

Molecular association complex of urea with polyethylene:

3. Structural studies of the complex

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The crystal structure of urea-polyethylene complex in the hexagonal form, obtained by one of our preparation methods, is analysed by X-ray power diffractometry. In this analysis, the fixed molecular parameters of urea are used, and three models with respect to rotational disorder of the guest polyethylene molecule are assumed. It is shown that the host lattice structure constructed by urea molecules is essentially the same as that of urea-n-paraffin complex. Effects of the disorder structure of the guest on X-ray scattering of the complex are presented. However, there is a difficulty in identifying the disorder structure by X-ray analysis. With the aid of a potential energy calculation between the hexagonal urea tunnel and the guest molecule, a rotational disorder model is preferred.

Keywords Urea; polyethylene; complex; adduct; inclusion compound; crystal structure; thermal properties; potential energy

INTRODUCTION

Our preliminary morphological studies^{1,2} of urea-polyethylene complex revealed that the complex consists of large lamellar crystals of the order of 1000 Å in size, and the guest polyethylene molecules are enclosed perpendicularly to the lamella, as extended chains in the host urea tunnels. Urea-n-paraffin complex is a single needle-like crystal, in which the guest paraffins are longitudinally stacked with van der Waals contacts of the end groups³.

The solid phase transition^{4,5} of urea-n-paraffin complex between orthorhombic (low-temperature form) and hexagonal (high-temperature form) has been revealed such that, in the former, the guest molecules exhibit a definite orientation about the tunnel axis, while in the latter, they have a rotational disorder around the axis. Such a type of transition was also discovered in urea-polyethylene complex by X-ray and thermal analyses⁶. It has been indicated that the transition temperatures increase with increasing chain length, e.g. those for urea complexes with n-hexadecane, n-hexatriacontane and polyethylene are -121°C ⁷, -55°C ⁵ and 8°C ⁶, respectively.

Here, the crystal structure of urea-polyethylene complex in the hexagonal form is analysed by X-ray powder diffractometry. It is assumed that guest polyethylene molecules have one of the rotational disorders whose models^{3,5} have been proposed for guest paraffin molecules in urea-n-paraffin complex. Preceding the X-ray analysis, the effects of the disorders on X-ray scattering will be presented. A potential energy calculation between the host urea tunnel and the guest polyethylene molecule will also be carried out in order to confirm the disorder structure.

EXPERIMENTAL

Preparation of urea complexes

A commercial linear polyethylene of viscosity average molecular weight 59 000 was used to prepare urea-polyethylene complex. The powder complexes were obtained from one of our preparation systems²: solid tetragonal urea with seeds and polyethylene solution in xylene at 120°C for 48 h. The complexes were used for the d.s.c. thermal analysis, and their milled fine powder for the X-ray measurements.

Urea complexes with n-paraffins whose carbon numbers are 28, 32, 36, 40 and 44 were prepared from urea-isopropanol-n-paraffin system. These complexes were provided for the d.s.c. thermal analysis.

D.s.c. thermal analysis

A Perkin-Elmer differential scanning calorimeter (DSC-1) was used for thermal analysis of the complexes. The temperature and amplitude scales were calibrated by using indium at the same scanning rate as the sample, $5^{\circ}\text{C min}^{-1}$.

X-ray powder diffractometric measurements

An X-ray powder diffractometer with Ni-filtered Cu K α radiation (wavelength 1.5418 Å) was used for recording the diffraction intensities of urea-polyethylene complex, with continuous scanning techniques. At smaller ($2\theta < 36^{\circ}$) and larger ($2\theta > 32^{\circ}$) Bragg angles, the symmetrical transmission and symmetrical reflection methods were applied respectively. The overall peak intensity between 32° and 36° , which was measured by these two methods, was utilized for the scaling of all the other intensities. The powder pattern in the 2θ range up to

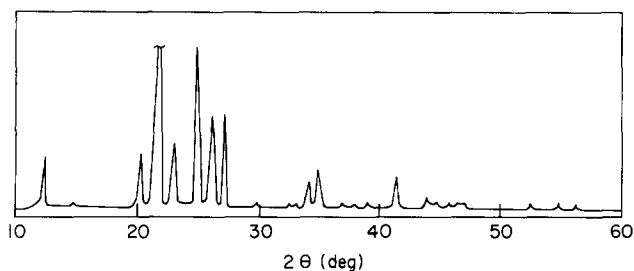


Figure 1 Schematic representation of X-ray diffraction pattern of urea-polyethylene complex in the region $2\theta = 10-60^\circ$

about 60° was used for the analysis. Its schematic representation is shown in Figure 1.

Observed structure factors

The observed structure factors were evaluated after the corrections of the measured intensities for the Lorenz polarization, the absorption and the multiplicity. Preceding these evaluations, however, some partly superimposed reflections, which were in the range $2\theta > 32^\circ$, were separated into component peaks by the least-squares method⁸. Then, the modified Lorentz function with an asymmetrical parameter was used as a shape function⁹ for the diffraction profile. Measurement by the symmetrical reflection method gave a largely distorted asymmetrical profile, due to many instrumental factors¹⁰. This function exhibited satisfactory curve fitting to the observed profiles. The observed structure factors about the completely superimposed reflections were subjected to the relation $F_0 = F_c \sqrt{I_0 / \sum m F_c^2}$ where I_0 is the overall observed intensity and m is the multiplicity.

BASIS OF THE X-RAY ANALYSIS

Representation of the host lattice structure

In this analysis, the molecular parameters of urea in the hexagonal urea-polyethylene complex are assumed as follows: bond lengths C=O, 1.270 Å; C-N, 1.326 Å; and N-H, 0.88 Å and 0.68 Å; and bond angles OCN, 121.0° ; and CNH, 119° and 109° . These were given by Caron and Donohue¹¹ for the tetragonal urea. Then, the determination of the host urea structure of the hexagonal urea complex with space group $P6_122$ is attributed to that of the following two parameters about one of six urea molecules in the unit cell: the molecular displacement along the twofold axis at the C=O bond and the molecular orientation around this axis.

First, let us represent the atomic coordinates in the urea molecule by the Cartesian coordinate system (X_1, Y_1), where the molecular plane is in the $X_1 Y_1$ plane and the C=O bond is directed along the X_1 axis, as shown in Figure 2a. Secondly, this coordinate system is attached to the hexagonal coordinate system (X_2, Y_2, Z_2) such that the origin in the former system is situated at a special point ($a/3, 2a/3, c/4$) and the X_1 axis is directed along the twofold axis, as shown in Figure 2b. (This figure represents the disposition of the three urea molecules whose C=O levels are at $c/4$; the tunnel structure of the host lattice is constructed by the symmetry operation of 6_1 screw axis around c -axis; for details, see ref. 3.) Then the molecule is allowed to displace along the X_1 axis and to rotate around the axis. Here, let u denote a position of the oxygen atom projected into the cavity from the above point, and φ a

rotation angle of the planar urea molecule measured relative to the $X_2 Y_2$ plane. According to procedures of coordinate transformation, we have the relation about the atomic coordinates of the urea molecule

$$\begin{pmatrix} X_2 \\ Y_2 \\ Z_2 \end{pmatrix} = \begin{pmatrix} 1/\sqrt{3} & -\cos \varphi & \sin \varphi \\ 2/\sqrt{3} & 0 & 0 \\ 0 & \sin \varphi & \cos \varphi \end{pmatrix} \begin{pmatrix} X_1 \\ Y_1 \\ 0 \end{pmatrix} + \begin{pmatrix} a/3 \\ 2a/3 \\ c/4 \end{pmatrix}$$

where X_1 in each atom is expressed as a function of u and Y_1 is a constant derived from only the molecular parameters given above. In this study, the host lattice parameters u and φ are determined by the least-squares refinement.

Effects of rotational disorder of guest molecules on X-ray scattering

In the hexagonal urea-*n*-paraffin complexes, three models^{3,5} of the rotational disorder of guest molecules have been proposed. In the first, guest molecules rotate

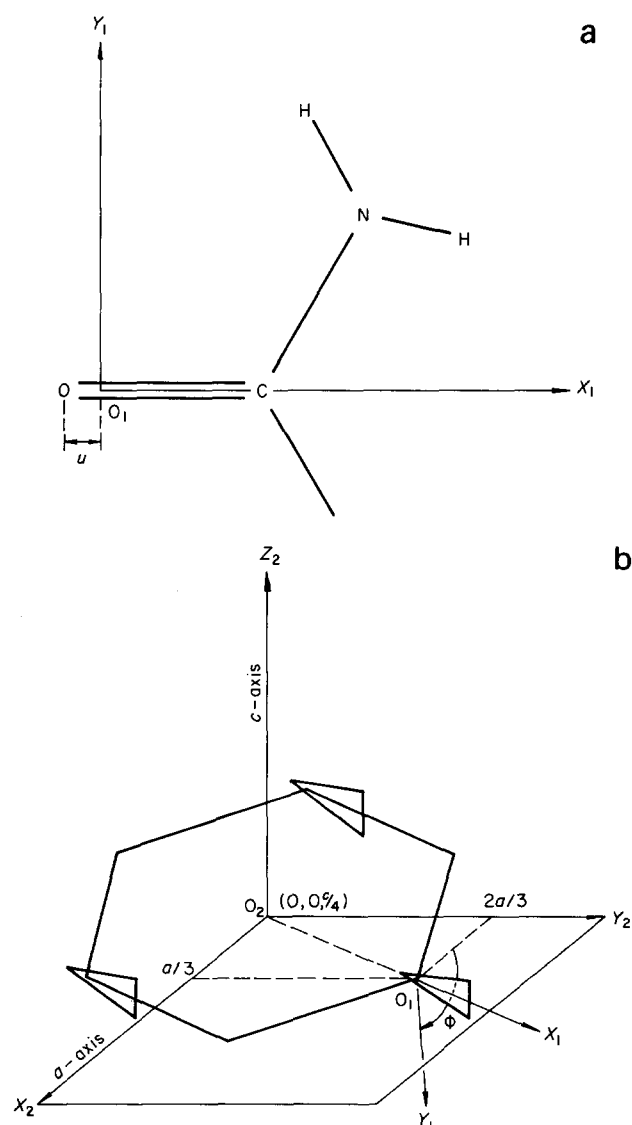


Figure 2 Schematic representation about coordinate transformation of urea molecule. (a) Representation of the atomic coordinates by the Cartesian coordinate system. (b) Relation between this system and the hexagonal coordinate system; triangles denote urea molecules

freely around the long axis independently of each other (here, let us call this free rotator model, Model I). In the other two, guest molecules are disposed statistically around the long axis with a sixfold rotation symmetry: zigzag plane of a guest molecule parallel to the a - c plane is Model II (see ref. 5); that with an angle of 30° relative to the a - c plane is Model III (see ref. 3). In any model, it is assumed that guest chain molecules behave as a rigid rotator and there is no phase relationship of the molecular orientation between the different tunnels.

In the early X-ray work by Smith³, the formula of the structure factor for Model I was derived by using the expression given by Bijvoet and Ketelaar¹² for a free rotator. That for Model III was represented by the procedure in which the statistically possible positions of a chain were projected along orthohexagonal a and b axes and then the Fourier transform of these configurations was made. In the recent X-ray work by Chatani *et al.*,⁵ the formula for these three models was shown by using the equation given by Cochran, Crick and Vand¹³ for a helical molecule. In this section, according to the ordinary structure factor equation, the expressions of the structure factor for the guest polyethylene which has the rotational disorders indicated above are presented, and then the effects of these disorders on X-ray scattering are mentioned.

The structure factor of a lattice containing one molecule in a urea tunnel can be expressed by the form

$$F_G(h,k,l_G) = \sum_j f_j \exp\{2\pi i [Rr_j \cos(\psi - \varphi_j) + l_G z_j / c_G]\} \quad (2)$$

Here the subscript G refers to the guest molecule, and j to the constituent atoms in one ethylene unit. R , ψ and l_G/c_G are the cylindrical coordinates of a point in the reciprocal space. f_j is the atomic scattering factor. r_j , φ_j and z_j are the cylindrical coordinates of the j th atom, which are based on the assumption of the molecular parameters of polyethylene: bond lengths C-C, 1.54 Å; and C-H, 1.09 Å; and bond angles CCC=HCH=tetrahedral angle, $109^\circ 28'$. Then the fibre period $c_G = 2.515$ Å is derived.

For convenience, let us introduce a variable χ which denotes a rotation angle of the zigzag plane measured relative to the z - c plane. Then, φ_j in (2) is rewritten as $\chi + \varphi_j$, and hence φ_j is defined as an intramolecular parameter. Now, since the polyethylene molecule has the 2_1 helical conformation, a pair of (r_j, φ_j, z_j) and $(r_j, \varphi_j + \pi, z_j + c_G/2)$ necessarily appears. Any of the above rotational disorder models is regarded as a kind of rotator with a statistical evenfold symmetry around the long axis; a pair of χ and $\chi + \pi$ exists. If these conditions are substituted in (2), we have the structure factor averaged over the possible orientations, in the form

$$\langle F_G(h,k,l_G) \rangle_\chi = \sum_j f_j [1 + \exp(i\pi l_G)] \langle \exp\{2\pi i Rr_j \cos[\psi - (\chi + \varphi_j)]\} \rangle_\chi \exp(2\pi i l_G z_j / c_G) \quad (3)$$

where j refers to one methylene. According to the definition for the models, this equation gives the formulae for the structure factor per methylene as follows.

(a) Model I

l_G even

$$\langle F_G(h,k,l_G) \rangle_\chi = \sum_j f_j J_0(2\pi Rr_j) \exp(2\pi i l_G z_j / c_G) \quad (4a)$$

where J_0 is the Bessel function of order zero.

l_G odd

$$\langle F_G(h,k,l_G) \rangle_\chi = 0 \quad (4b)$$

(b) Model II and Model III

l_G even

$$\langle F_G(h,k,l_G) \rangle_\chi = \frac{1}{3} \sum_{j=1}^3 \sum_{n=1}^3 f_j \cos(2\pi Rr_j \cos\{\psi - [\chi_0 + \frac{1}{3}\pi(n-1) + \varphi_j]\}) \times \exp(X\pi i l_G z_j / c_G) \quad (5a)$$

l_G odd

$$\langle F_G(h,k,l_G) \rangle_\chi = 0 \quad (5b)$$

where χ_0 is named the setting angle⁵; $\chi_0 = 0$ for Model II and $\chi_0 = \pi/6$ for Model III.

Equations (4b) and (5b) indicate an extinction law of the Bragg scattering from a lattice containing one 2_1 helical molecule which has a rotational disorder with a statistical evenfold symmetry around the long axis. In the X-ray rotation photograph of urea-polyethylene complex¹⁴, the Bragg scattering on the first layer line about the fibre period of the guest was not observed; instead, we observed only faint diffuse streaks, whose position in the reciprocal space was interpreted by the fibre period assumed here.

In this study, the powder diffraction pattern which is measured in the 2θ region below 60° is used. Then, the orders of layer lines with respect to the fibre period which should be taken into account are $l_G = 0$ and ± 1 , as in the case of Cu K α radiation, $2\theta \geq 35.7^\circ$ for $l_G = \pm 1$ and $2\theta \geq 75.6^\circ$ for $l_G = \pm 2$. The background intensity levels in the powder pattern are smooth against 2θ . The diffuse scatterings resulting from the first layer line will be distributed over the wide 2θ range as a background in the powder pattern.

Since the equatorial structure factor of the guest molecule is combined with that of the host urea lattice, the structure factor of the complex in the equator is given by

$$F(h,k,0) = F_H(h,k,0) + m \langle F_G(h,k,0) \rangle_\chi \quad (6)$$

where the subscript H denotes the host lattice. The second term corresponds to (4a) or (5a), and m is the number of methylenes per host unit cell, which is estimated to be 8.76 by using the c dimension of the host,² 11.02 Å, and the fibre period, 2.515 Å. Such different identity periods along the c -axis give the independent layer reflections of each lattice. Then, the structure factor of the complex has no contribution from the guest lattice, and hence can be written by

$$F(h,k,l) = F_H(h,k,l) \quad (7)$$

Table 1 Observed and calculated structure factors of urea-polyethylene complex

$h k \cdot l$	$ F_o $	$ F_c $	$h k \cdot l$	$ F_o $	$ F_c $
1 0 · 0	14.2	15.6	3 1 · 1	14.2	15.9
1 0 · 1	3.7	3.2	1 1 · 5	8.1	9.1
1 0 · 2	20.8	21.7	2 2 · 2	14.2	15.9
1 1 · 0	77.4	75.5	2 1 · 4	9.8	11.0
1 1 · 1	27.9	29.5	2 0 · 5	7.0	8.0
2 0 · 0	65.2	65.5	3 1 · 2	5.1	5.9
2 0 · 1	38.7	39.6	0 0 · 6	7.3	8.3
1 1 · 2	14.5	13.3	3 0 · 4	11.6	12.3
1 0 · 3	37.6	34.4	2 2 · 3	4.0	4.3
2 0 · 2	7.3	7.9	4 0 · 0	3.0	3.3
1 1 · 3	5.8	6.7	1 0 · 6	6.0	6.4
2 1 · 0	11.6	14.1	4 0 · 1	9.2	9.8
2 1 · 1	21.0	23.5	3 1 · 3	12.3	13.1
1 0 · 4	24.2	22.2	2 1 · 5	5.6	5.6
2 0 · 3	32.2	29.6	4 0 · 2	11.5	11.5
2 1 · 2	8.6	8.1	1 1 · 6	25.3	25.2
3 0 · 0	13.9	11.9	2 2 · 4	1.7	1.8
3 0 · 1	1.2	1.2	3 2 · 0	13.3	13.8
1 1 · 4	16.6	16.5	2 0 · 6	21.8	22.7
3 0 · 2	3.8	3.7	3 2 · 1	7.2	7.6
2 0 · 4	3.8	3.7	3 0 · 5	3.1	3.2
2 1 · 3	28.1	27.4	3 1 · 4	6.6	6.8
2 2 · 0	37.2	37.4	4 0 · 3	7.3	7.6
2 2 · 1	23.6	24.2			
3 0 · 3	4.2	4.3			
3 1 · 0	18.0	18.6			

Least-squares refinement

In the least-squares refinement, the normal equations are repeatedly solved until the corrections to the parameters become sufficiently small. Then, the derivatives of $K|F_c|$ with respect to the parameters K , u and φ are required, where K is the scale factor; F_c corresponds to (6) or (7); u and φ are the host lattice parameters defined before. We can show here the following equation

$$\frac{\partial K|F_c|}{\partial p_j} = \sum_i \frac{\partial K|F_c|}{\partial x_i} \frac{\partial x_i}{\partial p_j} \quad (8)$$

where p_j is u or φ ; x_i denotes the fractional coordinates with respect to x , y and z components of constituent atoms C, O, N, H(1) and H(2) in the urea molecule, and can be readily derived from (1), as a functional form. Equation (8), together with $\partial K|F_c|/\partial K = |F_c|$, will be used in the normal equations.

RESULTS AND DISCUSSION

X-ray analysis

In Table 1 we show a comparison of the observed and calculated structure factors of urea-polyethylene complex in the case of the rotational disorder model of the guest, Model III, which gives the smallest reliability factor ($R = \sum(|F_o| - |F_c|)/\sum|F_o|$). The temperature factors used for urea and polyethylene are 4 \AA^2 and 6 \AA^2 , respectively³. It is difficult to conclude here, however, which model is most preferable, because the differences of the calculated structure factors of the guest molecule among the three models are small, as shown in Table 2. There is no substantial difference of R factors of the complex among the models: 5.7% for Model I, 5.7% for Model II, and 5.7% for Model III. In urea-n-hexadecane complex, Smith³ adopted Model III with R factor 9.7%. It was

pointed out by Chatani *et al.*⁵ that the differences of the equatorial structure factors of the guest among these three models are so small that it is difficult to determine the disorder structure from R factors alone. Chatani *et al.*, in this complex, adopted Model II from R factors, $F_o - F_c$ syntheses and positions of energy minima for the rotation of the guest n-hexadecane molecule in the hexagonal urea tunnel.

We should note from such small R factors that the molecular parameters of urea used in this analysis, which are those in tetragonal form of urea, are correct. If four hydrogens in the planar urea molecule are neglected, R factors become 7.8% for Model I, 7.8% for Model II and 7.8% for Model III. If they are included, R factors are improved over those given above. From these results, it is expected that the hydrogens are not deviated largely from the plane formed by the other atoms, although there is a degree of freedom about the rotation of two kinds of hydrogens around the C-N bond. Smith³ determined the positions of the hydrogen atoms of urea in the hexagonal urea-n-hexadecane complex such that they were placed midway between the nitrogen and oxygen atoms. The bond distances and the bond angles derived from his fractional coordinates with respect to the carbon, oxygen and nitrogen atoms are C=O, 1.28 Å; C-N, 1.35 Å; and OCN bond angle, 122°; these are substantially the same as those used here.

In Table 3, the host lattice parameters of urea-polyethylene complex are shown, compared with those of urea-n-hexadecane complex. Good agreement is found between the parameters of both complexes. The cell dimensions of urea-polyethylene complex and those of urea-n-hexadecane complex agree well with each other; $a = 8.22 \text{ \AA}$, $c = 11.02 \text{ \AA}$ for the former complex²; $a = 8.230 \text{ \AA}$, $c = 11.005 \text{ \AA}$ after Smith³ and $a = 8.227 \text{ \AA}$, $c = 11.015 \text{ \AA}$ after Chatani *et al.*⁵ for the latter complex. According to the definition for the parameters u and φ , they are related

Table 2 Comparison of calculated structure factors of ($h k \cdot 0$) reflections of the guest polyethylene molecule about three models

$h k \cdot 0$	Model I	Model II	Model III
1 0 · 0	55.0	55.0	55.0
1 1 · 0	35.4	35.4	35.4
2 0 · 0	29.0	28.9	29.0
2 1 · 0	17.3	17.3	17.2
3 0 · 0	13.0	12.8	13.2
2 2 · 0	9.1	9.4	8.8
3 1 · 0	8.2	8.2	8.2
4 0 · 0	6.1	5.7	6.5
3 2 · 0	4.6	4.9	4.3

Table 3 Host lattice parameters of urea complexes: the values marked * are calculated from the fractional coordinates given by Smith

Guest molecule	u (Å)	φ (deg)	Hydrogen bond distances (Å)	Reference
Polyethylene	0.19	82.4	2.98 3.04	This paper
n-Hexadecane	0.20*	82.6*	2.93 3.04	Smith (3)

Table 4 Thermal properties of urea complexes

Guest molecule	Melting point (°C)	Heat of fusion		
		(cal g ⁻¹)	(kcal per mole of guest)	(kcal per mole of CH ₂)
n-Paraffin				
<i>n</i> = 28	135	60.5	98.8	
<i>n</i> = 32	138	61.3	113.8	
<i>n</i> = 36	138	61.5	127.6	3.59
<i>n</i> = 40	139	61.6	141.5	
<i>n</i> = 44	140	62.4	156.9	
Polyethylene	150	64.4	—	3.55

n = carbon number of n-paraffin

to the cross-sectional area of the host urea cavity in which the guest molecule is enclosed. From the similarities of the cell dimensions and the host lattice parameters *u* and ϕ in urea-polyethylene complex to those in urea-n-hexadecane complex, it is suggested that the guest polyethylene molecules are subjected to the same spatial restriction from the host lattice and are probably forced to have the same extended chain conformation as paraffin molecules in urea-paraffin complexes. It was indicated by Chatani *et al.* that the shape of the cross section of the guest molecule affects whether or not a complex undergoes the phase transition between orthorhombic and hexagonal. Both urea complexes with sebasic acid and poly(1,4-butadiene) do not show the phase transition⁵; these guest molecules possess cylindrical cross sections. On the other hand, urea complexes with n-paraffin type compounds including polyethylene exhibit the phase transition⁶; it was suggested that even a long polyethylene molecule has a planar zigzag conformation as a whole in a urea tunnel.

The similarities in the two kinds of N-H...O hydrogen bond distances of urea-n-hexadecane complex and urea-polyethylene complex, as shown in Table 3, will be attributed to similarities in *u*, ϕ and cell dimensions. It seems that such magnitudes of hydrogen bond distances are commonly recognized in urea complexes with space group *P*6₁22, if the cell dimensions are almost the same as those given in Table 3, e.g. urea-poly(1,3-butadiene) complex¹⁵ has the cell dimensions *a* = 8.22 Å and *c* = 11.01 Å, and the two kinds of hydrogen bond distances are 2.98 Å and 3.00 Å. However, in urea complexes with a series of 2-methyl paraffins whose principal chains have carbon number ranging from *n* = 10 to *n* = 20, the *a*-axes are particularly expanded due to the bulky methyl branch. Their cell dimensions¹⁶ vary with the chain length, e.g. *a* = 8.280 Å and *c* = 11.03 Å for *n* = 10, and *a* = 8.258 Å and *c* = 11.04 Å for *n* = 20. The decreases in the heat of formation of these complexes, compared with that of the complexes with the corresponding n-paraffins, were ascribed to the increases in the hydrogen bond distances.

D.s.c. thermal analysis

In Table 4, we show the thermal properties of urea-n-paraffin complexes and urea-polyethylene complex. These complexes show a single endothermic peak. But, urea complexes with n-paraffins whose carbon numbers are lower than *n* = 20 gave two distinct endothermic peaks, the lower and higher ones of which corresponded to the decomposition of the complex into the constituents

and the melting of the resultant tetragonal urea, respectively¹⁷. It is found from this table that the melting point of urea-n-paraffin complexes increases with the chain length, and that of urea-polyethylene complex reaches 150°C. Similarly, the heat of fusion increases with the chain length. Such a chain-length dependence of the thermal properties will be attributed to effects of the methylene repeating parts and end groups on the thermal stability.

Here, we show the heat of fusion of urea-n-paraffin complexes per mole of guest (the fourth column in Table 4), which was obtained from the measured heat of fusion per gram of complex (the third column) by using the equation³:

$$\text{mole ratio of urea/n-paraffin} = 0.6848(n - 1) + 2.181$$

where *n* is the carbon number. These values indicate a linear relationship *versus* carbon number, the slope of which gives the heat of fusion per mole of methylene (the last column). This estimate will be regarded as that of urea complex with infinite chain length of polyethylene, since, in this, the thermal contributions from the end groups are absent. Setting $n \approx \infty$ in the above equation, from the measured heat of fusion of urea-polyethylene complex per gram, we have the heat of fusion per mole of methylene (the last row). It is found that these two estimates agree well with each other. This suggests the structural similarity of urea complexes among the different chain lengths of the guest molecules.

Potential energy analysis

The curve of potential energies between the host urea tunnel and the guest polyethylene molecule, plotted against the rotation angle χ of the guest around the long axis, is shown in Figure 3, where the Lennard-Jones 6-12 equations with intermolecular energy constants in set II proposed by Parsonage and Pemberton¹⁸ were used for the calculation. Then, the energies were obtained by averaging potential energies between the host lattice and one ethylene over the *z* coordinates of one host unit cell; the constituent ethylenes of the polyethylene are expected to be disposed at any *z* level, because of the non-integral ratio of the repeating distances of these two components along the *c*-axis.

This curve has a relatively low energy barrier, which

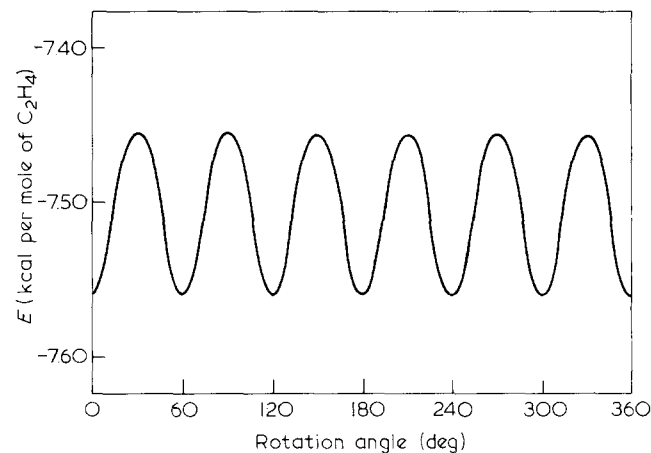


Figure 3 Potential energy for the rotation of a polyethylene molecule in a hexagonal urea tunnel

suggests the facilitation of rotational motion around the long axis. The broad-line n.m.r. measurement of urea-polyethylene complex showed that marked line-narrowing occurred at a temperature higher than about the transition point by d.s.c. thermal analysis, indicating an appreciable rotational motion¹⁹. Whenever their set I and set II energy constants were used, the features of energy curves were the same; the curve profiles displayed a sixfold symmetry against the rotation angle; the energy minima were situated at the positions 0° and multiples of 60°. Such results support Model II, as in this model the zigzag plane is statistically disposed at the positions of these energy minima. In urea-n-hexadecane complex, results similar to ours were given by Chatani *et al.*,⁵ which favoured Model II, in accordance with their X-ray results.

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REFERENCES

- 1 Monobe, K. and Yokoyama, F. *J. Macromol. Sci. B* 1973, **8**, 277
- 2 Yokoyama, F. and Monobe, K. *Polymer* 1980, **21**, 968
- 3 Smith, A. E. *Acta Crystallogr.* 1952, **5**, 224
- 4 Chatani, Y., Taki, Y. and Tadokoro, H. *Acta Crystallogr. B* 1977, **33**, 309
- 5 Chatani, Y., Anraku, H. and Taki, Y. *Mol. Cryst. Liq. Cryst.* 1978, **48**, 219
- 6 Yokoyama, F. and Monobe, K. *J. Polym. Sci., Polym. Lett. Edn.* 1981, **19**, 91
- 7 Pemberton, R. C. and Parsonage, N. G. *Trans. Faraday Soc.* 1965, **61**, 2112
- 8 Schwartz, L. M. *Anal. Chem.* 1971, **43**, 1336
- 9 Cox, D. E. and Khattak, C. P. *J. Appl. Crystallogr.* 1977, **10**, 405
- 10 Klug, H. P. and Alexander, L. E. 'X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials', 2nd Edn., Wiley, New York, 1974, p. 271
- 11 Caron, A. and Donohue, J. *Acta Crystallogr. B* 1969, **25**, 404
- 12 Bijvoet, J. M. and Ketelaar, J. A. A. *J. Am. Chem. Soc.* 1932, **54**, 625
- 13 Cochran, W., Crick, F. H. C. and Vand, V. *Acta Crystallogr.* 1952, **5**, 581
- 14 Yokoyama, F., Ochi, Y., Shinohara, M. and Monobe, K. *Polym. Prepr. Jpn.* 1979, **28**, 1862
- 15 Chatani, Y. and Kuwata, S. *Macromolecules* 1975, **8**, 12
- 16 Oshima, Y., Chida, F. and Ohnuma, H. *Nippon Kagaku Kaishi* 1978, 99
- 17 Monobe, K., Murakami, Y. and Yokoyama, F. *Mem. School Eng. Okayama Univ.* 1971, **6**, 57
- 18 Parsonage, N. G. and Pemberton, R. C. *Trans. Faraday Soc.* 1967, **63**, 311
- 19 Hori, Y., Tanigawa, T., Shimada, S. and Kashiwabara, H. *Polym. J.* 1981, **13**, 293