776 *Macromolecules* **1992,** *25,* 776-782

Poly(tetrahydrofuran)-Urea Adduct: A Structural Investigation

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Received July 8, 1991; Revised Manuscript Received September 30, 1991

ABSTRACT: PTHF and urea form a crystalline complex of the host-guest type whose structure has been established from three-dimensional X-ray data. The crystal belongs to the hexagonal system, space group $P6_1$, and has a unit cell of dimensions $a = b = 8.199$ (1) Å and $c = 11.032$ (2) Å. The crystal structure was established by direct methods from 410 unique reflections. The refinement of the atomic coordinates and the temperature factors converged to an agreement index, R, of 0.046. The stoichiometry of the adduct is $[(CH_2)_4O]_{1.8}[\text{urea}]_6$. In this structure, the urea molecules (the host) are linked to one another through hydrogen bonds, and the resulting network consists of hexagonal channels much like a honeycomb. The PTHF chain, the guest, fits within the hexagonal channel. The C and O atoms are indistinguishable, and there is a crystallographic disorder about the chain axis. The PTHF chain is in the trans conformation, but there is a small twist of 24° about each bond so that the chain is coiled. The morphology of the crystals, as revealed by scanning electron microscopy, consists of hexagonal prisms, for low $\bar{M}_w$. When $\bar{M}_w$ increases, the crystal consists of stacks of hexagonal platelets. DSC measurements indicate that there is no phase change as the temperature is lowered to -150 °C. The melting temperature, which varies with $\bar{M}_w$, is slightly higher than that of pure urea. The enthalpy of melting, ΔH_m, has a value of 14.4 kJ/mol $[(CH_2)_4O]$. The values of $\bar{M}_w$, $\bar{M}_n$, and the $\bar{M}_w/\bar{M}_n$ ratio were measured before and after complex formation. It was found that the polymolecularity index improves significantly, from 1.59 to 1.20 for PTHF of $\bar{M}_w = 1000$ and from 1.82 to 1.39 for PTHF whose $\bar{M}_w$ is 2000.

Introduction

It is a well-established fact that urea, the host, may form complexes of the "host-guest" type when the guest is a linear molecule (n-paraffin) such as n-hexadecane.[1] It has also been shown that linear polymers, such as polyethers[2,3] or polyethylene,[4,5] could form adducts with urea, while polybutadiene-urea adducts have been obtained by polymerization of the parent monomer already present in the urea channels.[6,7] The urea molecules constitute, through an extensive network of hydrogen bonds, a hexagonal host lattice much like a honeycomb. The guest molecule (n-paraffin or polymer) finds its place in each of the hexagonal channels.

PEO-urea and PE-urea complexes have been investigated in detail by X-ray diffraction, infrared spectroscopy, and ^{13}C NMR.[8-11] However, since no suitable polymer-urea single crystal was available at the time, and because of the disordered nature of the guest caused by the highly symmetrical host lattice, no conclusive answer could be reached as to the position and/or the conformation of the polymer itself within the channel. In a recent investigation[12] we obtained good single crystals of the PEO-urea adduct and we were able to establish through a three-dimensional structure analysis that this complex has the stoichiometry of four CH_2CH_2O units per nine urea molecules and that, contrary to all previous reports, there are two kinds of urea molecules. Some of them contribute to the makeup of the pseudo-hexagonal host lattice (*wall-forming* urea molecules), while the others (*internal* urea molecules) are located within the channels together with the PEO chains to which they are hydrogen-bonded. The *internal* urea molecules are also hydrogen-bonded to the *wall-forming* urea molecules. Thus, the PEO chain is well anchored to the channels. We also established that, in the complex, PEO adopts a helical conformation that differs only slightly from that reported for the uncomplexed PEO.[13] A few years ago, Suehiro et al.[11] described the preparation of adducts formed between poly(tetrahydrofuran) (PTHF) and urea. These authors indicated that their diffraction pattern could be indexed with a hexagonal unit cell similar to that reported by Smith for the normal alkane-urea adducts.[1] They concluded that the PTHF chains have the same all-trans conformation as that of polyethylene in its urea adduct[4,14] or n-alkanes complexed with urea.[15-19] Although this seems reasonable, it has not been unequivocally demonstrated. We decided to reinvestigate the PTHF-urea system for the following reasons: the stoichiometry of the adduct is uncertain; the diffraction patterns of the urea adducts with n-paraffins show streaks indicating a high degree of disorder for the paraffin molecules; and some authors claim that, particularly in the case of the n-alkane adducts,[20] there may be some kind of conformational defects whereby some of the torsion angles could be gauche.[21] The present report is part of a systematic analysis of polymer-urea adducts. It sets out the conditions required to obtain good single crystals suitable for an X-ray analysis. The three-dimensional crystal structure of the PTHF-urea adduct is established, and various possibilities of disorder of the guest molecules are examined.

Experimental Section

Adduct Preparation. The adduct is obtained at room temperature after dissolving PTHF [poly(tetramethylene ether glycol); $\bar{M}_w = 650$, 1000, 2000; Polysciences, Inc., Warrington, PA] in an isopropyl alcohol solution saturated in urea [Anachemia Chemicals Ltd., Montreal]. Crystals appear almost immediately. In order to grow the good single crystals required for an X-ray analysis, the first grown crystals are slowly redissolved by warming their suspension in isopropyl alcohol. The solution is maintained at 45 °C in a thermostated bath until well-developed single crystals appear, usually after 48 h. The crystals are then filtered and dried at room temperature.

Scanning Electron Microscopy. The morphology of the adduct crystals ($\bar{M}_w = 650$, 1000, 2000) was examined using the JEOL-820 scanning electron microscope equipped with an Everhart-Thornely detector effective to secondary electrons. The crystals, grown directly onto the sample holder, were coated with a 500-Å layer of the Au-Pd eutectic to ensure good electrical conduction to eliminate the charging effect.

The morphology of a number of crystals of the PTHF-urea adduct was examined by scanning electron microscopy. Typical

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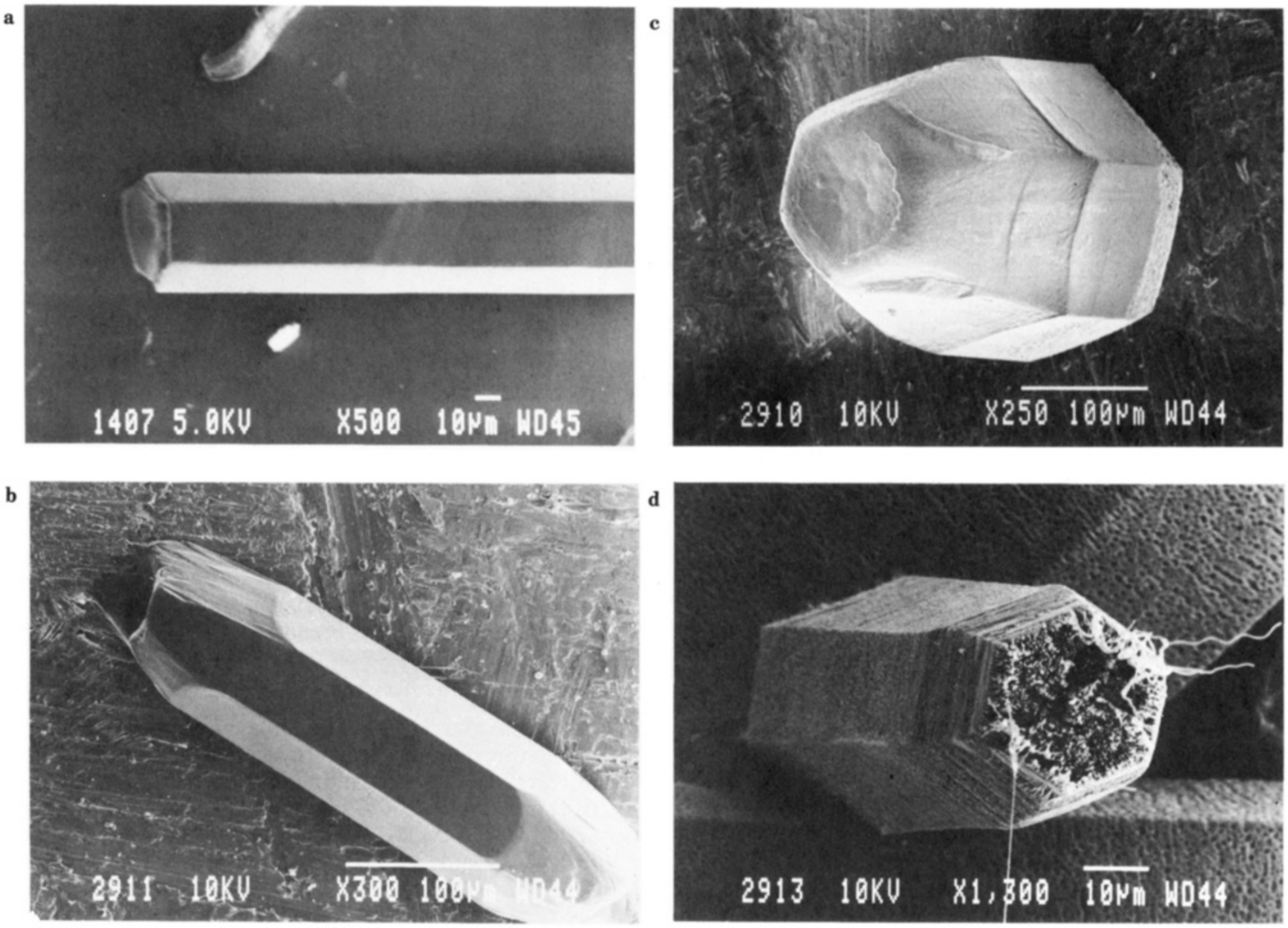

Figure 1. Scanning electron micrographs of single crystals of the poly(tetrahydrofuran)-urea adduct; all crystals were grown at 45 °C: (a) PTHF-urea, $\bar{M}_w = 650$. (b) PTHF-urea, $\bar{M}_w = 1000$. (c) PTHF-urea, $\bar{M}_w = 1000$. (d) PTHF-urea, $\bar{M}_w = 2000$.

micrographs are illustrated in Figure 1 for PTHF-urea adducts with $\bar{M}_w = 650$, 1000, and 2000. In all cases, the crystal growth proceeds along the *c* axis. Exceptionally well-developed hexagonal prisms are observed especially for $\bar{M}_w = 650$ and 1000. For $\bar{M}_w = 2000$ the faces of the crystal are not as smooth. Although the overall morphology is the same, it seems that, in this case, one has hexagonal platelets stacked on top of one another. Such a lamellar structure was reported for PE-urea[4,5] and PEO-urea ($\bar{M}_w > 1000$)[12] adducts. Hexagonal prisms with very smooth lateral faces were observed for normal alkane-urea and PEO-urea ($\bar{M}_w < 1000$) adducts. Thus, there is a direct relationship between the molecular weight of the polymer and the morphology of the complex.

Gel Permeation Chromatography. The polydispersity index, $\bar{M}_w/\bar{M}_n$, of the PTHF sample used here ($\bar{M}_w = 650$, 1000, and 2000), and that of the PTHF obtained after having decomplexed the adduct, was examined by gel permeation chromatography, GPC. The equipment, from the Waters Co., consisted of three Ultrastyragel columns, with minimum porosity of 10^3, 10^4, and 10^5, respectively, and a refractometer, Waters Model R401. The columns are mounted in series and kept at 30 °C while the temperature of the refractometer is maintained at 33 °C. The rate of flow of the eluent (THF) is 1 mL min^{-1}. The calibration curve required for the analysis of the distribution of the molecular masses was obtained from commercial poly(ethylene oxide) glycols and poly(ethylene oxide) of very low polydispersities.

The values of $\bar{M}_w$, $\bar{M}_n$, and the ratio $\bar{M}_w/\bar{M}_n$ for the commercial PTHF as well as for PTHF recovered from the adduct crystallized at 45 °C are given in Table I. The average molecular weight before adduct formation is $\bar{M}_w = 1851$ (formally 1000) while it is 4309 for the PTHF recovered after the adduct was formed. For the PTHF formally labeled $\bar{M}_w = 2000$, one measured $\bar{M}_w = 5133$ and 7906 before and after adduct formation, respectively. This implies that, at the crystallization temperature of 45 °C, the smaller fractions are not complexed. This may be due to their shorter chain lengths. That the polymolecularity index $\bar{M}_w/\bar{M}_n$ improves significantly, in both cases, confirms the suggestion offered by Schmidt et al.[28] that polymer-urea adducts be used as a means to fractionate the polymer.

Table I
Comparison of the Polymolecularity Index of PTHF before and after Adduct Formation

	PTHF	
	commercial before adduct formation	recovered after adduct formation
$\bar{M}_w$(formal)	1000	
$\bar{M}_n$	1160	3572
$\bar{M}_w$	1851	4309
$\bar{M}_w/\bar{M}_n$	1.59	1.20
$\bar{M}_w$(formal)	2000	
$\bar{M}_n$	2800	5657
$\bar{M}_w$	5133	7906
$\bar{M}_w/\bar{M}_n$	1.83	1.39

Differential Scanning Calorimetry. The analysis of the thermal behavior of the PTHF-urea adduct was carried out on a Perkin-Elmer DSC Model 1B with a heating or a cooling rate of 10 °C/min. The samples, weighing 5-10 mg, were crimped in small aluminum containers. The temperature scale was calibrated with respect to the melting point of indium, 429.6 K.

X-ray Diffraction. The experimental value of the density is obtained by the flotation method using a benzene-chloroform mixture. The quoted value is the result of six independent measurements.

Preliminary examination (unit cell dimensions and space group determination) of PTHF-urea single crystals was done on a Nonius X-ray generator fitted with a Super precession camera. The nickel-filtered copper radiation was used throughout (λ(Cu

Table II
Crystal Data of Interest and Variations of the Unit Cell Dimensions of the PTHF–Urea Adduct as a Function of the Temperature

Crystal Data (Room Temperature)

$[CO(NH_2)_2]_6[(CH_2)_4O]_{1.8}$ FW = 490.126 $F(000) = 264e$
$a = b = 8.199$ (1) Å $c = 11.032$ (3) Å $V = 642.3$ (4) Å^3
hexagonal $P6_1$ (No. 169) $Z = 1$
$d_o = 1.262$ g cm^{-3} $d_c = 1.267$ g cm^{-3} μ(Cu $K\bar{\alpha}$) = 8.43 cm^{-1}
λ(Cu $K\bar{\alpha}$) = 1.54178 Å

T, °C	a, Å	c, Å	V, Å^3	ref
25	8.199 (1)	11.032 (3)	642.3 (4)	this work
−11	8.194 (1)	11.032 (3)	639.9 (4)	this work
−48	8.164 (2)	11.031 (3)	636.7 (5)	this work
−89	8.136 (2)	11.030 (3)	632.3 (5)	this work
−112	8.135 (2)	11.019 (2)	631.5 (5)	this work
RT	8.20 (1)– 8.22 (2)	11.08 (2)– 11.01 (1)	641 (2) 648 (4)	Schmidt et al.[28]
RT	8.230 (4)	11.005	645.5 (9)	paraffin–urea adduct, Smith[1]
RT	8.22	11.02	645	polyethylene–urea adduct, Yokoyama & Monobe[4]

$K\bar{\alpha}$) = 1.54178 Å). In order to establish whether diffraction streaks are present or not, a PTHF–urea single crystal was mounted in a Weissenberg camera. Once the crystal was aligned (along its c axis), the diffraction pattern was recorded in the rotation mode. Exposures of up to 200 h were taken at room temperature on Kodak Industrex AA5, a diffraction film of very low background.

A well-developed single crystal (dimensions: 0.45 × 0.17 × 0.15 mm) of the PTHF–urea adduct ($\bar{M}_w = 1000$) was mounted on the Enraf-Nonius CAD4 diffractometer. The unit cell dimensions were measured at increasingly colder temperatures, from room temperature down to −112 °C. In all cases, the cell parameters were refined using the same 25 reflections for which $40° \leq 2\theta \leq 50°$. The unit cell dimensions and other crystal data of interest are given in Table II.

The intensity data collection was performed at room temperature with the graphite-monochromatized Cu $K\bar{\alpha}$ radiation, using the ω scan mode and a scan width defined by $\Delta\omega = (1.00 + 0.14 \tan\theta)°$. The stability and the orientation of the crystal were monitored with seven reference reflections. Their intensities were measured every 100 reflections and their orientation every 1 h. The crystal was not affected by the X-ray beam since there were only random fluctuations of the standards' intensities (maximum fluctuation 0.6%). The data collection included all reflections within the diffraction sphere limited by $2\theta_{max} \leq 140.0°$ and $-10 \leq h \leq 10$, $-10 \leq k \leq 10$, and $0 \leq l \leq 13$. The intensity data were placed on a common scale and corrected for Lorentz and polarization effects as well as for absorption.[22] The extreme values of the transmission factor were 0.86–0.91. The averaging of the equivalent reflections yielded 416 unique reflections where R(ave) = 0.018.

The structure was solved by direct methods using the SHELXS86 program.[23] The atomic coordinates and the isotropic temperature factors of the urea molecules were refined. The agreement index, R, converged to 0.21. After the anisotropic refinement of the urea molecules, a series of structure factor calculations and difference Fourier syntheses yielded the atomic coordinates of the PTHF chain within the urea channel. As the oxygen atoms could not be identified (see Results and Discussion), all chain atoms were treated as carbon atoms and refined anisotropically. The coordinates of the hydrogen atoms were calculated (d(C–H) = 1.00 Å, θ(C–C–H) = 109°). The refinement process was completed when the R, R_w, and S ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, and $S = [\Sigma w(|F_o| - |F_c|)^2/(m - n)^{1/2}$) indicators converged to $R = 0.046$, $R_w = 0.052$, and $S = 2.85$ for 410 observed reflections. In the last refinement cycle, the average (Δ/σ) ratio was 0.03 (maximum value of $(\Delta/\sigma) = 0.15$) and the extreme fluctuations of the residual electron density on the final difference Fourier synthesis were in the range −0.41 to +0.32 e Å^{-3}. The quantity minimized was $\Sigma w\Delta F^2$, and weights were derived from the counting statistics. The scattering curves were taken from refs 24 and 25.

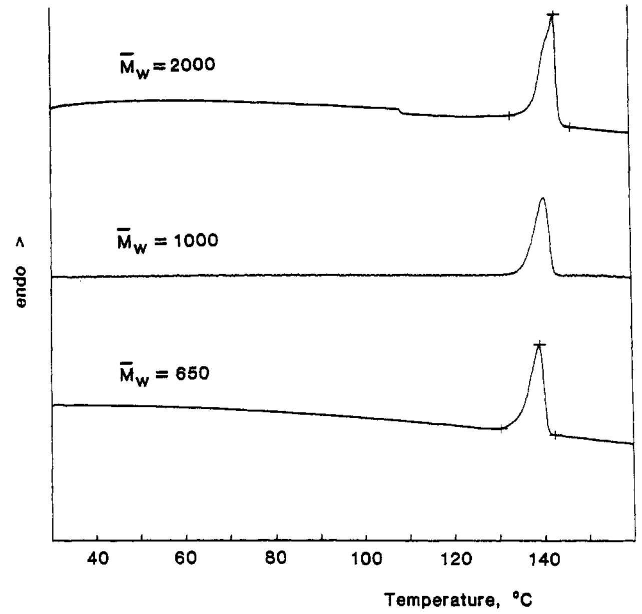

Figure 2. Differential scanning calorimetry curves of the PTHF–urea adduct, $\bar{M}_w$ = 650, 1000, and 2000.

Results and Discussion

Thermal Analysis. The DSC curves of the PTHF–urea complexes, recorded between room temperature and 433 K, reveal only one endotherm. The temperature of this thermal event depends upon the average molecular weight, $\bar{M}_w$, of PTHF. Thus, the peaks are observed at 408.7, 411.2, and 412.6 K for the complexes obtained with PTHF whose $\bar{M}_w$ = 650, 1000, and 2000, respectively (Figure 2). Since these temperatures are higher than the melting point of uncomplexed urea, mp = 405.8 K, it is thought that the polymer within the urea channels reinforces the structure slightly, thus retarding the melting of urea. It has been shown[26] that inclusion compounds formed between normal alkanes and urea decompose according to

$$\text{urea–alkane(s)} \rightarrow \text{urea(s)} + \text{alkane(l)}$$

For this process to take place the guest molecule must acquire enough vibrational–rotational energy to escape from the channels. In our case, maybe because the chains are longer, the complex remains stable up to and beyond the melting point of urea, and then it collapses to yield the two original constituents in the liquid state.

Flory and Vrij[27] have shown that, for pure oligomers, the melting temperature is related to the degree of polymerization in the following way:

$$1/T_m = 1/T_m° + 2R/\Delta H_m(1/P_n)$$

where T_m is the melting temperature (K) of the oligomer whose degree of polymerization is P_n (number average); $T_m°$ is the melting temperature (K) of the polymer with infinite chain length, ΔH_m is the molar heat of melting; and R is the universal gas constant.

Schmidt et al.[28] have used the above relationship to calculate the enthalpy of melting of the urea–PTHF complex. They obtained a value of 14.2 kJ/mol $[(CH_2)_4O]$. Using the degrees of polymerization derived from our GPC measurements, one arrives at a ΔH_m value of 14.4 kJ/mol $[(CH_2)_4O]$. This value compares extremely well with the experimental quantities obtained from the DSC scans, which were 14.9, 14.5, and 14.5 kJ/mol $[(CH_2)_4O]$ for PTHF with $\bar{M}_w$ = 650, 1000, and 2000, respectively.

When the same approach is applied to the melting of the urea–PEO complexes, one calculates ΔH_m = 8.05 kJ/

mol [$(CH_2)_2O$]. This in turns agrees very well with the DSC values of 8.23–8.64 kJ/mol [$(CH_2)_2O$].

The variation of the unit cell dimensions has been studied between room temperature and −112 °C. The results, reported in Table II, indicate that there is no phase change as the adduct crystal is cooled. This is confirmed by the DSC study of the adduct, which does not show any thermal event between room temperature and −150 °C. However, the hexagonal unit cell undergoes a slight contraction which is mostly observed in the *ab* plane of the unit cell ($100\Delta a/a = -0.78$) while very little change occurs in the *c* direction ($100\Delta c/c = -0.12$).

The anisotropic nature of the contraction indicates that the PTHF chain is very tightly enclosed in the urea channel and that the chain is sufficiently rigid so that its conformation does not change upon cooling. It should be pointed out that the opposite situation was encountered in the case of the PEO–urea adduct.[12] There, the PEO chain adopted a helical conformation and the urea channels contained not only the PEO chain but also some extra urea molecules. These were hydrogen-bonded to both the guest PEO chain and the host lattice, thus preventing contraction in the *ab* plane, while allowing for a slight shrinkage in the *c* direction.

Stoichiometry. The experimental density, $d_o = 1.262 \pm 0.005$ g cm^{-3}, is significantly different from the value calculated ($d_c = 1.304$ g cm^{-3}) on the basis of six urea molecules for every two [$(CH_2)_4O$] units. Furthermore, for this stoichiometry, one would expect a *c* dimension of 12.030 Å for the polymer in the trans conformation. Since, the observed *c* is only 11.032 Å long, either the PTHF chain is not in a fully extended conformation or there must be some kind of structural disorder.

All studies on aliphatic–urea adducts point to a situation where the aliphatic guest is in a trans conformation; the size of the channel does not allow the chain torsion angles to deviate very much from 180°. Thus, we assume that the PTHF chain is confined to the channel in a nearly trans conformation. The possibility of a disorder is examined next.

In a rational adduct, such as those formed between thiourea and a cyclic molecule, there is a well-defined stoichiometry, for example, three thiourea molecules for every guest molecule.[29] If this were the case here, the length of the chemical repeat of the polymer chain should be in a simple ratio of integers with the period of the host lattice. However, if this is not the case, the structure is incommensurate.

Many, if not all, the urea adducts with linear molecules have incommensurate structures. The most obvious indication of such a situation is revealed by continuous intensity streaks superimposed on the diffraction pattern of the adduct. In order to check on the existence of an incommensurate structure in the PTHF–urea adduct, we recorded the diffraction pattern of the complex in a Weissenberg camera. In normal exposure conditions no streaks were visible on the diffraction film. However, when the X-ray pattern was recorded on a very low background film and with exposure times as long as 200 h, very faint streaks could be detected (Figure 3). The presence of diffuse bands superimposed on a normal spot pattern is indicative of a one-dimensional disorder; in this case the translational disorder is along the *c* axis.[1] Thus, it seemed that if there is a chain disorder, i.e., random position along the *c* axis, it is not a major feature of the structure since the streaks have a very weak intensity. Indeed, for many adducts where an incommensurate situation has been reported, the characteristic streaks appear in as little as 4 h of exposure.[1,30]

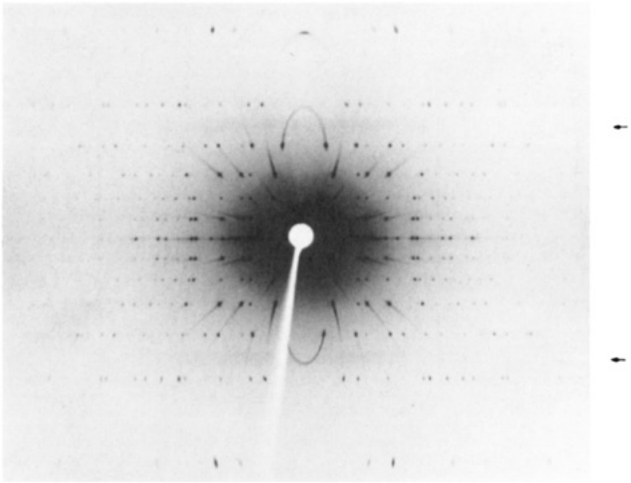

Figure 3. X-ray diffraction film of the poly(tetrahydrofuran)–urea adduct showing very weak diffraction streaks.

Since none of those possibilities seem to fit the observations, another interpretation must be sought. Although the diffraction streaks are very weak, their positions can be measured. They correspond to a repeat of 2.452 Å in the direct space, a value close to the repeat found in polyethylene (PE) in the fully trans conformation [p(PE) = 2.534 Å;[31] p(PE) = 2.547 Å[32]]. In other words, what is observed here is a stepwise or incremental translational disorder by increments of 2.452 Å. This type of disorder is schematically illustrated in Figure 4. The consequence of this incremental translational disorder is that one cannot distinguish a CH_2 group from an oxygen atom. Thus, the PTHF chain is perceived by the X-rays as a PE chain. This interpretation is further supported by the value of the ratio of the *c* dimension to the observed repeat of the streaks: 11.032/2.452 = 4.5 indicating that there are 9 CH_2 groups instead of 10 atoms as in [$(CH_2)_4O]_2$. Consequently, the stoichiometry of the PTHF–urea adduct is $[CO(NH_2)_2]_6[(CH_2)_4O]_{1.8}$ for which the calculated density is 1.267 g cm^{-3} in excellent agreement with the experimental measurement of 1.262 g cm^{-3}.

Crystal Structure. The fractional atomic coordinates resulting from the X-ray analysis are given in Table III while the numbering of the atoms is schematically represented in Figure 5. Because of the various types of disorder, there could be some doubt as to the location of the PTHF chain. In order to ascertain that the orientation and the position of the chain along *c* were correctly established in the X-ray analysis, two calculations were performed. In both cases the atomic coordinates of the urea molecule were kept at their refined values, i.e., the host lattice remained unchanged.

In the first case the *R* factor was computed as the chain was rotated, within the channel, by 10° increments. The variation of *R* as a function of the chain's rotation angle is shown in Figure 6a. There is one very strong and clear minimum at 0°, that is, for the chain in its original X-ray established orientation which is thus confirmed.

In the second case, the *R* value was computed as the chain was moved within the channel along the *c* direction. The resulting variation of *R* is shown in Figure 6b. Here again the position of the chain with respect to the host lattice is clearly that obtained in the X-ray analysis.

A PTHF chain in its cage is shown in the stereopair of Figure 7. As indicated earlier, the structure of this PTHF–urea adduct is constructed of hexagonal channels made up of urea molecules linked through N–H···O hydrogen bonds while the channels are occupied by the PTHF chain. The urea host lattice is shown, in projection along the *c* axis, in Figure 8.

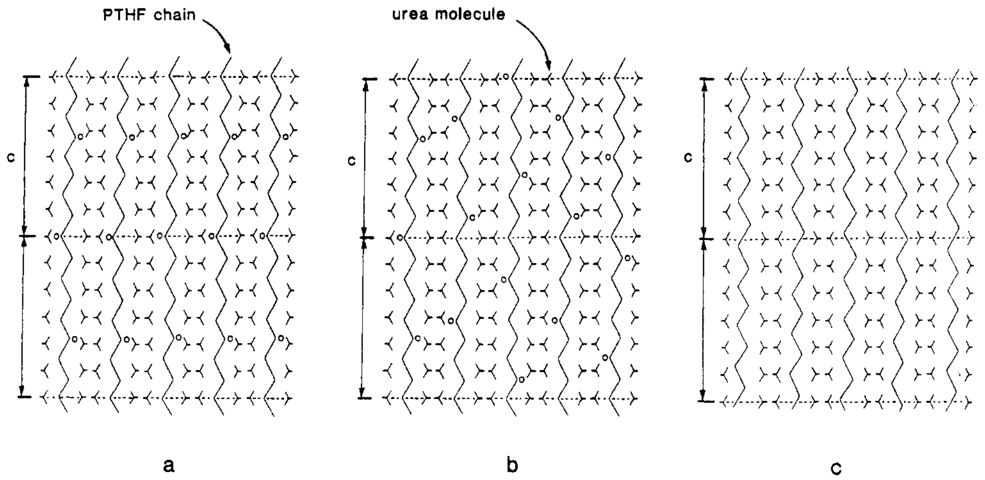

Figure 4. Schematic representation of the urea channels and the various modes of their occupation by the PTHF chains. (a) All PTHF chains are in register; thus, there is a three-dimensional ordering. (b) The polymer chains are still in register, but the oxygen atoms and the CH_2 groups are indistinguishable. In this situation, the chains are displaced by increments of 2.45 Å along the *c* axis. (c) Translational disorder of the polymer chains. The chains in the channels are displaced from one another by any amount. This situation gives rise to strong streaks in the diffraction film.

Table III
Fractional Atomic Coordinates and Their Esd's for the PTHF–Urea Adduct (×10⁴) and U_{eq} or U_{iso} (×10³, Å²)[a]

atom	x	y	z	U_{eq}/U_{iso}
O	6806 (2)	3611 (2)	81 (4)	47
C	5920 (3)	1838 (2)	85 (4)	43
N(1)	5659 (3)	874 (3)	−945 (4)	59
N(2)	5215 (3)	879 (3)	1107 (4)	59
H(1A)	6036 (9)	1537 (8)	−1639 (5)	63 (1)
H(1B)	5198 (9)	−379 (3)	−950 (9)	74 (1)
H(2A)	4652 (9)	−386 (3)	1124 (9)	63 (1)
H(2B)	5436 (9)	1531 (8)	1802 (5)	66 (1)
C(1)	216 (8)	−240 (7)	10298 (5)	75
C(2)	356 (8)	783 (8)	9174 (5)	75
C(3)	−179 (9)	−415 (8)	8075 (5)	95
C(4)	547 (8)	557 (8)	6910 (6)	88
C(5)	−525 (8)	−546 (8)	5845 (5)	88
C(6)	554 (8)	173 (8)	4712 (5)	83
C(7)	−610 (8)	−393 (8)	3605 (5)	93
C(8)	479 (8)	−165 (8)	2498 (5)	76
C(9)	−50 (8)	545 (8)	1437	84

[a] $U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j$.

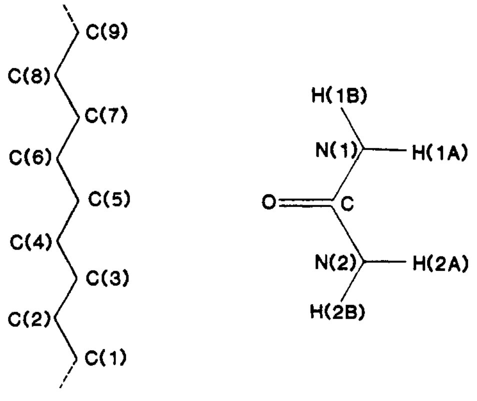

Figure 5. Atomic numbering adopted for the poly(tetrahydrofuran)–urea adduct.

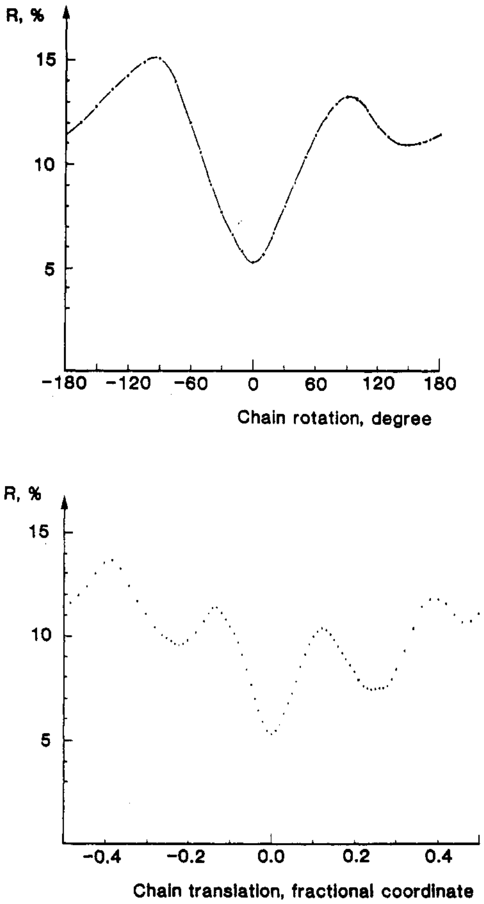

Figure 6. Variation of the *R* factor (a) as the chain is rotated around its axis within the channel and (b) as the chain is translated along the *c* axis.

The bond distances and angles of the urea molecules in this complex are compared, in Table IV, to those found in free urea and in the PEO–urea adduct. All these quantities are in good agreement. The N–H···O distances form two groups (Table V). Two distances are relatively short, ~2.97 Å, while the two others have slightly longer values, at 3.03 Å. Simultaneously, the two N–H···O angles ~160° are associated with the two "short" distances, while for the "long" distance, the two N–H···O angles are near 173°. A similar observation was reported for the PEO–urea adduct.[12]

The bond distances, bond angles, and torsion angles for the PTHF chain are given in Table VI. Because of the translational disorder, no atom could be identified as an oxygen and all peaks in the difference Fourier synthesis were treated as carbons with two hydrogen atoms attached. Thus, the bond distances reflect this ambiguity and are slightly shorter than one would expect for CH_2–CH_2 bonds. What is observed here is some kind of weighted average between C–O and C–C bond lengths. The actual values range from 1.468 (8) to 1.482 (8) Å and average 1.474 Å.

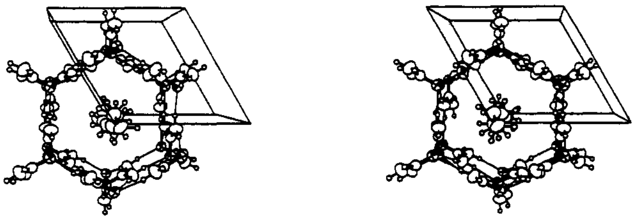

Figure 7. Stereopair showing the poly(tetrahydrofuran) chain within the urea cage.

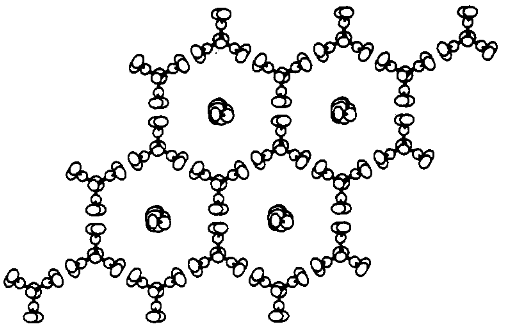

Figure 8. Hexagonal host lattice and its guests seen in projection down the *c* axis.

Table IV
Comparison of the Bond Distances (Å) and Bond Angles (deg) of Urea Molecules in Complexes or in the Pure State

			urea	
	PTHF–urea: 298 K (this work)	PEO–urea: 173 K (12)	123 K (28)	295 K (29)
C–O	1.259 (2)	1.255 (4)–1.258 (4)	1.258 (1)	1.260 (3)
C–N	1.330 (6), 1.339 (6)	1.335 (3)–1.344 (3)	1.341 (1)	1.352 (2)
O–C–N	120.6 (3), 121.0 (3)	121.3 (3)–121.9 (2)	121.5 (1)	121.7 (1)
N–C–N	118.4 (3)	116.6 (2)–116.8 (2)	117.0 (1)	116.6 (1)

Table V
Hydrogen Bonds between Urea Molecules Forming the Channels

	distances, Å		angles, deg
	N···O	H···O	N–H···O
N(1)–H(1A)···O (11$\bar{1}$)3	3.032 (5)	2.134	176
N(1)–H(1B)···O (00$\bar{1}$)5	2.974 (3)	2.124	157
N(2)–H(2A)···O (0$\bar{1}$0)6	2.977 (3)	2.110	161
N(2)–H(2B)···O (100)2	3.031 (5)	2.138	171

The bond angles in the range of 112.0 (5)–117.0 (5)° are similarly affected by the translational disorder.

The conformation of the PTHF chain is all-trans. However, some of the torsion angles deviate significantly from 180°. The observed value range from −140.5 (6) to −162.7 (6)° and average −156.1°. Although the torsion angles deviate somewhat from 180°, they are far from being gauche (±60°), as was suggested by Imashiro et al.[21] for the alkane chain conformation (C_nH_{2n+2} with $n = 7–10$) in alkane–urea adducts. In our case, the PTHF chain is slightly contracted in order to match the *c* dimension of the unit cell. The interactions between the urea molecules and the PTHF chain are essentially of the van der Waals type. Since in terms of electron densities an oxygen atom and a CH_2 group are fairly comparable, the PTHF chain behaves like a PE chain. Not surprisingly, the *c* dimension of the PE–urea adduct has a value of 11.005 Å,[5] which is very close to our value of 11.032 (3) Å for the PTHF–urea complex.

Table VI
Bond Distances (Å), Bond Angles, and Torsion Angles (deg) and Their Esd's in the PTHF Chain of the Adduct[a]

bond	distances	bond	angles
C(1)–C(2)	1.471 (8)	C(9″)–C(1)–C(2)	117.0 (5)
C(2)–C(3)	1.482 (8)	C(1)–C(2)–C(3)	113.4 (5)
C(3)–C(4)	1.474 (9)	C(2)–C(3)–C(4)	116.6 (6)
C(4)–C(5)	1.476 (9)	C(3)–C(4)–C(5)	114.0 (6)
C(5)–C(6)	1.473 (9)	C(4)–C(5)–C(6)	112.0 (5)
C(6)–C(7)	1.476 (9)	C(5)–C(6)–C(7)	114.2 (5)
C(7)–C(8)	1.470 (9)	C(6)–C(7)–C(8)	113.0 (5)
C(8)–C(9)	1.468 (8)	C(7)–C(8)–C(9)	115.5 (5)
C(9)–C(1′)	1.477 (7)	C(8)–C(9)–C(1′)	115.5 (5)

bond	torsion angles
C(1)–C(2)–C(3)–C(4)	−158.4 (6)
C(2)–C(3)–C(4)–C(5)	−159.3 (6)
C(3)–C(4)–C(5)–C(6)	−161.7 (6)
C(4)–C(5)–C(6)–C(7)	−159.4 (6)
C(5)–C(6)–C(7)–C(8)	−162.7 (6)
C(6)–C(7)–C(8)–C(9)	−140.5 (6)
C(7)–C(8)–C(9)–C(1′)	−147.4 (6)
C(8)–C(9)–C(1′)–C(2′)	−160.2 (6)
C(9)–C(1′)–C(2′)–C(3′)	−155.7 (6)

[a] Primed and doubly primed atoms are obtained by translations of −*c* or +*c*, respectively.

Table VII
Comparison of the Fiber Repeat, Bond Distances, and Bond Angles of the Pure PTHF Chain and PTHF–Urea Complex

	PTHF			
		Cesari et al.[36]		
	Imada et al.[35]	model 1	model 2	PTHF–urea: this work
fiber repeat, Å	12.07	12.25		12.258[a]
advance per $(CH_2)_2$ along the chain axis, Å	2.414	2.450		2.452
bond distances				
C–C	1.518	1.542, 1.515	1.536, 1.529	
C–O	1.403	1.425	1.424	
weighted av	1.472	1.490	1.490	1.474[b]
bond angles				
C–C–C	110.5	109.8	113.6	
C–C–O	110.0	110.0	108.5	
C–O–C	109.6	114.8	109.6	
weighted av	110.1	110.9	110.8	114.5[b]

[a] Calculated for a 10-atom chain, $[(CH_2)_4O]_2$. [b] C and O are indistinguishable; values averaged from those in Table V.

The crystal structure of the uncomplexed PTHF has been investigated by Imada and co-workers[35] and, at the same time, by Cesari et al.[36] The two groups, using X-ray fiber diffraction, propose that the PTHF chain is in the trans conformation. However, there are some small differences between their results (with limited diffraction data) and between theirs and ours (three-dimensional X-ray data).

There are three types of parameters that may be adjusted in order to match the observed fiber repeat; they are the bond distances, the bond angles, and the torsion angles. The two groups[35,36] reported on the structure of pure PTHF chosen to keep all the torsion angles at 180°; thus, their PTHF chain is in the fully extended conformation. The fit to the observed fiber repeat was obtained by small adjustments of the bond distances and angles.

The observed fiber repeat and the selected bond distances and angles used to build the polymer chain are compared in Table VII with the corresponding quantities derived from the single-crystal X-ray analysis. The calculated "equivalent fiber repeat" for a 10-atom chain, using our own data, is 12.258 Å, a value identical to that reported by Cesari.[36] The fiber repeat reported by Imada et al.[35] is significantly smaller (12.07 vs 12.25–12.26 Å).

The weighted averages of the bond distances and the bond angles for the two models proposed by Cesari coincide but differ from our observed averages. Our structural analysis is clearly different in the sense that we did not have to fix the torsion angles at 180°. The values that are obtained by the structure determination and the refinement are all of the same sign, and all deviate, on the average,

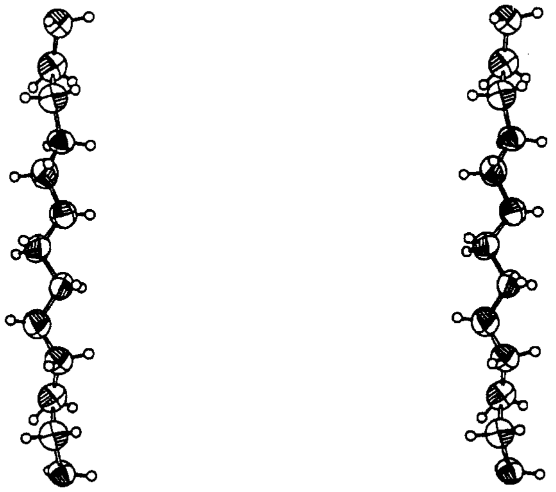

Figure 9. Stereopair showing the slight twist of the PTHF chain.

by 24° from the exactly trans value of 180°. Thus, the PTHF chain in the urea channel is slightly helical or coiled. In a first approximation one can say that the chain adopts a trans conformation, but it is not fully extended. This twist around the chain axis may be appreciated in the stereopair of Figure 9.

The situation reported here is to be contrasted with what was observed in the case of the PEO–urea adduct.[12] In this particular complex the oxygen atoms were identified and there was no chain disorder other than that imposed by the symmetry of the crystal. This was attributed to the presence of hydrogen bonds between the PEO chain and the urea molecules. In other words, the chain was anchored, at regular intervals, to the channel through hydrogen bonds.

Conclusion

The PTHF–urea complex was prepared and characterized by gel permeation chromatography, scanning electron microscopy, and scanning differential calorimetry as well as single-crystal X-ray diffractometry. There are no phase changes as the PTHF–urea adduct is heated from −150 to 160 °C, except for the melting of the compound at 135–139 °C. This melting temperature increases slightly with the average molecular weight, $\bar{M}_w$, of the polymer, and one finds that the enthalpy of melting has a value of 14.4 kJ/mol [$(CH_2)_4O$]. The PTHF–urea complex crystallizes in hexagonal prisms with well-developed faces when $\bar{M}_w$ is small. The density measurement and the X-ray crystal structure analysis indicate a stoichiometry of 9 [$(CH_2)_4O$] units for every 30 urea molecules, or $[(CH_2)_4O]_{1.8}[urea]_6$. The structure may be described in terms of a host–guest type association. The host urea molecules form, through N–H···O hydrogen bonds, a hexagonal lattice similar to a honeycomb. The guest PTHF chain is in the trans conformation, but since the torsion angles deviate by up to 20° from 180°, the chain is slightly twisted rather than fully extended.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for its financial support. We also thank Dr. M. Simard and Mrs. F. Bélanger-Gariépy for collecting the X-ray intensities. We also want to acknowledge the help of Professor J. Prud'homme and Alain Vallée in carrying out the DSC and GPC experiments. We also want to acknowledge the cooperation of the Centre de Caractérisation Microscopique des Matériaux of the École Polytechnique de Montréal in the recording of the scanning electron micrographs.

Supplementary Material Available: Tables listing anisotropic temperature factors and their esd's and hydrogen atom coordinates (2 pages); a table of observed and calculated structure factors (2 pages). Ordering information is given on any current masthead page.

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