Structural Investigations of Urea–Aliphatic Polyester Adducts

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ABSTRACT: Linear aliphatic polyesters and urea form crystalline complexes of the host–guest type. Crystals of such complexes were obtained and the structures of the urea–poly(trimethylene adipate) (PTA) and the urea–poly(trimethylene glutarate) (PTG) adducts were established from three-dimensional X-ray data. The crystals belong to the hexagonal system, space group $P6_1$, and the unit cells have the following dimensions: a = 8.222(6) Å and c = 11.004(2) Å for the urea–PTA adduct and a = 8.191(5) Å and c = 11.041(2) Å for the urea–PTG adduct. The crystal structures were established by direct methods from 416 unique reflections in the first case and from 406 unique reflections in the second one. The stoichiometries of these adducts are: $[urea]_6{\cdot}[O{-}(CH_2)_3{-}O{-}CO{-}(CH_2)_4{-}CO{-}]_{0.82}$ and $[urea]_6{\cdot}[O{-}(CH_2)_3{-}O{-}CO{-}(CH_2)_3{-}CO{-}]_{0.90}$. The urea molecules forming the host structure are linked to one another through H bonds, and the resulting network consists of hexagonal channels much like a honeycomb. The PTA or the PTG aliphatic polyester chain, the guest, is located within the hexagonal channel. As in the case of the urea–PTHF adduct, which is "isostructural", the C and O atoms are indistinguishable. The PTA and PTG polyester chains are in the nearly *all-trans* conformation. The morphology of the crystals, as revealed by scanning electron microscopy, 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 temperatures are clearly higher than that of pure urea while the enthalpies of melting, ΔH_m, expressed per atom in the main chain, indicate a certain dependency upon the chain parity. The values of $\bar{M}_n$, $\bar{M}_w$, and the ratio $\bar{M}_w/\bar{M}_n$ measured before and after adduct formation indicate that the polydispersity indices decrease significantly, from 1.40 to 1.23 for PTA and from 1.90 to 1.37 for PBA. Thus the complexation is selective and has a purification effect on the considered polymer.

Introduction

The formation of inclusion compounds between urea and certain linear polymers such as polyethylene,[1,2] $(CH_2)_n$, polyethers,[3–9] $[(CH_2)_m{-}O]_n$ with $m \geq 2$, or polybutadiene,[10,11] $(CH_2{-}CH{=}CH)_n$, has been reported in previous accounts. Urea complexes with polyethers (m = 2 and 4) and those obtained with polyethylene have been studied mainly from the structural and conformational aspects of the guest molecules. On the other hand, formation of such compounds with linear polyesters has remained virtually unexplored, except for a brief report by Kohler et al.[12] in 1964. The authors indicated that aliphatic polyesters in benzene solution may be absorbed by finely pulverized urea and thus form stable adducts. On the basis of X-ray powder patterns, the authors concluded that the adduct has a hexagonal unit cell quite similar to that established by Smith[13] for the combinations of urea and normal saturated hydrocarbures. Since we succeeded in obtaining single crystals of urea–PEO and urea–PTHF adducts and were able to establish the crystal structure of the complexes, we decided to investigate the formation of such adducts where the guests are aliphatic polyesters and then to characterize them using X-ray diffractometric measurements rather than powder patterns.

The polyesters investigated are represented by the following formula: $[-O{-}(CH_2)_x{-}O{-}CO{-}(CH_2)_y{-}CO{-}]_n$, where x = 2, 3, or 4 and y = 4 and x = 3 and y = 3. They are respectively poly(ethylene adipate), PEA, poly(trimethylene adipate), PTA, poly(1,4-butylene adipate), PBA, and poly(trimethylene glutarate), PTG.

Experimental Section

Adduct Preparation. The urea inclusion compounds with aliphatic polyesters were prepared following two distinct methods.

Crystallization. The adducts were obtained at room temperature after dissolving the selected aliphatic polyester [PEA and PBA, Eastman Kodak, Co., and PTA and PTG, Scientific Polymer Product, Inc.] in a nitromethane solution saturated in urea [Anachemia Chemicals Ltd., Montréal]. The crystals appeared after some hours, were removed from the solution, and then air dried.

Absorption. The finely milled urea was added to a benzene solution of aliphatic polyesters (PEA or PBA) (2–5% by weight), and the mixture was stirred for about 2 weeks. Urea absorbed the polymer from the solution and formed the corresponding inclusion compound. In the end, the solid phase was removed by filtration and washed many times with hot benzene, in order to eliminate all traces of uncomplexed polyester. The solid residue was then air dried.

Scanning Electron Microscopy. The morphology of the adduct crystals 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 Au–Pd eutectic to ensure good electrical conduction to dissipate the charging effect.

Gel Permeation Chromatography. The polydispersity indices, $\bar{M}_w/\bar{M}_n$, of the starting polyesters and those of the polyesters (PEA and PBA) recovered after decomplexation were examined by gel permeation chromatography, GPC. The equipment, of the Waters Co., consisted of three Ultrastyragel columns with a minimum porosity of 10^3, 10^4, and 10^5, respectively, and a refractometer, Model Waters R401. The columns were mounted in series and kept at 30 °C, while the temperature of the refractometer was maintained at 33 °C. The rate of flow of the eluent (THF) was 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.

X-ray Diffraction. The experimental values of the densities were obtained by the flotation method using a benzene–chloroform mixture. Each value is the result of six independent measurements.

A single crystal of the urea–polyester adduct was mounted on the Enraf-Nonius CAD4 diffractometer. The unit cell dimensions were measured at room temperature and at low temperature. In all cases, the cell parameters were refined using the same 25 reflections for which $40° \leq \theta \leq 50°$. The unit cell dimensions and other crystal data of interest are given in Table I. The intensity data were collected at room temperature for the urea–PTA adduct and at low temperature for the urea–PTG adduct, with graphite-monochromatized Cu K$\bar{\alpha}$ radiation, using the ω scan mode and

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Table I. Comparison of Unit Cell Dimensions of the Urea–Polyester Adducts with Those of Urea–*n*-Alkane[13] and Urea–Polyethylene, PE[1,2]

polyester	cryst syst	*a*, Å	*c*, Å	*V*, Å^3	*T*, K
PEA	hexagonal	8.185(5)	11.021(5)	639.8	293
PTA	hexagonal	8.222(6)	11.004(2)	644.3	293
	hexagonal	8.160(7)	10.979(3)	633.2	193
PTG	hexagonal	8.191(5)	11.041(2)	641.5	293
	hexagonal	8.107(6)	11.019(3)	627.2	163
n-alkane[13]	hexagonal	8.230(4)	11.005	645.5	293
PE[1,2]	hexagonal	8.22	11.02	645	293

a scan width defined by $\Delta\omega = (1.00 + 0.14 \tan\theta)°$. In each case, the stability and the orientation of the crystal were monitored with 7 reference reflections. Their intensities were measured every 100 reflections and their orientations every hour. The crystals were not affected by the X-ray beam since there were only random fluctuations of the standard's intensities (0.6% for the urea–PTA adduct and 3.8% for the urea–PTG adduct). The measured intensity 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 $-13 \leq l \leq 13$ for the urea–PTA complex and $-9 \leq h \leq 9$, $-9 \leq k \leq 9$, and $-13 \leq l \leq 13$ for the urea–PTG complex. The intensities were placed on a common scale and then corrected for Lorentz and polarization effects.[14] The averaging of the equivalent reflections yielded 426 unique reflections with R(av) = 0.035 for the urea–PTA complex and 417 unique reflections with R(av) = 0.097 for the urea–PTG complex.

The structures were solved by direct-methods using the SHELX86 program.[15] The atomic coordinates and the isotropic temperature factors of the urea molecules were refined by a full-matrix least-squares procedure. After convergence ($R \simeq 0.20$), a series of structure factor calculations and difference Fourier syntheses yielded the atomic coordinates of the polyester chain within the urea channel. The coordinates of the hydrogen atoms were calculated, d(C–H) = 1.00 Å, θ(C–C–H) = 109°. The refinement process converged, for the urea–PTA complex, when $R = 0.032$, $R_w = 0.044$, and $S = 2.05$ for 416 observed reflections and, in the case of the urea–PTG adduct, for $R = 0.071$, $R_w = 0.076$, and $S = 2.57$ with 406 observed reflections. [$R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, and $S = [\sum w(|F_o| - |F_c|)^2/(m-n)]^{1/2}$, where m is the number of reflections and n is the number of refined parameters]. In the last refinement cycle, the average (Δ/σ) was 0.02 (maximum = 0.09) in one case, and 0.03 (maximum = 0.10) in the other, while the extreme fluctuations of the residual electron densities on the final difference Fourier synthesis were in the ranges −0.11 to +0.12 and −0.23 to +0.20 e Å^{-3} for the PTA and PTG complexes, respectively. The quantity minimized was $\sum w\Delta F^2$ and weights were derived from the counting statistics. The scattering curves were taken from refs 16 and 17.

Results and Discussion

Scanning Electron Microscopy. Morphological aspects of urea–aliphatic polyester adduct crystals have been examined by scanning electron microscopy. Typical micrographs of these crystals are shown in Figure 1. The crystals clearly consist of more or less elongated stacks of hexagonal platelets. This lamellar morphology has been already observed in the urea–polyethylene,[1,2] urea–poly(ethylene oxide),[8] and urea–poly(tetrahydrofuran)[9] adducts, when the polymer molecular weight becomes high enough. However, the crystals of the urea–PEA adduct have been found to be much smaller in the direction of the platelets stack than in the lateral one. The crystals have a width of 70–100 μm and a thickness of 15–20 μm. There is a marked similarity between the crystals of the urea–PBA, urea–PTA, and urea–PTG complexes. Although the widths are similar to that of urea–PEA adduct crystals, they are more elongated and the platelet stacks can reach up 0.5 mm. We have noticed that the crystals of urea–PEO and urea–PTHF adducts, obtained with lower molecular weight polymers, have very well-developed and perfectly smooth faces and edges. In the case of urea–aliphatic polyester adducts, we could not obtain such well-developed crystals. This could be explained by the fact that the molecular weight distributions of the polyesters are not as homogeneous as in the case of the PEO and PTHF polymers (see below).

Gel Permeation Chromatography. Polymers before Complexation. The average molecular weight, $\bar{M}_w$ and $\bar{M}_n$, as well as the polydispersity indices of the polyesters in their original forms were established by gel permeation chromatography. The chromatograms, shown in Figure 2a indicate clearly that the molecular weight distributions are not homogeneous, especially for PEA, PBA, and PTA. The distribution curves for PEA and PTA present two maxima which are associated with the presence of two polymers with distinct average molecular weights. The distribution curve of PBA reveals that this polyester is composed of four polymers of different average molecular weights. As for the PTG, it has a normal distribution approaching that of a Gaussian curve.

Polymers after Complexation. The aliphatic polyesters, PEA and PBA, have been recovered from their relative adducts by dissolving the urea matrix in an appropriate solvent (H_2O or CH_3OH). Then, these recovered polyesters have been examined by GPC. The chromatograms, shown in Figure 2b, indicate that the molecular weight distribution curves now have a Gaussian form. The comparison of this result with that obtained for the polyesters, PEA and PBA, before complexation, clearly indicates that the complexation of the polymers with urea has a purification effect. Furthermore, the average molecular weights and the polydispersity indices, listed in Table II, reveal a preferential complexation of urea with the longer chain fractions. It is a fact that for a given polymer, the stability of its urea complex increases with the length of the complexed chain. These preliminary results confirm the usefulness of urea–adduct complexation in order to decrease the polydispersity index of a polymer.

Differential Scanning Calorimetry. The thermograms shown in Figure 3 illustrate the thermal behavior, recorded between room temperature and 160 °C, of the inclusion compounds of urea with the aliphatic polyesters PEA, PBA, PTA, and PTG. Each of these curves shows the existence of a unique endothermic transition in a small temperature range, between 137.9 and 145.4 °C. The melting temperature and the enthalpy of fusion of the urea–aliphatic polyester adducts, are listed in Table III. The melting temperatures of the inclusion compounds are clearly higher than that of pure urea (132.7 °C) and than those of the corresponding polyesters (38–60 °C). The melting temperatures of the aliphatic polyesters in their pure state are also given in Table III. It seems that the polymers' melting temperatures are dependent upon the parity of the aliphatic chain. This is more obvious when the enthalpy of melting is expressed in terms of the number of atoms in the main chain because one finds two groups of values which are 3.25 and 3.57 kJ/atom for the urea–PEA and urea–PBA adducts and 2.70 and 2.72 kJ/atom for urea–PTA and urea–PTG adducts. One concludes that the urea–PEA and urea–PBA adducts are more stable than urea–PTA and urea–PTG adducts. The often observed parity effect in the polymers, with at least one aliphatic chain part, influences certain physical properties such as melting temperature, enthalpy and entropy of transformation, and the crystal structure of the polymer.[18,19] It has been reported that the reorientation of the polymer chain during the melting or crystallization process plays a determinant role in the dependency of the

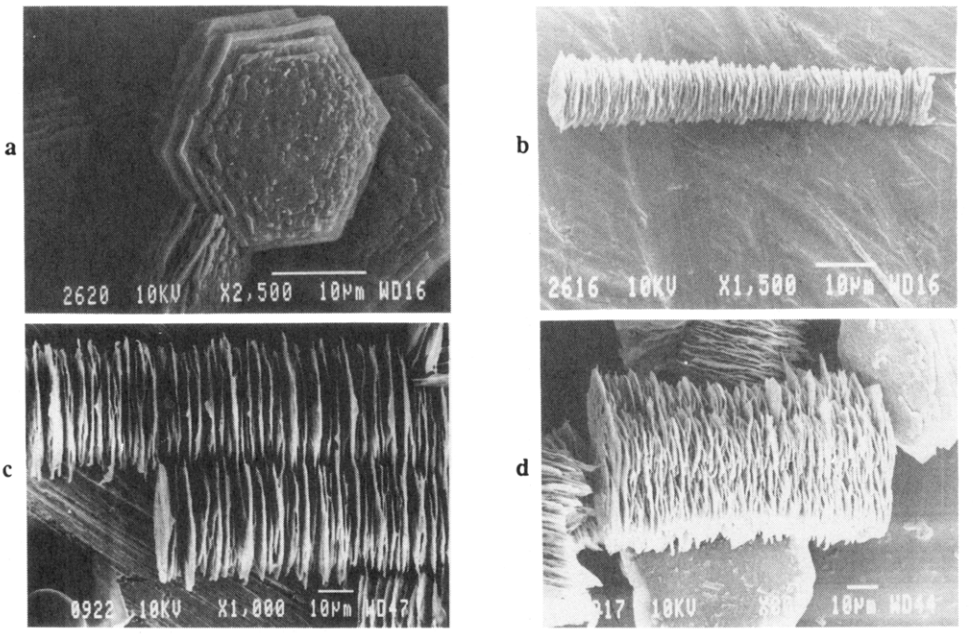

Figure 1. Scanning electron micrographs of crystals of the urea–polyester adducts: (a) crystal of urea–PEA adduct; (b) crystal of urea–PBA adduct; (c) crystal of urea–PTA adduct; (d) crystal of urea–PTG adduct.

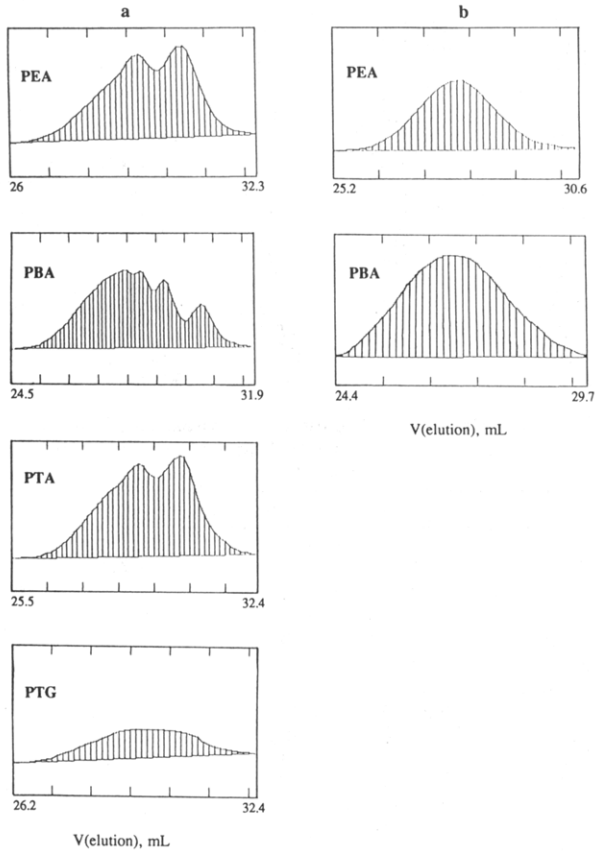

Figure 2. Elution volume in GPC of aliphatic polyesters: (a) polymer before the urea complex formation; (b) polymer after the urea complex formation.

temperature or the enthalpy of fusion on the parity of the aliphatic chain parts.[18] This does not seem to apply in our case, since the polymeric chains are oriented in the same manner in the channels and there are no chain–chain interactions. However, we have found that the enthalpy of fusion of the urea–polyester adducts is also related to the parity in the glycolic segment of the polyester. We thus conclude that the chain reorientation is not the dominant factor in this phenomenon, as was indicated.[18]

Table II. Molecular Mass Distributions and Polydispersity Indices of Polyesters before and after Formation of Urea Complexes

	PEA		PBA			
polyester	before	after	before	after	PTA	PTG
$\bar{M}_n$	2281	5888	5041	9624	2467	2285
$\bar{M}_w$	3211	7248	9605	13204	3645	3264
$\bar{M}_w/\bar{M}_n$	1.40	1.23	1.90	1.37	1.47	1.42

X-ray Diffraction Analysis. Unit Cell Determination. The unit cell dimensions of the compounds obtained with urea and PEA, PTA, and PTG aliphatic polyesters are listed in Table I. These data indicate that the three complexes crystallize in the hexagonal system already established by Smith[13] for the urea–*n*-alkane adducts. We have confirmed the existence of a unique crystal phase in the considered temperature range by thermal analysis. However, we noticed that during cooling, the cell contraction is more important in the lateral plane *ab* than in the *c* direction, $\Delta a/a = -0.85$ (PTA) and -1.0% (PTG) $\Delta c/c = -0.2\%$, for both urea–PTA and urea–PTG complexes. These results are comparable to that obtained in the case of the urea–PTHF adduct.[9]

The stoichiometry of these complexes is described as six urea molecules per *m* chemical units of the polymer: $[\text{urea}]_6{\cdot}[\text{O–(CH}_2)_x\text{–O–CO–(CH}_2)_y\text{–CO–}]_m$. Table IV shows that the calculated densities for $m = 1$ are clearly higher than those obtained by flotation. This leads us to think that there is less than a complete fully-extended chemical unit in the *c*-dimension of the unit cell. In other words only a fraction of the polymer chemical unit is present in the unit cell. We established this fraction to be $9/n$, where *n* is the number of atoms of the main chain of the aliphatic polyester chemical repeat, since the length of the chain, with nine carbon atoms, in its *trans* conformation is very close to the *c*-dimension. In this way the calculated densities are closer to those experimentally established (see Table IV). It has been shown, in the case of the urea–PTHF adduct,[9] that besides the polymer chains orientation disorder due to crystallographic symmetry there is also an incremental disorder, which makes it impossible to distinguish between oxygen and carbon atoms of the polymer chain. We have a similar situation in the case of urea

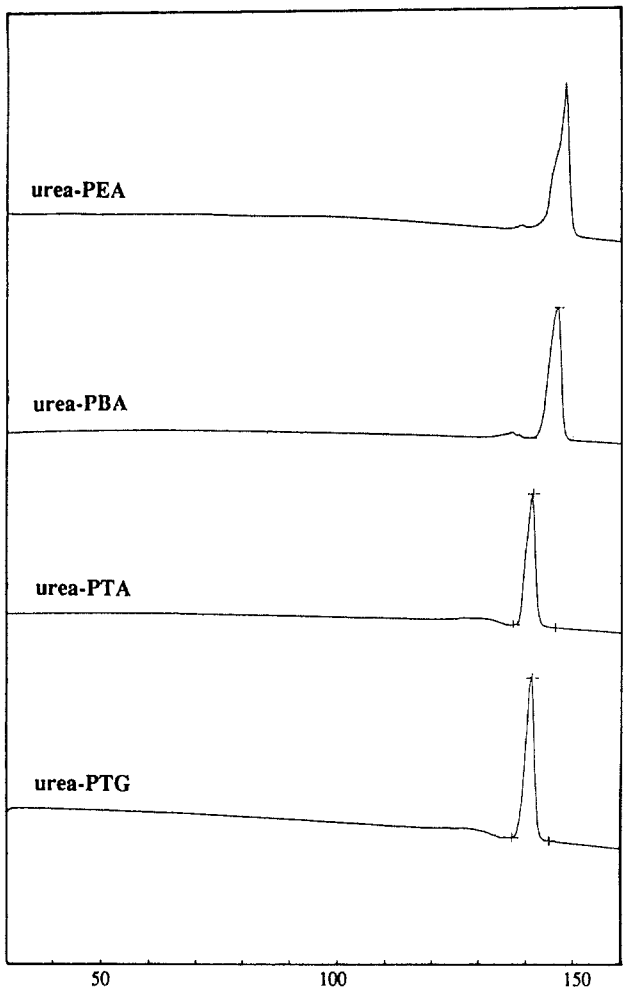

Figure 3. Thermal analysis curves of the urea–polyester adducts.

Table III. Thermal Analysis of Urea–Polyester Adducts[a]

	complexed polyester			
polyester	t_f	ΔH_f	$\Delta H_f'$	pure polyester t_f
PEA	145.4	34.24	3.25	52–54
PBA	143.5	42.85	3.57	56–60
PTA	137.9	29.74	2.70	38
PTG	138.2	27.22	2.72	39

[a] Comparison of the melting temperature, t_f (°C) and the enthalpy of fusion, ΔH (kJ/chemical unit) and $\Delta H'$ (kJ/chain atom).

Table IV. Stoichiometry of Urea–Polyester Complexes $[urea]_6\cdot[O-(CH_2)_x-O-CO-(CH_2)_y-CO)-]_m$

	urea–PEA		urea–PTA		urea–PTG	
density	$x = 2$, $m = 1$	$y = 4$, $m = 0.90$	$x = 3$, $m = 1$	$y = 4$, $m = 0.82$	$x = 3$, $m = 1$	$y = 3$, $m = 0.90$
d_{exp}	1.323		1.271		1.301	
d_{cal}	1.381	1.325	1.406	1.320	1.378	1.330

inclusion compounds with aliphatic polyesters. The hydrogen-bonded urea molecules impose the c value of the host cell. This value is, in most cases, independent of the chemical nature of the guest chain. The existence of the relatively weak interactions of the van der Waals type, between the urea molecules and the guest chain, explains this relative autonomy of the guest polyester. On the basis of these considerations, we have undertaken the determination of the crystal structures of the urea–PTA and urea–PTG adducts.

Crystal Structure Determinations. The crystal structures of the urea–PTA and urea–PTG adducts, were

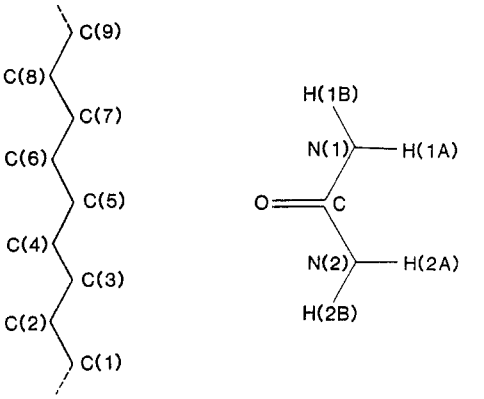

Figure 4. Atomic numbering adopted for the urea–PTA and urea–PTG adducts. The O(10) and O(11) carbonyl atoms cannot be represented since they are distributed statistically along the polymer chain.

Table V. Fractional Atomic Coordinates and Their Esd's for the Urea–PTA Adduct (×10⁴) and U_{eq} or U_{iso} (×10³, Å²), at Room Temperature

atom	x	y	z	U_{eq}
O	3198(3)	6805(3)	1278(2)	45
C	4079(3)	5921(3)	1278(2)	41
N(1)	4819(4)	5697(4)	258(3)	59
N(2)	4308(4)	5194(4)	2302(3)	60
H(1Au)	5549(13)	5170(13)	295(15)	71
H(1Bu)	4569(15)	6050(15)	-459(10)	82
H(2Au)	5137(12)	4780(14)	2279(15)	78
H(2Bu)	3825(15)	5386(15)	2986(11)	81
C(1)	-215(15)	-522(14)	10585	210
C(2)	1046(13)	573(15)	9576(8)	162
C(3)	58(13)	426(14)	8429(8)	105
C(4)	647(12)	-227(13)	7348(8)	69
C(5)	-170(13)	47(13)	6224(8)	81
C(6)	-33(14)	-857(13)	5101(8)	86
C(7)	29(16)	229(13)	4008(8)	184
C(8)	-411(16)	-806(13)	2847(7)	162
C(9)	200(16)	445(13)	1773	146
O(10)	-1397	-231	12072	149
O(11)	1363	-437	11778	159

Table VI. Fractional Atomic Coordinates and Their Esd's for the Urea–PTG Adduct (×10⁴) and U_{eq} or U_{iso} (×10³, Å²), at 161 K

atom	x	y	z	U_{eq}
O	3175(5)	6838(6)	1341(13)	67
C	4066(8)	5934(8)	1341(13)	66
N(1)	4858(8)	5755(8)	332(13)	75
N(2)	4267(8)	5152(8)	2368(12)	76
H(1Au)	5729(21)	5375(25)	308(29)	111
H(1Bu)	4622(29)	6226(28)	-344(19)	127
H(2Au)	5186(20)	4833(26)	2360(29)	84
H(2Bu)	4081(30)	5491(29)	3112(17)	119
C(1)	-158(26)	-501(25)	10585	277
C(2)	1161(20)	506(24)	9566(10)	106
C(3)	240(24)	458(27)	8406(11)	178
C(4)	982(22)	-30(26)	7313(11)	80
C(5)	-76(23)	-50(26)	6212(12)	86
C(6)	282(25)	-796(24)	5081(11)	101
C(7)	-341(26)	-197(25)	3982(11)	207
C(8)	13(29)	-854(22)	2815(10)	228
C(9)	415(29)	451(22)	1773	225
O(10)	-2074	9407	1908	98
O(11)	1615	1085	3956	127

established in the $P6_1$ space group. We used the diffractometric data recorded at room temperature for the urea–PTA adduct and those at low temperature (−112 °C) in the case of the urea–PTG adduct. As mentioned above, we considered the stoichiometries which gave the densities closest to the observed values. The urea adduct formulas are thus $[urea]_6\cdot[O-(CH_2)_3-O-CO-(CH_2)_4-CO-]_{0.82}$ for the urea–PTA adduct and $[urea]_6\cdot[O-(CH_2)_3-O-CO-(CH_2)_3-$

Table VII. Comparison of the Bond Distances (Å) and Bond Angles (deg) of the Urea Molecule in the Complexes or in the Pure State

	urea–PTA 298 K	urea–PTG 161 K	urea–PTHF[9] 298 K	pure urea[19] 295 K	urea–POE[8] 173 K
C–O	1.257(4)	1.260(5)	1.259(2)	1.260(3)	1.256(4)–1.257(3)
C–N(1)	1.333(4)	1.329(9)	1.330(6)	1.352(2)	1.336(3)–1.335(3)
C–N(2)	1.331(3)	1.347(9)	1.339(6)		1.342(3)
O–C–N(1)	121.0(2)	120.9(9)	121.0(3)	121.7(7)	121.7(2)–121.8(2)
O–C–N(2)	120.7(2)	120.9(9)	120.6(3)		121.3(2)
N(1)–C–N(2)	118.3(3)	118.2(9)	118.4(3)	116.6(1)	116.6(2)–116.9(2)

Table VIII. Comparison of the Hydrogen Bonds between Urea Molecules Forming the Channels, in Urea–PTA, Urea–PTG, and Urea–PTHF Adducts

	distance N---O, Å			angle N–H---O, deg		
	PTA	PTG	PTHF	PTA	PTG	PTHF
N(1)–H(1a)---O(01$\bar{1}$)3[a]	3.033(3)	3.002(9)	3.032(5)	175	163	176
N(1)–H(1b)---O(00$\bar{1}$)5	2.988(4)	2.949(7)	2.974(3)	149	154	157
N(2)–H(2a)---O(100)6	2.991(4)	2.927(7)	2.977(3)	162	155	161
N(2)–H(2b)---O(110)2	3.029(3)	3.008(9)	3.031(5)	162	168	171

[a] Symmetry code: 2, $-y, x-y, z+{}^1/_3$, $-x+y, -x, z+{}^2/_3$; 5, $y, -x+y, z+{}^5/_6$; 6, $x-y, x, z+{}^1/_6$.

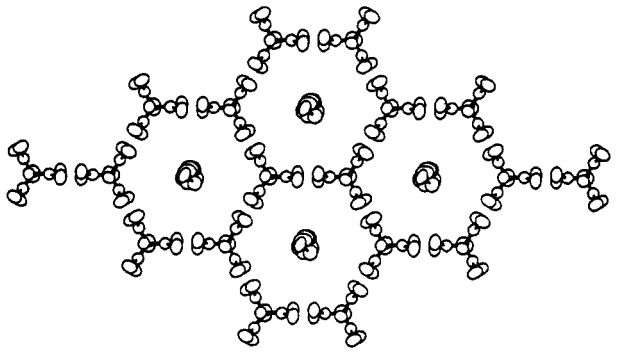

Figure 5. View down the *c*-axis of the urea molecule channels occupied by the PTA or PTG polyester chains. The hydrogen atoms have been omitted for clarity.

Table IX. Bond Distances (Å) and Bond Angles (deg) and Their Esd's in the PTA and PTG Polyester Chains Complexed with Urea Molecules

	distance			angles	
	PTA	PTG		PTA	PTG
C(1)–C(2)	1.478(13)	1.482(2)	C(1)–C(2)–C(3)	114(1)	115(1)
C(2)–C(3)	1.473(14)	1.471(20)	C(2)–C(3)–C(4)	117(1)	116(1)
C(3)–C(4)	1.482(14)	1.485(20)	C(3)–C(4)–C(5)	111(1)	111(1)
C(4)–C(5)	1.477(14)	1.481(20)	C(4)–C(5)–C(6)	118(1)	118(2)
C(5)–C(6)	1.476(13)	1.476(20)	C(5)–C(6)–C(7)	111(1)	113(2)
C(6)–C(7)	1.483(13)	1.484(20)	C(6)–C(7)–C(8)	115(1)	116(2)
C(7)–C(8)	1.477(12)	1.474(20)	C(7)–C(8)–C(9)	113(1)	115(2)
C(8)–C(9)	1.478(10)	1.483(16)	C(8)–C(9)–C(1′)	115(1)	115(1)
C(9)–C(1′)[a]	1.479(6)	1.472(10)	C(9)–C(1′)–C(2′)	116(1)	116(1)

[a] Primed atoms are obtained by translation of $-c$.

CO–]$_{0.90}$ for the urea–PTG adduct. The final atomic coordinates and their equivalent thermal parameters U_{eq} are listed in Tables V and VI, while the numbering of the atoms is schematically represented in Figure 4.

Because of the existence of the translational disorder of the guest chain and the equivalence of an oxygen atom and a methylene group (CH_2), in terms of electronic density, it is impossible to distinguish them. The oxygen atoms of the carbonyl groups cannot be localized within the channel because of their high disorder level. Thus all the main chain atoms are viewed as carbon atoms. The type of disorder encountered here has been already described for the urea–PTHF adducts[9] and was illustrated by Figure 4 in that reference. During the refinement process, the bond distances, d(C–C), and the bond angles, θ(C–C–C), of the polyester chains were subjected to constraints, such as $d(C_I–C_{I+1}) = 1.48 \pm 0.01$ Å and $d(C_I–C_{I+2}) = 2.46 \pm 0.02$ Å. The oxygen atoms of the two carbonyl groups were considered but with their initial coordinates in the atom list. Since we cannot distinguish or recognize specifically the atoms of the main chain, the oxygen atoms of the CO groups are distributed statistically along the chain. Instead of placing them on the nine positions, with very low occupancy factors, we decided to put each of them at a position corresponding to the highest residual electronic density. It is interesting to point out that the thermal parameters associated with the atoms of the polymer chains are not much larger than those of the urea molecules. The description of the disorder is thus further supported.

Table X. Torsion Angles (deg) in the PTA and PTG Polyester Chains in Their Urea Complexes

	PTA	PTG
C(1)–C(2)–C(3)–C(4)	−124.0(9)	−133(2)
C(2)–C(3)–C(4)–C(5)	−168.9(9)	179(2)
C(3)–C(4)–C(5)–C(6)	−168.3(9)	−171(2)
C(4)–C(5)–C(6)–C(7)	−151.0(9)	−162(2)
C(5)–C(6)–C(7)–C(8)	−162.2(9)	179(2)
C(6)–C(7)–C(8)–C(9)	−163.1(9)	−148(3)
C(7)–C(8)–C(9)–C(1′)[a]	−179.7(9)	−151(2)
C(8)–C(9)–C(1′)–C(2′)	−153.5(9)	−141(2)
C(9)–C(1′)–C(2′)–C(3′)	−136.3(9)	−140(2)

[a] Primed atoms are obtained by translation of $-c$.

Urea Molecules. The urea molecules in the urea–PTA and the urea–PTG adducts, as in the urea inclusion compounds with *n*-alkanes[13] and PTHF,[9] are placed in such a way that they form hexagonal channels parallel to the *c*-axis. A view down the *c*-axis of the channel is shown in Figure 4. The urea molecules are connected to one another by hydrogen bonds. The bond distances and angles in the urea molecules are comparable to those found in pure urea[19,20] or in other urea adducts, as shown in Table VII. Low temperature or room temperature measurements do not show significant variations in the bond distances or the bond angles. The N···O hydrogen-bonded distances listed in Table VIII, in the range 2.927–3.033 Å, are fairly similar to those found in the urea–PTHF adduct, indicating the existence of relatively strong hydrogen bonds. The urea molecule is planar, and its mean plane is tilted from the *c*-axis by about 10° for the urea–PTA adduct and 11° for the urea–PTG adduct. A comparison can be made with the urea–PTHF adduct,[9] in which the mean plane of the urea molecule was tilted from the *c*-axis by about 9°.

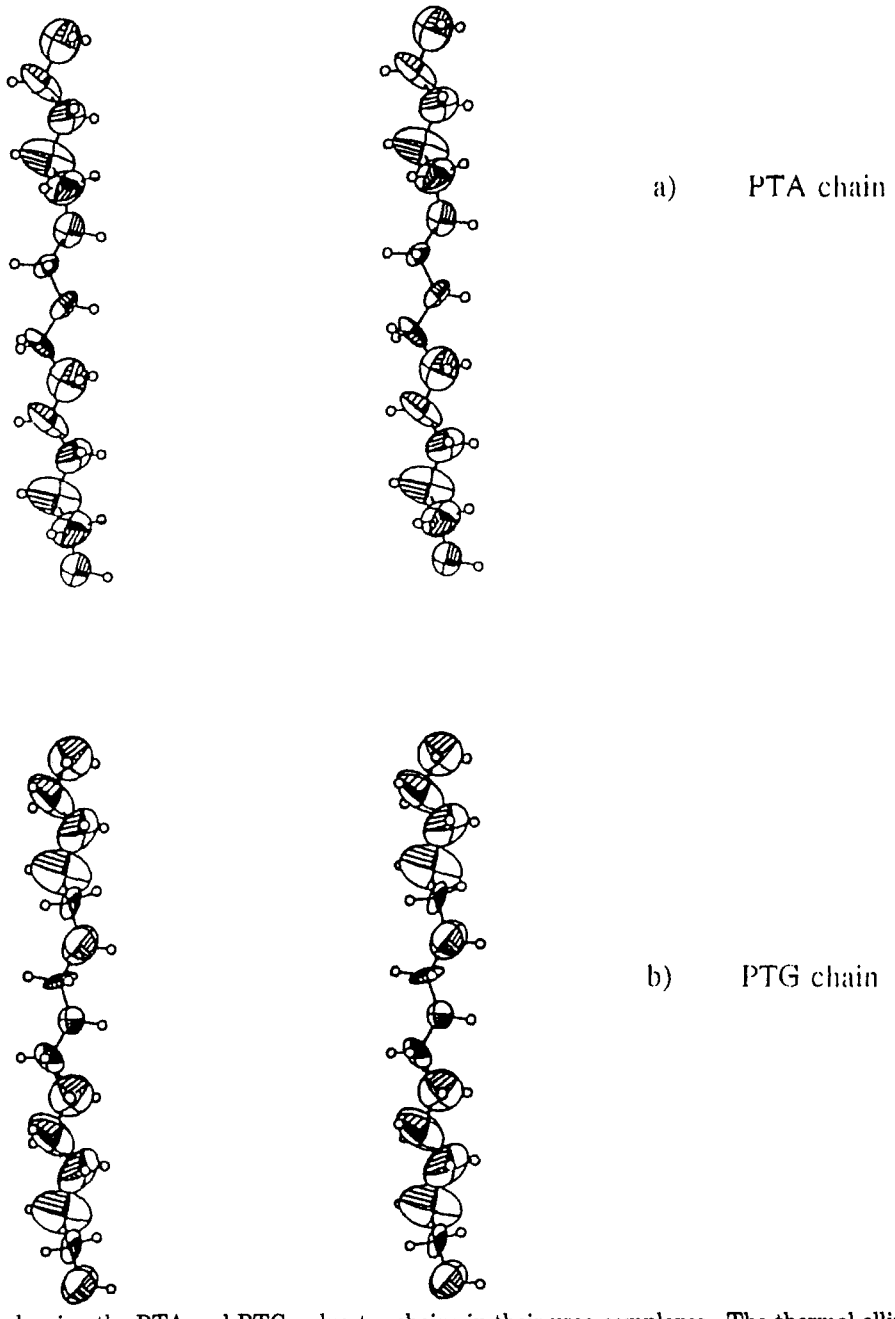

Figure 6. Stereopairs showing the PTA and PTG polyester chains in their urea complexes. The thermal ellipsoids correspond to a 50% probability.

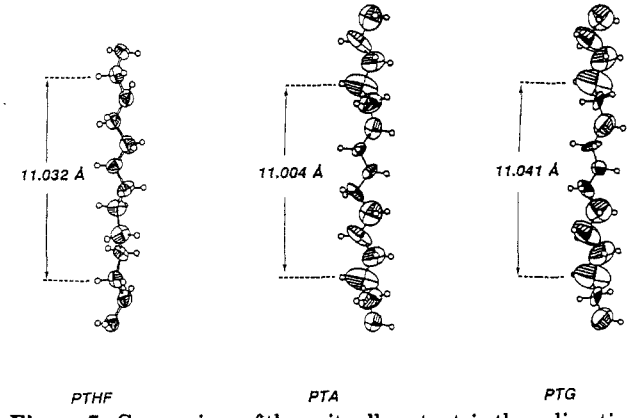

Figure 7. Comparison of the unit cell content, in the *c*-direction, of three "isostructural" urea–polymer adducts.

Aliphatic Polyester Chain. The aliphatic polyester chain is clearly located within the channel formed by the urea molecules (Figure 5). The 6_1 rotation axis coincides with the polymer chain axis. Since the polymer chain does not have the 6_1 symmetry and only one chain can exist in one channel, the chain occupies $^1/_6$ in each of the six symmetry related positions. Since, as indicated earlier, one cannot distinguish an oxygen atom from a CH_2 group, all the atoms in the asymmetric unit are identified as carbon atoms. The bond distances and valence angles in the polymer chain, such as listed in Table IX, are in fact the weighted averages of distances, $C(sp^3)$–$C(sp^3)$, $C(sp^3)$–$C(sp^2)$, $C(sp^3)$–$O(sp^3)$, and $C(sp^2)$–$O(sp^3)$, and of angles, $C(sp^3)$–$C(sp^3)$–$C(sp^3)$, $C(sp^3)$–$C(sp^3)$–$C(sp^2)$, $C(sp^3)$–$C(sp^3)$–$O(sp^3)$, $C(sp^3)$–$C(sp^2)$–$O(sp^3)$, and $C(sp^2)$–$O(sp^3)$–$C(sp^3)$. The torsion angles which have values in the range 125–180° for the PTA chain and from 133 to 181° for the PTG chain (see Table X), indicate that although there are some large deviations, on the whole the polymer chains within the channels have a nearly *trans* conformation. The aliphatic polyester chains in their urea complexes are then

only affected by slight distortions, as illustrated by Figure 6.

In this conformation the lengths of PTA and PTG chemical units, i.e., the fiber repeats, are calculated as 13.449 and 12.256 Å, respectively, which differ considerably from the values of 10.8 and 7.7 Å reported by Fuller et al.[21] for these polymers in their pure state. These authors have also indicated that, in the trimethylene family of polyesters, the chain conformation consists of two parts, an acid one which is entirely *trans* and a glycol part whose conformation is probably *trans gauche gauche trans*.

Our results show that the PTA and PTG aliphatic polyester chains in their urea complexes underwent significant modifications, which took place essentially in the glycolic part. Indeed, without the conformation transformation from *tggt* to a nearly *trans* conformation of the glycolic part, the polymer chain could not be accommodated within the urea channel. The aliphatic polyester chains in their complexes adopt a nearly *trans* conformation, which is favored by the smallness of the channel diameter and the known flexibility of the aliphatic polyester chains.[22,23]

It is of interest to note that the structures of the urea–PTA, urea–PTG and urea–PTHF[9] are to all intents identical. In all three adducts the polymer chain is in a nearly fully *trans* conformation. The important point though is that whether the guest polymer is a polyester or a polyether, it appears in the adduct as a polyethylene chain. The three polymer chains are drawn side by side in Figure 7. The polymer content of the unit cell is dictated by the value of the *c*-dimension, and in all three examples, the polymer backbone is seen to have only 9 atoms although the chemical repeats in PTA, PTG, and PTHF contain 11, 10, and 10 atoms, respectively. To all intents, these three urea–polymer adducts are isostructural. Thus when the host–guest interactions are essentially of the van der Waals type, the *c*-dimension is independent of the nature of the included chain. However, the existence of hydrogen bonds, as in the case of the urea–PEO adduct, brings about a totally different type of structure.[8]

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Supplementary Material Available: Tables listing hydrogen atom coordinates and anisotropic temperature factors with their esd's (4 pages); two tables of observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Monobe, K.; Yokoyama, F. *J. Macromol. Sci.—Phys.* **1973**, *B8*, 277.
(2) Yokoyama, F.; Monobe, K. *Polymer* **1980**, *21*, 968.
(3) Parrod, J.; Kohler, A. *J. Polym. Sci.* **1960**, *48*, 457.
(4) Bailey, F. E., Jr.; France, H. G. *J. Polym. Sci.* **1961**, *49*, 397.
(5) Tadokoro, H.; Yoshihara, T.; Chatani, Y.; Murahashi, S. *Polym. Lett.* **1964**, *2*, 363.
(6) Suehiro, K.; Nagano, Y. *Makromol. Chem.* **1983**, *184*, 669.
(7) Suehiro, K.; Urabe, A.; Yoshitake, Y.; Nagano, Y. *Makromol. Chem.* **1984**, *185*, 2467.
(8) Chenite, A.; Brisse, F. *Macromolecules* **1991**, *24*, 2221.
(9) Chenite, A.; Brisse, F. *Macromolecules* **1992**, *25*, 776.
(10) Brown, F. J., Jr.; White, D. M. *J. Am. Chem. Soc.* **1960**, *82*, 5678.
(11) Chatani, Y.; Nakatani, S.; Tadokoro, H. *Macromolecules* **1970**, *3*, 481.
(12) Kohler, A.; Mayer, R.; Hild, G.; Parrod, J. *Compt. Rend. Acad. Sci. Paris* **1964**, *258*, 5439.
(13) Smith, A. E. *Acta Crystallogr.* **1952**, *5*, 224.
(14) Ahmed, F. R.; Hall, S. R.; Pippy, M. E.; Huber, C. P. *J. Appl. Crystallogr.* **1973**, *6*, 309.
(15) Sheldrick, G. M. *SHELX86, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1986.
(16) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321.
(17) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.
(18) Ueberreiter, K.; Karl, V. H.; Altmeyer, A. *Eur. Polym. J.* **1978**, *14*, 1045.
(19) Ober, Ch. K.; Jin, J.; Lenz, R. W. *Adv. Polym. Sci.* **1984**, *59*, 103.
(20) Pryor, A.; Sanger, P. L. *Acta Crystallogr.* **1970**, *A26*, 543.
(21) Fuller, C. S.; Frosh, C. J.; Pape, N. R. *J. Am. Chem. Soc.* **1942**, *42*, 154.
(22) Daubeny, R. De P.; Bunn, C. W.; Brown, C. J. *Proc. R. Soc.* **1954**, *226*, 531.
(23) Turner-Jones, A.; Bunn, C. W. *Acta Crystallogr.* **1962**, *15*, 105.