Order-Disorder Transition in Urea-Polyethylene Complex

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SYNOPSIS

The phase transition of urea complexes whose guest components range from n-paraffin to polyethylene was investigated by DSC thermal analysis. The transition temperatures increased with increasing the chain length; the related heats did not change much with the chain length. An X-ray powder diffractometry for urea-polyethylene complex revealed that the complex undergoes the same kind of phase transition between orthorhombic and hexagonal as urea-n-paraffin complex. The transition is interpreted in terms of an order-disorder transition with respect to the orientation of the guest molecule.

1. INTRODUCTION

From heat capacity measurements for some urea complexes with n-paraffins whose carbon numbers range from $n = 10$ to $n = 20$, Pemberton and Parsonage\textsuperscript{1,2} first showed that in each case the heat capacity curve had at least one region of high heat anomaly in a low temperature. They considered that this phenomenon was attributed to an order-disorder transition of the guest molecule around the chain axis. However, they did not take account of the structural change in the

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host urea lattice. It was found that the transition temperatures increased with the chain lengths of the guest molecules.

Recently, from X-ray and differential thermal analyses, Chatani et al.\textsuperscript{3,4} indicated that the ordinary hexagonal complexes (denoted as high-temperature form) transform commonly into orthorhombic complexes (low-temperature form) except for a few complexes. The transition was regarded as an order-disorder transition of the guest chain molecules, accompanied by structural changes in the host urea lattice. In the former form\textsuperscript{5}), the guest chains in the tunnels rotate around the long axis independently of each other; while in the latter form\textsuperscript{3,4}), they are disposed in a definite orientation about the tunnel axis. In our previous work\textsuperscript{6}), urea-polyethylene complex was shown to exhibit the similar phase transition to urea-n-paraffin complex. Umemoto and Danyluk\textsuperscript{7}) indicated that the marked line narrowing temperatures in broad line NMR of several urea-d\textsubscript{4} complexes with n-paraffins correspond nearly to the transition temperature obtained by the heat capacity measurements, indicating the motional changes of the guest molecules around the tunnel axis. Hori et al.\textsuperscript{8}) investigated molecular motion of polyethylene molecules in urea-polyethylene complex by broad line NMR, related to the phase transition.

In this study, the phase transition of urea complex with n-paraffin and that of urea complex with polyethylene are studied by thermal analysis and X-ray powder diffractometry. The transition phenomena for a series of the urea complexes will be discussed from a structural point of view.

2. EXPERIMENTAL

2.1 Materials

The complexes of urea with n-tetracontane, n-tetratetracontane, and those with polyethylenes were prepared by the method presented by us\textsuperscript{9}). Here, polyethylenes used were Hiwax 200P of Mitsui Petrochemical Industries, Ltd. (denoted as PE(A), $M_v = 2300$), Hiwax 400P (PE(B), $M_v = 5800$) and Sholex 6050 of Showa Denko Co. (PE(C), $M_v = 59000$). All the complexes were provided for DSC thermal analysis. The urea complex with polyethylene (PE(C)) was provided for X-ray analysis. The complex of urea with n-paraffin(mp. 42~44°C) was also prepared and used for obtaining the X-ray diffraction pattern.
2.2 DSC thermal analysis

A Perkin Elmer differential scanning calorimeter (DSC-1) was used for the measurements of the thermal properties of the complexes. Both temperature and amplitude scales were calibrated by using mercury (melting point: -38.9°C, heat of fusion: 43.2 cal/g\(^{10}\)) and water (0°C, 79.8 cal/g), with the same scanning rate 10°C/min as the sample.

2.3 X-ray analysis

Preceding the X-ray measurements, urea-polyethylene (PE(C)) complex was milled to fine powder of the particle size less than 145 mesh. An X-ray powder diffractometer with Ni-filtered Cu-K\(_\alpha\) radiation, the usual optical arrangement, and a vacuum chamber for the setting of the sample was used for the identification of the crystal types at 23, -12, and -190°C; determination of the unit cell constants at -190°C; evaluation of the integral breadth of line profiles at 23 and -190°C. The known diffraction peaks of hexagonal urea-polyethylene complex at 23°C were used to correct diffraction angles. The evaluation of the integral breadth of line profiles at 23 and -190°C for the complex of urea with n-paraffin (mp.42~44°C) was also carried out.

3. RESULTS AND DISCUSSION

3.1 Thermal analysis

In Fig. 1, we show the transition temperatures of urea complexes with n-paraffins and polyethylenes, together with those of pure n-paraffins and melting points of polyethylenes, plotted against the carbon number. The transition temperatures of urea complexes with n-paraffins increase with the chain length in an irregular manner, significantly differing from those of even or odd-membered pure paraffin crystals\(^{11}\). This feature was ascribed to the fact that the increment of paraffin chain length of about 2.5 Å or the fiber period does not fit into the integral of urea spiral repeating distance, 1.83 Å (=11.0 Å/6) along the urea tunnel axis. The various temperature-widths of transition about urea-n-paraffin complexes indicated in Tab. 1 also may be related to such a structural character.

The transition temperatures of three urea-polyethylene complexes approach the room temperature; DSC thermograms of these complexes show endothermic peaks at 5~8 °C, which agrees nearly with the marked
Figure 1. Transition temperature versus carbon number of the guest molecule (Δ: even, ▲: odd, ○: polyethylene). Transition temperatures of pure n-paraffins\(^{11}\) (○: even, ●: odd) and melting temperatures of polyethylenes (□) are also shown. The latters were estimated by the relation\(^{11}\): \(T_m(\text{°K}) = 414.3(n - 1)/(n + 5)\).

We find from the figure that the transition temperatures of the complexes are situated nearly 100 °C lower than those of the corresponding pure paraffin crystals or melting points of the corresponding pure polyethylene crystals. This will be attributed to a very weak interaction resulting from a large interguest distance, 8.2 Å, which is about twice the intermolecular distance in pure paraffin or polyethylene crystals.
Table 1. Comparison of thermal properties with respect to the transition among the urea complexes.

<table>
<thead>
<tr>
<th>Guest</th>
<th>$T_t$ (°C)</th>
<th>$\Delta H$ cal/g of complex</th>
<th>$\Delta S$ cal/deg·g of complex</th>
<th>Width of transition (°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>n=10</td>
<td>-162</td>
<td>0.32* (203)</td>
<td>0.003* (1.94)</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>n=12</td>
<td>-150</td>
<td>0.35* (265)</td>
<td>0.003* (2.26)</td>
<td>4</td>
<td>Pemberton and Parsonage</td>
</tr>
<tr>
<td>n=16</td>
<td>-121</td>
<td>0.43* (422)</td>
<td>0.003* (2.91)</td>
<td>2</td>
<td>Parsonage</td>
</tr>
<tr>
<td>n=20</td>
<td>-84</td>
<td>0.56* (667)</td>
<td>0.003* (3.61)</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>n=40</td>
<td>-61</td>
<td>0.36</td>
<td>0.002</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>n=44</td>
<td>-50</td>
<td>0.39</td>
<td>0.002</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>PE(A)</td>
<td>+5</td>
<td>0.48</td>
<td>0.002</td>
<td>7</td>
<td>This work</td>
</tr>
<tr>
<td>PE(B)</td>
<td>+7</td>
<td>0.51</td>
<td>0.002</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>PE(C)</td>
<td>+8</td>
<td>0.53</td>
<td>0.002</td>
<td>8</td>
<td></td>
</tr>
</tbody>
</table>

* We derived these values from the corresponding ones in the parentheses given by Pemberton and Parsonage; using the relationship: mole ratio of urea/n-paraffin = 0.6848(n - 1) + 2.181, n: carbon number.

** We estimated this quantity as the half-width of the endothermic peak profile.
Figure 2. X-ray powder diffraction patterns of urea-polyethylene complex: (a) at 23 °C, (b) at -12 °C, (c) at -190 °C.

Pemberton and Parsonage\(^1\) showed that urea-2-methyl penta­decane complex had not the phase transition; the bulky methyl group hinders the rotational jumping from one site to another around the chain axis. Chatani et al.\(^4\) reported that the absence of the phase transition in urea-sebASIC acid complex and in urea-poly(1,4-butadiene) complex is resulted from the cylindrical shape of these guest molecules in the urea tunnel. In this study, urea-polyethylene complex did show the phase transition. Then, the conformation of the guest polyethylene molecules in the tunnel is expected to be zigzag one as a whole.
In Tab. 1, the thermal properties about the solid-phase transition of urea complexes are summarized. The heat and entropy of transition of any of three urea-polyethylene complexes are 0.5 cal/g and 0.002 cal/deg g, respectively, which are on the same order as those for urea-n-paraffin complexes. It is expected from such small values for urea-polyethylene complex that changes in the host lattice structure and those in thermal motion of the guest molecule accompanied with the transition will be as small as in the case of urea-n-paraffin complexes. In fact, it has been shown by Chatani et al.\textsuperscript{4)\textsuperscript{4}} that the orthorhombic form of urea-n-hexadecane complex is attained by a small deformation of urea tunnel from hexagonal, and that the temperature factor of the guest molecule is significantly high even below the transition temperature, 2.8 \textsuperscript{\AA}\textsuperscript{-2} at -175°C\.\textsuperscript{12})

3.2 X-ray analysis

In Fig. 2 are shown the X-ray diffraction patterns of urea-polyethylene complex at 23, -12 and -190°C; the similar patterns to those at 23°C and -190°C were obtained for urea-n-paraffin complex, at the respective temperatures. We find that the pattern at 23°C in (a) is ascribed to the hexagonal form as already shown in our work\textsuperscript{9}), while the patterns at -12°C in (b) and -190°C in (c) are ascribed to the orthorhombic one. The transition from hexagonal to orthorhombic results in the splitting of the diffraction peaks, because of the reduction of symmetry from the space group P\textsubscript{6}1\textsubscript{2}2\textsubscript{2} to P\textsubscript{2}1\textsubscript{2}1\textsubscript{2}1\textsubscript{2}1,\textsuperscript{4}) e.g. (10·0) in the former form becomes (110) and (020) in the latter form. The splittings of the other reflexions are found in the figure. Evaluations of integral breadths of the following equatorial reflexions are presented later: (11×0) and (20×0) in the hexagonal form and the corresponding reflexions in the orthorhombic form; a pair of (200) and (130), and of (220) and (040).

By using the following reflexions in Fig. 2 (c): (112), (200), (130), (201), (131), (220), (040), and (221), orthorhombic unit cell constants of urea-polyethylene complex at -190°C were obtained: \(a = 8.30 \text{ Å}, b = 13.81 \text{ Å}, c = 11.00 \text{ Å}\). The superposition of many pairs of the splitting reflexions at -12°C makes it difficult to evaluate the cell constants. The above constants agree well with those of urea-n-hexadecane complex at the same temperature: \(a = 8.272 \text{ Å}, b = 13.824 \text{ Å}, c = 10.988 \text{ Å}\), in which \(a\) and \(b\) dimensions were derived from the thermal expansion equations, given by Chatani et al.\textsuperscript{4)}}
a = 8.178[1 - 6.08 \times 10^{-5}(T - 273.15)] \text{ Å} \quad [1a]

b = 14.091[1 + 9.96 \times 10^{-5}(T - 273.15)] \text{ Å} \quad [1b]

where T is expressed in °K; they reported that a drastic change in the c-dimension at the phase transition temperature (-175°C) was not recognized within the experimental accuracy. The above agreement implies that the orthorhombic crystal of urea-polyethylene complex has not only the similar host lattice structure but also the similar molecular orientation of the guest about the tunnel axis, to those in urea-n-hexadecane complex; in the latter complex\(^4\), the host lattice is deformed gradually with lowering the temperature by such an anisotropic thermal expansion that the linear coefficient for a-axis is negative and that for b-axis is positive, as indicated in Eq. 1; then the orientational change of the guest molecules, whose overall rotation about the chain axis is forbidden by the relatively high energy barriers, proceeds cooperatively with the deformation and with the zigzag plane being almost parallel to the long axis of the ellipsel-shaped cross section as shown in Fig. 3. In structural studies of the complex\(^{13}\), on the other hand, we have indicated by the X-ray and potential energy analyses that the hexagonal form of urea-polyethylene complex is characterized by the overall rotation of the guest molecule around the long axis.

In Tab. 2, integral breadths of X-ray line profiles of urea-polyethylene complex and those of urea-n-paraffin complex between corresponding equatorial reflexions about orthorhombic and hexagonal crystal forms are compared; these were evaluated after the elimination of the \(\alpha_1\alpha_1\) doublet by Keating's method\(^{14}\). In each complex, we cannot recognize the difference between crystal types within the experimental errors; smaller breadths for all reflexions in urea-n-paraffin complex will be due to a larger crystallite size. Then, it is expected that in the orthorhombic form, there is no generation of lattice distortion to cause the line broadening, even when longer polyethylene molecules are enclosed as guests. In the melt-crystallized polyethylene\(^{15}\), the lattice distortion of equatorial direction increased with lowering the temperature, indicating the increase in the broadening of X-ray line profile. In the
Figure 3. Schematic representation of structural change of the urea complex in the solid-phase transition. The orthorhombic and hexagonal host lattices are symbolized by ellipses and circles, respectively. The planar zigzag molecules are denoted by lines.

Table 2. Comparison of integral breadths (degree) of X-ray line profiles between hexagonal and orthorhombic, for urea–n-paraffin complex and urea–polyethylene complex. The values for the former complex are given in the parentheses.

<table>
<thead>
<tr>
<th>Hexagonal (23°C) (hk-0)</th>
<th>Breadth</th>
<th>Orthorhombic (-190°C) (hk0)</th>
<th>Breadth</th>
</tr>
</thead>
<tbody>
<tr>
<td>(11-0)</td>
<td>0.32 (0.25)</td>
<td>(200)</td>
<td>0.29 (0.25)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(130)</td>
<td>0.33 (0.23)</td>
</tr>
<tr>
<td>(20-0)</td>
<td>0.32 (0.25)</td>
<td>(220)</td>
<td>0.34 (0.22)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(040)</td>
<td>0.34 (0.24)</td>
</tr>
</tbody>
</table>
urea-poly-ethylene complex, on the contrary, the accumulation of
distortion energy of lattice in a low temperature is avoided through
the cooperative deformation process mentioned above. The narrowness
of transition given in the fifth column in Tab. 1 suggests that the
transition is strongly cooperative irrespective of chain length. The
reason why the transition for urea-n-hexadecane complex is very sharp
is now obscure.

Since the equatorial reflexions of urea-polyethylene complex
originate from the combined structure factor of both host and guest
lattices, the X-ray diffraction line profiles involve the information
about degrees of orderings of the combined lattice. The conformation
of polyethylene molecules around which the host urea lattice is
constructed should be strictly related to disorders of the complex
lattice. In this respect, the results given in Tab. 2 suggest that
polyethylene molecules in the orthorhombic complex are as fairly
accommodated to the tunnel cavity in the form of extended-chains, much
as in the hexagonal complex.

4. CONCLUSIONS

The solid-phase transition of urea-polyethylene complex was
revealed by thermal analysis and X-ray powder diffractometry, and we
had the following conclusions.
1) Urea-polyethylene complex exhibited the phase transition between
orthorhombic (low-temperature form) and hexagonal (high-temperature
form), at -8°C. The heat and entropy of transition were about 0.5
cal/g and 0.002 cal/deg g, respectively, which were on the same order
as those in urea-n-paraffin complexes.
2) The transition has been regarded as an order-disorder transition
of the guest molecule, accompanied by the structural change in the
host urea lattice; in the orthorhombic form, the guest molecule has
a definite orientation about the tunnel axis, and while in the
hexagonal form, its overall rotation around the axis is facilitated.
3) The existence of the transition of urea-polyethylene complex
suggested that even a long polyethylene molecule has a planar zigzag
conformation as a whole in an urea tunnel.
4) No generation of the host lattice distortion near liquid nitrogen
temperature implied that the guest polyethylene molecules in the
orthorhombic complex are as fairly accommodated to the tunnel cavity
in the form of extended-chains, much as in the hexagonal complex.

5) The narrowness of transition suggested that the transition is strongly cooperative regarding structural changes in the host and guest lattices, irrespective of chain length.

REFERENCES

9) F. Yokoyama and K. Monobe, Polymer, 21 (1980), 968.
13) F. Yokoyama and K. Monobe, Polymer, 24 (1983), 149.