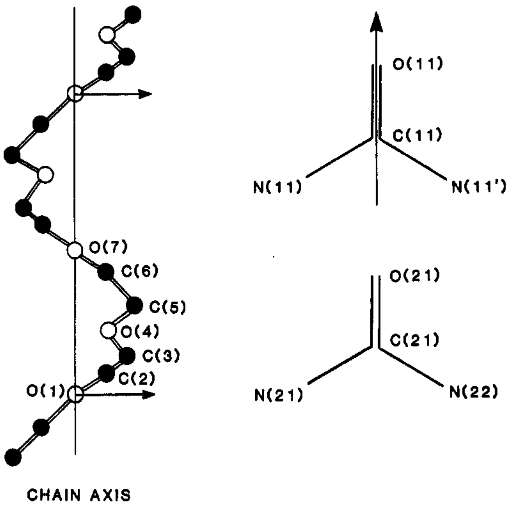

Figure 2. Atomic numbering for the PEO chain and the urea molecules in the crystal structure of the adduct.

C atom to which they are bonded. Convergence was reached at $R = 0.052$, $R_w = 0.064$, and $S = 3.84$ for 639 observed reflections. ($R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, $S = [\sum w(|F_o| - |F_c|)^2/(m-n)]^{1/2}$.) The refinement was based on F's, and the quantity minimized was $\sum w\Delta F^2$. In the final least-squares refinement cycle, the average parameter/shift ratio was 0.02σ (maximum 0.20σ). The extreme fluctuations of the residual electron density, as shown on the final difference Fourier synthesis, were −0.31 and 0.21 e Å^{-3}. The scattering factors used were taken from refs 12 and 13 for non-hydrogen and hydrogen atoms, respectively.

Scanning Electron Microscopy. The morphology of single crystals of the PEO–urea adducts with $\bar{M}_w$ = 1000, 6000, 35 000, and 100 000 was examined on a JEOL-820 scanning electron microscope equipped with an Everhart-Thornely detector. Crystals of the adducts were grown directly onto the specimen holder. They were then coated with a 500-Å layer of the Au–Pd eutectic.

Results and Discussion

The average molecular weight of the various PEO samples at our disposal was found by GPC to be within the specifications given by the suppliers.

Scanning electron micrographs of various PEO–adduct crystals are shown in the series of photographs of Figure 1. The observed morphology is identical for all the specimens studied. The crystals all appear as elongated pseudohexagonal prisms. However, one notices that the faces of the prisms are very smooth for the lowest molecular weight specimen and they become more corrugated as $\bar{M}_w$ increases. For the higher $\bar{M}_w$ values, the morphology is comparable to a stack of hexagonal platelets rather than that of a tall prism. Figure 1a shows a typical crystal of the PEO–urea adduct obtained with PEO of low molecular weight ($\bar{M}_w$ = 1000). This crystal has very smooth lateral sides and very sharp edges. However, none of the crystals examined show a well-defined end. In Figure 1b, the crystal is shown down the c axis. This view reveals the pseudohexagonal contour and the pattern of a spiral growth with the screw axis coincident with the c axis. The crystal of Figure 1c, grown from PEO(6000) and urea, is still "pseudohexagonal", but the faces are not as smooth as for that obtained with PEO(1000). There are signs that in fact the crystal is made up of a stack of thick prisms. The end of the crystal still shows the spiral growth pattern. For the PEO(35 000)–urea and PEO(100 000)–urea adducts (Figure 1d,e) it becomes very clear that the crystals consist of stacks of platelets. Thus the morphology changes progessively as $\bar{M}_w$ increases. This situation is very reminiscent of that observed in the polyethylene–urea complex.[14,15]

The unit-cell dimensions of the PEO–urea adducts, obtained for PEO of average molecular weight, $\bar{M}_w$, in the range 300–100 000 are listed in Table III. Although there is a very slight decrease in the unit cell volume as $\bar{M}_w$ increases, one may conclude that the crystal structure

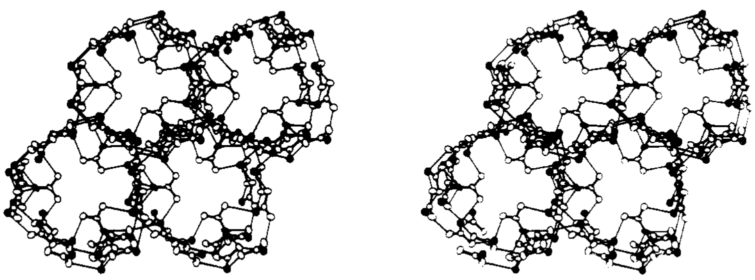

Figure 3. Stereopair showing the channels formed by hydrogen-bonded urea molecules and the extra urea molecule present in the channels.

Table VI
Bond Distances (Å) and Angles (deg) in the PEO Chain

bond	dist	angle	angle
O(1)–C(2)	1.421 (6)	C(2′)–O(1)–C(2)	111.6 (4)
C(2)–C(3)	1.498 (11)	O(1)–C(2)–C(3)	109.8 (5)
C(3)–O(4)	1.420 (9)	C(2)–C(3)–O(4)	104.6 (6)
O(4)–C(5)	1.426 (10)	C(3)–O(4)–C(5)	107.7 (6)
C(5)–C(6)	1.499 (11)	O(4)–C(5)–C(6)	110.3 (7)
C(6)–O(7)	1.427 (12)	C(5)–C(6)–O(7)	105.1 (7)
		C(6)–O(7)–C(6′)	108.1 (7)

Table VII
Comparison of the Torsion Angles (deg) of the PEO Chain in This Complex and Uncomplexed

torsion angle	PEO–urea adduct	uncomplexed PEO[16]
C(2′)–O(1)–C(2)–C(3)	–178.4 (5)	188.2
O(1)–C(2)–C(3)–O(4)	56.6 (7)	65.0
C(2)–C(3)–O(4)–C(5)	–177.6 (6)	188.2
C(3)–O(4)–C(5)–C(6)	175.9 (6)	
O(4)–C(5)–C(6)–O(7)	50.0 (8)	
C(5)–C(6)–O(7)–C(6′)	–175.1 (6)	

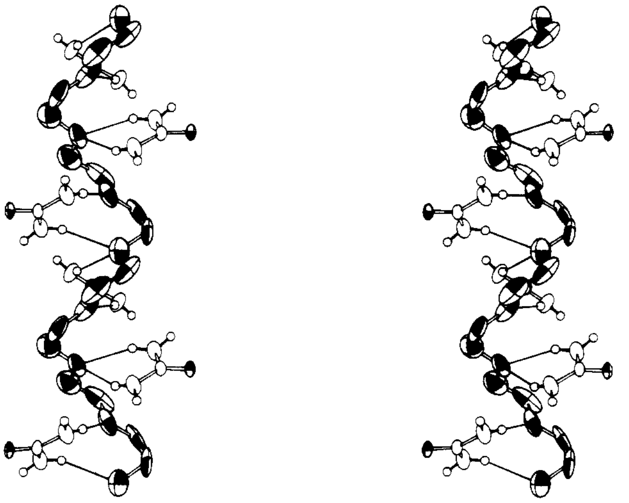

Figure 4. Stereopair showing the association of PEO and urea molecules in the channel.

described below for the complex PEO–urea where the average molecular weight of PEO is 1000 also applies to the complexes with higher $\bar{M}_w$ values. It is to be noted that upon cooling to 173 K, the contraction of the unit cell is anisotropic. The *a* dimension decreases by only 0.2%, whereas at the same time the *c* dimension was reduced by 1.7%.

The final atomic coordinates and the equivalent thermal parameters *U* are listed in Table II. The atomic numbering is shown schematically in Figure 2. The stoichiometry of the PEO–urea adduct is $(-CH_2CH_2O-)_4\cdot(\text{urea})_9$. For this stoichiometry, the observed density, although measured at room temperature, agrees very well with its calculated value. As indicated earlier there are two kinds of urea molecules: those that constitute the walls of the channels (2/3) and those that are located within the channels (1/3).

From a crystallographic point of view, the unit cell contains six urea molecules in the 6(c) general position and the other three urea molecules occupy the 3(a) position of space group $P3_121$. Thus the latter molecules possess a 2-fold axis of rotation which passes along the C=O bond.

Urea Channels. The bond distances and angles of the urea molecules are compared in Table IV to the corresponding quantities as found by neutron diffraction of pure urea at 123 K[17] and room temperature[18] and to those observed in a H_2O_2–urea complex.[19] All these quantities are in very good agreement. The urea molecules forming the walls of the channels are all hydrogen bonded to one another. The channels formed extend in the *c* direction and are associated in a honeycomblike pattern. The N···O distances (see Table V) are in the range of 2.951 (3)–2.990 (2) Å. Thus this indicates the existence of a relatively strong network of H bonds. Each urea molecule is planar within experimental error. However, their mean plane is not quite parallel to the *c* direction. They are tilted by about 27° with respect to the walls of the channels, which are thus slightly corrugated. A stereopair, shown down the *c* axis the channels formed by these urea molecules, reveals that the cross section of a channel is not quite hexagonal. This was to be expected since the structure has only a 3_1 crystallographic axis of rotation (Figure 3).

Occupants of the Channels. Two kinds of structural units are located within the channels: urea molecules and the polymer. These urea molecules within the channels are placed in such a way their C=O bonds are on 2-fold axes of rotation. The urea molecules are themselves planar but inclined by 32° with respect to the base plane *ab*. These urea molecules also form hydrogen bonds, toward the oxygen atoms of the PEO chain as well as with the other channel-forming urea molecules. The N···O distances, in the range 3.144 (3)–3.274 (8) Å, indicate that these H bonds are not as strong as those formed between the channel-forming urea molecules of the adduct. It is of interest to compare these distances to those found by Harkema et al.[20] in a 18-crown-6:urea complex with 1:5 stoichiometry. There, some urea molecules are not H bonded to the crown ether but to one another, thus forming layers. At the same time two other urea molecules are H bonded to the macrocycle through H bonds whose lengths are in the interval 2.848 (3)–3.282 (3) Å.

The PEO chain in the channel is on a 3_1 helicoidal axis of rotation. However, since there is only one chain per unit cell and only one chain can fit within a given channel, this means that the chains have three possible orientations. Furthermore, the oxygen atoms O(1) and O(7) are situated on 2-fold axes of rotation perpendicular to the chain axis, at $z = 0$ and $^1/_2$, respectively, and O(4) is in a general position. Thus the polymer chain may have six distinct orientations. The bond distances and bond angles of the PEO chain are given in Table VI, and the conformational

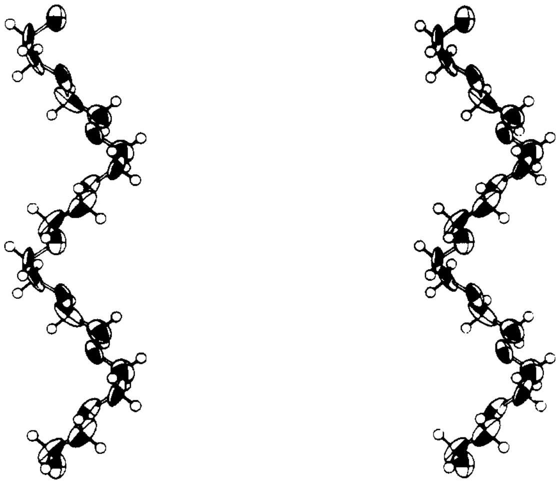

Figure 5. Stereopair showing the conformation of PEO in the PEO–urea adduct.

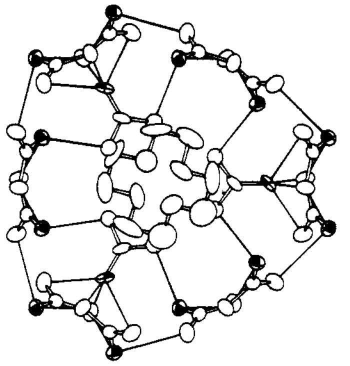

Figure 6. Projection of the PEO chain down the chain axis.

angles are compared in Table VII to the corresponding quantities in the structure of pure PEO. The stereopair of Figure 4 shows the PEO chain and the H-bonded urea molecules. This unit fits within the channel and is H bonded to it through its urea molecules. In their study of the structure of PEO, using the X-ray intensities of a fiber diagram and infrared absorption spectroscopy, Tadokoro et al.[16] arrived at conclusions that very nearly parallel our results. The model proposed by these authors assumes C–C and C–O distances of 1.54 and 1.43 Å and C–C–O = C–O–C = 109.47° for bond angles. The most likely model is a 7_2 helix, where the oxygen atoms lie on the inner part of the helix. They also find, as we have noted here, that the oxygen atoms lie on 2-fold axes of rotation.

The conformation of the PEO chain in the asymmetric unit of the adduct may be described, starting at atom C(2), as $(ttg)_2$ (Figure 5). The fiber repeat of PEO in the urea adduct is $p_o = c = 9.094\ (2)$ Å. Note that this value was measured at 173 K. At room temperature, $p_o = 9.252\ (2)$ Å. These values differ significantly from that calculated for an all-trans conformation ($p_c = 10.8$ Å). On the other hand, the quantity p_o is slightly shorter, although of the same order of magnitude, than half the p_o value, 19.30 Å, observed in pure PEO whose conformation is a 7_2 helix.[16] In the urea adduct, the conformation for one fiber repeat is $(ttg)_4$. Thus, one could say, in first approximation, that the conformation of PEO in the adduct is that of a 4_1 helix. However, when one takes into account the actual values of the torsion angles (Table VII), it becomes obvious that the conformation is only approximately 4_1. The nearly 4-fold helix and the location of the oxygen atoms at the inner side of the helix may be clearly appreciated in Figure 6. It may be the existence of the H-bonded urea molecules that makes the PEO chain more tightly bound in the complex than in the pure state.

In light of what was established here, it was tempting to interpret the data reported by Suehiro and Nagano.[21] These authors, studying the urea–ethylene oxide oligomer complexes, reported the existence of a new tetragonal form with a unit cell of dimensions $a = b = 7.30$ Å and $c = 19.51$ Å. Thus, we expect the PEO chain to have a perfect 4_1 conformation since the reported space group is $I4_1/amd$ and the c value is very close to that of pure PEO in the 7_2 conformation ($p_o = 19.30$ Å). However, the nonreversible transformation of form II to form I is not just a phase change since the stoichiometry of the complex changes from $(CH_2CH_2O)\cdot(\text{urea})$ to $(CH_2CH_2O)_4\cdot(\text{urea})_9$. To check on this, it would be very useful to undertake a full crystal structure determination. However, so far we have not been able to obtain a single crystal of this particular composition.

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Supplementary Material Available: Tables listing anisotropic thermal parameters and their esd's and the H-atom coordinates (2 pages); tables of observed and calculated structure amplitudes (3 pages). Ordering information is given on any current masthead page.

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