SYNTHESIS AND PROPERTIES OF POLY[ETHYLENE 4,4'-
(1,2-ETHANEDIYLDIOXY)BIS(3-ETHYLBENZOATE)]

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Synopsis

Poly[ethylene 4,4'-(1,2-ethanediyldioxy)bis(3-ethylbenzoate)] [o-Et type polyester-ether],
which is the ethylene glycol polyester of 1,2-bis(4-carboxy-2-ethylphenoxy)ethane having the ethyl
substituents in the ortho-position on the benzene nuclei to the ester linkages, was successfully
synthesized.

The crystallizability and the thermal properties of this polymer were investigated by use of
X-ray analysis, infrared analysis, differential scanning calorimetry and estimation of the rate of
crystallization.

It was shown that [o-Et] was crystalline and melt-spinnable. Its physical properties were as
follows. Crystal melting temperature, 170°C; Glass transition temperature, 52°C; Half-time crystal-
lation at 140°C, 5400 sec.; Fiber identity period, 18.7 Å.

Introduction.

The polyester-ether [o-Et] having the following
chemical formula was successfully prepared by
polycondensation of the dimethyl ester of bis(4-
carboxy-2-ethylphenoxy)ethane with ethylene
glycol.

\[
\begin{align*}
\text{OC} & \text{OCH}_2 \text{CH}_2 \text{O} \text{OCH}_2 \text{CH}_2 \text{O} \text{n} \\
C_2 \text{H}_5 & \text{H}_5 \text{C}_2 \\
\text{C}_2 \text{H}_5 & \text{OCH}_3
\end{align*}
\]  [o-Et]

As is well known, the ethylene glycol polyester
of 1,2-bis(4-carboxyphenoxy)ethane is crystalline
and melt-spinnable. Our further investigations
showed that fibers of this polyester-ether [B] have
high tenacity, high Young's modulus and remarka-
ble alkali-resistance.

Studies on the synthesis and properties of this
series of aromatic polyester-ethers with side sub-
stituents, viz., the methyl groups and the methoxy
groups as side group respectively, in the ortho-
position to the ether linkage on the benzene nuclei
have previously been reported. Results of the
studies have clarified that [o-Me] and [V] shown
below, were also crystalline and melt-spinnable.
The details of physical properties on [V] were
previously reported elsewhere by our associates.

\[
\begin{align*}
\text{OC} & \text{OCH}_2 \text{CH}_2 \text{O} \text{OCH}_2 \text{CH}_2 \text{O} \text{n} \\
\text{CH}_3 & \text{H}_3 \text{C} \\
\text{CH}_3 & \text{CO}
\end{align*}
\]  [o-Me]

The purpose of this work is to present a method
for the synthesis of [o-Et], and is to shed light on
the influence of the ethyl groups on crystallizabi-
ity and phase transition behaviors of [o-Et] in
comparison with those of the polyester-ether
homologs having various side substituents in the
benzene ring.

Experimental.

Materials.

Monomers were synthesized according to the
procedure in Scheme 1.

\[p\text{-Tolyl acetate (2)}\]

In a 1 L, three necked flask fitted with an air
condenser and mechanical stirrer was placed \(p\)-
cresol (108 g, 1.0 mole), acetic anhydride (153 g,
1.5 moles) and a small amount of conc. \(H_2SO_4\).
The flask and contents were heated with continu-
ous stirring at 120°C for half an hour, then cooled to room temperature, and the reaction mixture was washed with aqueous sodium hydrogen carbonate, with water, dried, and distilled under reduced pressure. The fraction boiling at 88°-89°/5 mmHg (lit. 5) 89°/5 mmHg was collected. The yield of p-tolyl acetate was 144 g. (96%). The 13C NMR spectrum was consistent with the structure.

6-Hydroxy-3-methyl-acetophenone (3)

(3) was prepared according to the method devised by Fries. To (2) (125 g, 0.83 mole) was placed in a 1 L, precooled three necked round bottom flask fitted with a thermometer and an air condenser, and finely powdered aluminum chloride (167 g, 1.25 moles) was cautiously added in small portions. When the addition was complete, the flask and contents were slowly heated to 125°C, held at this temperature for ten minutes, and then cooled. Then it was added to a stirred mixture of 250 g of ice and 150 cc. of conc. HCl. After the ice has melted, the solid product was filtered and dried. Recrystallization from petroleum ether produced pale yellow needles, mp 50°C (lit. 7). and yield was 125 g. (quantitative).

2-Ethyl-4-methyl-phenol (4)

Amalgamated zinc was covered with water (100 cc.), conc. HCl (100 cc.), and (3) (30 g, 0.2 mole) in a 1 L, three necked round bottom flask. The mixture was then heated under reflux for 10 hrs. Two or three additions of fresh conc. HCl were made during this period. After cooling the product was isolated by extraction with ether. The ether solution was washed with water and dried. After removing the ether, the product was distilled in vacuum to give an oily colorless distillate, bp 120°C/19 mmHg (lit. 9) 216°-218°C/760 mmHg. Yield, 101 g. (74%).

Bis(2-ethyl-4-methylphenoxo)ethane (5)

To a solution of NaOH (18 g, 0.45 mole) in water (20 cc.) was added a solution of (4) (54 g, 0.4 mole) in EtOH (250 cc.). The mixture was stirred on the steam bath for 2 hrs., followed by addition of ethylene dibromide (27 g, 0.15 mole) in EtOH (20 cc.) over a period of 15 hrs. After the reaction was complete, the mixture was concentrated by distillation of EtOH. The precipitate formed was collected by filtration, washed with water, and dried in vacuo. The crude product was recrystallized from EtOH to give colorless needles, mp 88°C (by DSC). Yield, 138 g (20%).

The infrared spectrum (KBr) exhibited an absorption at 1075 cm⁻¹ (ν = C-O-C).

Bis(4-carboxy-2-ethylphenoxo)ethane (6)

Glacial acetic acid (30 cc.), cobalt acetate tetrahydrate (5 g, 0.02 mole), and methyl ethyl ketone (8.4 g, 0.12 mole) were allowed to react with oxygen with efficient stirring at 90°C under atmospheric pressure. Following an induction period of approximately for 1 hr., the solution was characterized by a change in color from purple to dark green. To this solution, (5) (4 g, 0.046 mole) was added. After 5 hrs., the reaction mixture was
cooled and the product was filtered, washed with acetic acid and water. The resulting crude dibasic acid was dissolved in aqueous ammonia, and acidified with conc. HCl. The product was filtered, washed, and dried to give 9.0g (54% yield) of (6) with a melting point of 278°C (by DSC), and a neutral equivalent of 183 (calcd. 189). The infrared spectrum (KBr) exhibited an absorption at 1680cm⁻¹ (ν C=O) and the ¹³C NMR-spectrum was consistent with the structure.

ANAL. Calcd for C₂₀H₂₂O₆: C, 67.02%; H, 6.19%; Found: C, 66.97%; H, 6.24%.

Bis(4-carbomethoxy-2-ethylphenoxy)ethane (7)

(6) (7g, 0.02 mole), dry methanol (150cc.), and conc. H₂SO₄ (5cc.) were charged into a 500cc., three necked round bottomed flask fitted with a mechanical stirrer and air condenser. The mixture was refluxed for 8 hrs. at 80°C. The progress of the esterification reaction could be followed by observing the clarification of the turbid solution. After cooling to room temperature the crude products were separated by filtration. The filtrate was neutralized with potassium carbonate and the resulting potassium sulfate was removed by filtration. Then the filterate was concentrated. The resulting product was collected, washed thoroughly with cold diluted aqueous ammonia, followed by water, and was recrystallized from MeOH to produce 5.4g. (70% yield) of (7), mp 118°C (by DSC).

The infrared spectrum (KBr) exhibited an absorption at 1720 cm⁻¹ assigned to ester carbonyl (ν C=O).

ANAL. Calcd for C₂₂H₂₄O₆: C, 68.38%; H, 6.78%; Found: C, 68.33%; H, 6.78%.

Polycondensation.

The polycondensation was carried out in a glass ampule under dry nitrogen. In the first step, (7) (5g, 0.013 mole) was transesterified with ethylene glycol (8g, 0.13 mole) using zinc acetate dihydrate (14mg, 6.4 x 10⁻⁵ mole) as catalyst at 190°C for 3 hrs, under atmospheric pressure. The temperature was then raised progressively at 190~240°C over a period of 2 hrs. In the second step, the temperature of the reaction ampule was kept at 265°C. Then the pressure was reduced to about 10⁻¹ mmHg and heating continued, while a slow stream of nitrogen was bubbled through the reaction mass to facilitate removal of ethylene glycol. After 5 hrs., the reaction mixture was cooled and the transparent polymer was isolated by breaking the reaction ampule.

The intrinsic viscosity number [η] of the resulting polymer in phenol-tetrachlorethane mixed solvent (1:1 w/w) was 0.62 (dl./g.) at 30°C.

ANAL. Calcd for (C₂₂H₂₄O₆)ₙ: C, 68.73%; H, 6.29%; Found: C, 68.52%; H, 6.27%.

Polymer Characterization.

Thermograms were obtained with a Perkin-Elmer DSC-1 calorimeter. 10 mg. of sample was placed in an aluminum pan with a lid. The heating rate was 10°C/min under nitrogen flow of 40 cc/min.

The rate of crystallization was determined by maintaining the amorphous sample in a closely thermostatted density gradient column filled with ZnCl₂·H₂O solution at 140°C in which crystallization can occur and by recording the specific gravity as a function of time.

Wide angle X-ray diffraction diagrams were taken on the melt spun fibers [a], the stretched fibers [b], and the stretched and annealed fibers [c] using a Shimazu X-ray camera and filtered CuKα radiation. [b] were stretched in one direction to six times their original length. [c] were prepared by annealing of [b] under tension in boiling methanol for 6 hrs., followed by annealing in air at 115°C for 2 hrs.

Infrared spectra were taken with a Shimazu Model IR-27G recording spectrophotometer and the crystalline absorption bands were determined. Unoriented amorphous films were prepared by quenching the melt sheets with ice-water, and stretched and annealed films were prepared from the quenched films by stretching at 60°C by a factor of about six, and then, were annealed by immersing in boiling methanol under tension for 10 hrs., followed by holding in methanol at 20°C for 80 hrs. Crystallization was so difficult that the "solvent heating" technique was employed to induce crystallization.

Results and Discussion.

Crystal Melting Temperature [T_m] and Glass Transition Temperature [T_g].

The effects of introducing ortho ethyl groups on
the aromatic nuclei on \( T_m \) and \( T_g \), were examined by comparing \([\text{o-Et}]\) with \([\text{o-Me}]\) and \([\text{V}]\).

The \( T_m \) and \( T_g \) for \([\text{o-Et}]\), \([\text{o-Me}]\), \([\text{V}]\) and \([\text{B}]\) are shown in Table 1.

No marked differences are observed in \( T_m \) and \( T_g \) between \([\text{B}]\) and \([\text{o-Me}]\).

As is well known, \( T_m \) can be defined by equation \( T_m = \Delta H_m / \Delta S_m \), where \( \Delta H_m \) and \( \Delta S_m \) are the heat and entropy of fusion per mole of repeating unit, respectively. The steric interference by the methyl groups can impede the molecular motion, and their bulkiness can decrease the intermolecular forces. Consequently, it may be considered that in the case of \([\text{o-Me}]\), the decrease in the entropy factor \( \Delta S_m \) due to the former tends to cancel out the decrease in the heat factor \( \Delta H_m \) due to the latter factor.

As seen in Table 1, the \( T_m \) is 240°C for \([\text{B}]\) and 238°C for \([\text{o-Me}]\), while it is as low as 200°C for \([\text{V}]\).

\([\text{V}]\), which has the methoxy side substituents, is difficult to crystallize and its \( T_g \) is high as 82°C. The reason for high \( T_g \), presumably, is that the bulkiness of the methoxy groups might significantly make the molecular chain rigid. The low \( T_m \) of \([\text{V}]\) can be caused by the reduction in molecular density or symmetry.

Although the bulkiness of the ethyl groups is somewhat similar to that of the methoxy groups, the methoxy side substituents make raise the \( T_g \) of \([\text{V}]\), while the ethyl side substituents, on the contrary, lower the \( T_g \) of \([\text{o-Et}]\). The fact that the \( T_g \) of \([\text{o-Et}]\) is 52°C and is the lowerest of the polyester-ether homologs, may be mainly attributable to the lower intermolecular forces in \([\text{o-Et}]\).

**Table 1.** Melting temperature \((T_m)\) and glass transition temperature \((T_g)\) of polyester-ether homologs.

<table>
<thead>
<tr>
<th>Polyester-ethers</th>
<th>o-Et</th>
<th>o-Me</th>
<th>V</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_m) (°C)</td>
<td>170( ^a )</td>
<td>238( ^b )</td>
<td>200( ^c )</td>
<td>240( ^b )</td>
</tr>
<tr>
<td>(T_g) (°C)</td>
<td>52</td>
<td>72</td>
<td>82</td>
<td>71</td>
</tr>
</tbody>
</table>

The samples used were crystallized by, \( ^a \) immersing in boiling methanol for 10 hrs., followed by in benzene at 20°C for 60 hrs., \( ^b \) annealed in air at 160°C for 15 min., \( ^c \) annealed in air at 160°C for 2 hrs.

The ethyl side substituents may also cause chain packing difficulties. These effects would be expected to facilitate the degree of molecular flexibility.

The above results indicate that the effect of the methyl group, as regards \( T_m \), is less than of the ethyl group or the methoxy group, and the influence of the bulkiness of side groups on \( T_m \) and \( T_g \) seems to become appreciable in substituents as large as the methoxy or the ethyl groups.

**Rate of Crystallization.**

The variation of specific gravity of \([\text{o-Et}]\) as a function of time at 140°C is shown in Figure 1 together with results on \([\text{B}]\), \([\text{o-Me}]\), and \([\text{V}]\).

Half-time of crystallization obtained from specific gravity-time curves at 140°C is also shown in Table 2.

In the studies previously reported on estimation of the rate of crystallization for amorphous samples, the measurements were carried out at several fixed temperatures in the temperature range in which crystallization can occur and by recording the variation of specific gravity as a function of time at 140°C is shown in Figure 1.

**Table 2.** Half-time of crystallization\(^{16}\).

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Half-time of crystallization at 140°C (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{o-Et}])</td>
<td>5400</td>
</tr>
<tr>
<td>([\text{B}])</td>
<td>3</td>
</tr>
<tr>
<td>([\text{o-Me}])</td>
<td>105</td>
</tr>
<tr>
<td>([\text{V}])</td>
<td>1100</td>
</tr>
<tr>
<td>PET*</td>
<td>55</td>
</tr>
</tbody>
</table>

*poly(ethyleneterephthalate)
the specific gravity as a function of time\(^2,3\)). Half-time crystallization of \([B]\), \([o\text{-}Me]\), and \([V]\) at 140\(^\circ\)C was then compared with each other as a measure of the rate of crystallization. Those results clearly indicated that the ease of crystallization is in the sequence of \([B]\) > \([o\text{-}Me]\) > \([V]\). In this connection, half-time of crystallization for poly(ethylene terephthalate) was about 55 seconds at the same temperature\(^2\).

Half-time of crystallization of \([o\text{-}Et]\) at 140\(^\circ\)C in the present investigation was longer than those of \([B]\), \([o\text{-}Me]\), and \([V]\).

The induction period of crystallization of \([o\text{-}Et]\) was very long and the extent of variation of specific gravity of \([o\text{-}Et]\) was less than those of other three polymers. Obviously, \([o\text{-}Et]\) is not readily crystallizable.

**X-ray Diagrams.**

No attempt has been made to select the temperature in the above description at which the crystallization rate was maximum for each polymer. It could, however, be concluded from

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**Table 3. Spacing and fiber identity period of \([o\text{-}Et]\)\(^a\).**

<table>
<thead>
<tr>
<th>Diffraction spot</th>
<th>Relative diffraction intensity</th>
<th>Lattice spacing (Å)</th>
<th>Fiber identity period (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A(_1)</td>
<td>m</td>
<td>5.79</td>
<td></td>
</tr>
<tr>
<td>A(_2)</td>
<td>vs</td>
<td>4.87</td>
<td></td>
</tr>
<tr>
<td>A(_3)</td>
<td>ww</td>
<td>4.48</td>
<td></td>
</tr>
<tr>
<td>A(_4)</td>
<td>vs</td>
<td>3.49</td>
<td></td>
</tr>
<tr>
<td>A(_5)</td>
<td>vww</td>
<td>2.85</td>
<td></td>
</tr>
<tr>
<td>I(_2)</td>
<td>vs</td>
<td>6.76</td>
<td>18.1</td>
</tr>
<tr>
<td>I(_3)</td>
<td>s</td>
<td>3.88</td>
<td>17.9</td>
</tr>
<tr>
<td>II(_2)</td>
<td>vww</td>
<td>4.53</td>
<td></td>
</tr>
<tr>
<td>III(_1)</td>
<td>m</td>
<td>5.40</td>
<td>18.5</td>
</tr>
<tr>
<td>III(_2)</td>
<td>vww</td>
<td>4.53</td>
<td></td>
</tr>
<tr>
<td>IV(_0)</td>
<td>s</td>
<td>4.55</td>
<td>18.7</td>
</tr>
<tr>
<td>IV(_3)</td>
<td>m</td>
<td>3.58</td>
<td>18.6</td>
</tr>
<tr>
<td>VII(_0)</td>
<td>w</td>
<td>2.98</td>
<td>19.6</td>
</tr>
</tbody>
</table>

\(^a\) Stretched (60\(^\circ\)C in H\(_2\)O, x 5) and annealed (in boiling methanol, 6 hrs. and 115\(^\circ\)C in air, 2 hrs.) fiber.
qualitative observation that, in any case, \([\text{o-Et}]\) as well as the other members with side substituents could crystallize.

The crystallizability of \([\text{o-Et}]\) was confirmed by X-ray analysis. Figure 2 shows typical wide-angle X-ray diagrams obtained on the amorphous and crystallized fibers of \([\text{o-Et}]\). The unstretched amorphous fibers (a) show a very broad, diffuse ring. The stretched fibers (b) show slightly crystallized and oriented X-ray patterns. The stretched and annealed fibers (c) show well defined diffraction spots on crystallization and good orientation.

Spacing and fiber identity period of the stretched and annealed fibers are shown in Table 3. The fiber period calculated from the fiber diagrams of \([\text{o-Et}]\) is 18.6Å and this value is approximately the same as \([\text{B}]\) (18.4Å), \([\text{o-Me}]\) (18.7Å), \([\text{V}]\) (18.9Å). As the distance for the fully extended chain of one chemical unit in the calculation is 20.3Å, it seems reasonable to assume that there is little hindrance effect on the fiber period of \([\text{o-Et}]\) by introduction of the substituents into the benzene ring.

These facts suggest that, in the case of polyester-ether homologs which have a point of symmetry with respect to the centre of trans-\(-\mathrm{CH}_2\mathrm{CH}_2-\) lying between ether linkages, the effect of steric interference by side groups (viz., methyl-, ethyl-, and methoxy-groups) on the conformation of \(-\mathrm{CH}_2\mathrm{CH}_2-\) is scarcely observed and the side groups may influence to a lesser extent the planar structure of the polyester-ether molecular chain.

Infrared Absorption Spectra.

The typical spectra of amorphous and annealed sample for \([\text{o-Et}]\) are shown in Figure 3. Spectral changes due to crystallization are summarized in Table 4.

The effect of annealing is obviously seen in some of the bands which show greater intensity change, viz., the bands at 1000 and 1340 cm\(^{-1}\). Besides these, there are several bands whose intensities change slightly. These are the bands at 935 and 1435 cm\(^{-1}\).

Some new bands appear which did not exist in an amorphous sample. These are the bands at 965 and 1065 cm\(^{-1}\).

The bands at 920, 1050, 1375, and 1455 cm\(^{-1}\) become weaker, especially at 1375 cm\(^{-1}\).

We reported previously that the infrared spectrum of polyester-ether \([\text{B}]\) was analogous to that of poly(ethyleneterephthalate)\(^{10}\). The bands at 965, 1340, 1375, and 1455 cm\(^{-1}\) in \([\text{o-Et}]\) also correspond to the bands at 973, 1337, 1370, and 1453 cm\(^{-1}\) in poly(ethyleneterephthalate). Then

![Infrared spectrum of o-Et.](image)
Table 4. IR spectral changes due to crystallization

<table>
<thead>
<tr>
<th>Bands</th>
<th>Stretching and annealing</th>
<th>Mode $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1455</td>
<td>$-$</td>
<td>$\delta$ (CH$_2$)</td>
</tr>
<tr>
<td>1435</td>
<td>$+$</td>
<td>$\delta$ (CH$_2$)</td>
</tr>
<tr>
<td>1375</td>
<td>$-$</td>
<td>$\tau_w$ (CH$_2$)</td>
</tr>
<tr>
<td>1340</td>
<td>$++$</td>
<td>$\tau_w$ (CH$_2$)</td>
</tr>
<tr>
<td>1065</td>
<td>appears</td>
<td>$\nu_s$ (C–O–C)</td>
</tr>
<tr>
<td>1050</td>
<td>$-$</td>
<td>$\nu$ (C–O–C)</td>
</tr>
<tr>
<td>1000</td>
<td>$++$</td>
<td>aromatic, in plane C–H bending</td>
</tr>
<tr>
<td>965</td>
<td>appears</td>
<td>$\nu$ (C–O)</td>
</tr>
<tr>
<td>935</td>
<td>$+$</td>
<td>aromatic, out of plane C–H bending</td>
</tr>
<tr>
<td>920</td>
<td>$-$</td>
<td>$\tau_r$ (CH$_2$)</td>
</tr>
</tbody>
</table>

$^a$ +, intensity increase; $-$, intensity decrease
$^b$ $\nu_s$ = Symmetric stretching, $\delta$ = Bending, $\tau_w$ = Wagging, $\tau_r$ = Rocking

*These bands display the same spectral changes with changes of crystallization as is the case of poly(ethyleneterephthalate). Assignments for poly(ethyleneterephthalate) are given Miyake$^{11}$, Monley$^{12}$, Miller and Willis$^{13}$, and Tobin$^{14}$. The band at 1065 cm$^{-1}$ is assigned to a C–O–C symmetric stretching vibration and the band at 935 cm$^{-1}$ is assigned to an out-of-plane C–H deformation vibration. These two bands characteristically exist only in polyester-ether homologs and are not observed in poly(ethyleneterephthalate). Davison assigned a band at 1060 cm$^{-1}$ in poly(oxyethylene)glycol to a C–O–C symmetric stretching vibration.$^{15}$ The band at 1435 cm$^{-1}$ is the CH$_2$ deformation vibration in [o-Et] and can be observed as also in [o-Me] and [V], though there is no corresponding band in [B] and poly(ethyleneterephthalate). Therefore, this is the characteristic band in polyester-ether homologs with side substituents. The $^\text{--}$C–O–C symmetric stretching vibration at 1050 cm$^{-1}$ exist in [B], [o-Me], and poly(ethyleneterephthalate), and not in [V]. Although the intensity of this band in [B] increases with annealing, it decreases in [o-Et], [o-Me], and poly(ethyleneterephthalate). These results are inexplicable.*

Acknowledgement.

The authors wish to thank Emeritus Professor Rikizo Imamura of Kyoto University for his encouragement and valuable comments.

References.

ポリ(エチレン4,4′-(1,2-エタンジルオキシ)
ビス(3-エチルベンゾエート))の合成と物性

朝日工業大学応用化学教室　山本吉威、三軒　齊、岸本芳信、中野英彦

芳香族のオルト位にエチル置換基をもつ、1,2-ビス
(4-カルポキシ-2-エチルフェノキシ) エタンを新たに
合成し、これをエチレンジコールと重縮合反応させて、
ポリ(エチレン4,4′-(1,2-エタンジルオキシ)ビス(3-
エチルベンゾエート))を得た。得たポリマーの結晶性と
熱的性質を、X線回折、赤外分光分析、DSC、及び結晶
化速度の測定などにより検討した。

本ポリマーは結晶性をもち、溶融粘弾性が可能であった。
ポリマーの物性は、結晶融点：170℃、ガラス転移温度：
52℃、140℃における半結晶化時間：5400秒、溶融粘性
模様の繊維周期：187 Åであった。