Elastic modulus of crystalline regions of poly(ether ether ketone), poly(ether ketone) and poly(p-phenylene sulphide)

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Elastic moduli \( E_l \) of crystalline regions in the direction parallel to the chain axis were measured by X-ray diffraction for poly(ether ether ketone) (PEEK), poly(ether ketone) (PEK) and poly(p-phenylene sulphide) (PPS). \( E_l \) values of 71 GPa, 57 GPa and 28 GPa were obtained for PEEK, PEK and PPS, respectively. The calculated values for Treloar's method agreed well with these observed \( E_l \) values. These small \( E_l \) values were considered to be due to the fact that the lengths of the arms where the moment of force acts during the deformation are longer for these polymers than for polyethylene (PE). The deformation through bond angle bending at hetero atoms played an important contribution to the extension of the chains. The difference in \( E_l \) values among these polymers was found to depend on the difference in the bond angles and their force constants. Elastic moduli \( E_t \) of crystalline regions in the direction perpendicular to the chain axis were also measured for PEEK and PEK. These \( E_t \) values were somewhat larger than those for PE; however, strong intermolecular interactions were not considered to act in these polymers. The intermolecular cohesive energy and heat resistance of these super engineering plastics were able to be evaluated through the measurement of \( E_t \) values.

(Keywords: crystal modulus; poly(ether ether ketone); poly(ether ketone))

INTRODUCTION

The elastic moduli of polymer crystals provide us with important information on the molecular conformation and intermolecular forces in the crystal lattice, and on the relation of these to the mechanical properties of polymers\(^1-6\). We have been engaged in measuring the elastic modulus of crystalline regions of various polymers in the directions parallel \( (E_l) \) and perpendicular \( (E_t) \) to the chain axis by X-ray diffraction\(^1-6\). Examination of the data so far accumulated led us to success in relating the \( E_t \) value—viz, the extensivity of a polymer molecule—to the molecular conformation and the deformation mechanism of a polymer molecule in the crystal lattice. The values of \( E_t \) for polymers with a fully extending planar zigzag conformation, e.g. polyethylene (PE) and poly(vinyl alcohol) (PVA), were found to be 235 and 250 GPa, respectively. Knowing of the elastic modulus \( E_t \) of crystalline regions of polymers is also of importance in connection with the mechanical properties of polymers, because \( E_t \) gives the maximum value for the specimen modulus of a polymer. On the other hand, the elastic modulus \( E_t \) gives information on the intermolecular forces and their anisotropy. The value of \( E_t \) varies from 11.4 GPa for nylon 6 γ-form (intermolecular hydrogen bonds acting) to 2 GPa for isotactic poly-l-butene (van der Waals force acting).

Recently, many engineering plastics have been developed for wide practical usages as industrial and structural materials. In particular, poly(ether ether ketone) (PEEK), poly(ether ketone) (PEK) and poly(p-phenylene sulphide) (PPS) are in the limelight as super engineering plastics, because they are easy to process and have extremely high heat resistance and chemical resistance\(^7\). They are polymers in which para-positions of phenyl rings are linked with various atoms or groups (O, CO, S), and are reported to be crystalline polymers whose skeletons have a zigzag conformation in the crystalline regions\(^8\). PPS is also known to form electrically conducting complexes upon doping with electron acceptors or donors\(^9\).

In this paper, we measured the \( E_l \) values for PEEK, PEK and PPS and the \( E_t \) values for PEEK and PEK by X-ray diffraction, and then investigated the relationships between the mechanical properties, the conformation of molecular chains, and the intermolecular interactions of these polymers.

EXPERIMENTAL

Samples

A PEEK film (Sumitomo Chemical Co., Ltd, thickness 150 \( \mu \)m) was drawn 4 times at 170°C and kept at that length while being annealed at 300°C for 1 h. A PEK film, which had been previously drawn 4 times uniaxially, was drawn 1.2 times at 200°C and kept at that length while being annealed at 320°C for 1 h. PPS fibres (Toray Industries, Inc., fibre diameter 17 \( \mu \)m) were annealed at 250°C for 1 h at constant length.
by drawing the reciprocal lattice rotation diagrams from
the diffraction position of each spot. The number of
diffraction spots were 23, 30 and 26 for PEEK, PEK and
PPS, respectively. The precise fibre period (the fibre axis
is \( 'c' \) in all cases) was determined from the lattice spacing
of the 008 reflection by using a wide-angle X-ray
diffractometer (Rigaku Denki RAD-B System). The
spacings were calibrated by the spacings of reflections
of LiF.

Density

The density \( d \) of the specimen was obtained by a
flostation method (benzene–carbon tetrachloride system)
at 30°C. The degree of crystallinity \( X_c \) was calculated by
the following equation:

\[
\frac{1}{d} = \frac{X_c}{d_c} + \left(1 - \frac{X_c}{d_a}\right)
\]

where \( d_c \) is the crystal density and \( d_a \) is the amorphous
density.\(^8,10,11\)

Melting point and heat of fusion

The melting point \( T_m \) and the heat of fusion \( \Delta H \) of
each sample were measured using a differential scanning
calorimeter (Daini Seikosha, SSC-560S) at a sample
weight of ca. 10 mg, and a heating rate of 10°C min\(^{-1}\). \( T_m \)
and \( \Delta H \) were determined as a peak temperature and
area of the whole melting endotherm, respectively.

Specimen modulus

The macroscopic specimen modulus \( Y_l \) was measured
from the initial slope of the stress–strain curve by using
a tensile tester (Simadzu, Autograph IS-100) at 25°C.
The initial length of the specimen was 20 mm, and the
extension rate was 2 mm min\(^{-1}\). At the same time, the
tensile strength and the elongation at break were also
measured.

Degree of orientation

The degree of orientation \( \pi \) was defined by

\[
\pi = \frac{(180 - H^\circ)}{180}
\]

where \( H^\circ \) is the half-width of the intensity distribution
curve for the 008 reflection of each sample along the
Debye–Scherrer ring.

Crystallite size

Determination of the crystallite size \( D \) and the lattice
distortion of each sample along the chain direction was
performed by measuring the meridional profiles of the
002, 006 and 008 reflections for PEEK and PEK, and
the 002, 004, 006 and 008 reflections for PPS. The
observed integral width \( \beta \) of each reflection was corrected
for both the CuK\(_a\) doublet broadening (Jones’ method)
and the instrumental broadening \( b \) according to the
equation:

\[
\beta^2 = B^2 - b^2
\]

where \( \beta \) is the pure integral width of each reflection. The
integral width \( (\delta S) \) in the reciprocal lattice space was
given as follows:

\[
(\delta S) = \beta \cos \theta / \lambda
\]

where \( \theta \) is the Bragg angle and \( \lambda \) is the X-ray wavelength.

It has been said that there are two types of lattice
distortions, that is, the microcrystalline type distortion

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**Figure 1** X-ray fibre photographs of poly(ether ether ketone),
poly(ether ketone) and poly(\(p\)-phenylene sulphide)
Crystal modulus of PEEK, PEK and PPS: T. Nishino et al.

used for the measurement of $E_t$. On the other hand, the reflections used for the measurement of $E_t$ were three equatorial reflections (110, 200 and 020), which strongly appeared in the low angle region in Figure 1.

The lattice extension under a constant load was measured by means of an X-ray diffractometer equipped with a stretching device and a load cell. The strain $\varepsilon$ in the crystalline regions was estimated by use of the relation:

$$\varepsilon = \Delta d/d_0$$  \hspace{1cm} (6)

where $d_0$ denotes the initial lattice spacing, and $\Delta d$ is the change in lattice spacing induced by a constant stress. The experimental error in measuring the peak shift was evaluated ordinarily to be less than $\pm 0.01^\circ$ in 20 angle.

The stress $\sigma$ in the crystalline regions was assumed to be equal to the stress applied to the sample. This assumption of homogeneous stress distribution has been proven experimentally for PE, PVA, cellulose etc. poly(ethylene terephthalate)\textsuperscript{15}, poly (p-phenylene terephthalamide)\textsuperscript{16}, isotactic poly(4-methyl-pentene)\textsuperscript{17} etc.

The elastic moduli $E_t$ and $E_t$ were calculated as:

$$E = \sigma/\varepsilon$$  \hspace{1cm} (7)

Here $\sigma$ and $\varepsilon$ were not corrected for inclination of the lattice plane, because in this study we used the meridional reflections. A more detailed description of the measurements was given in earlier papers\textsuperscript{1-6,13,14}.

RESULTS AND DISCUSSION

Characterization of samples

Table 1 shows some characteristics of PEEK, PEK and PPS. Though all polymers had high melting points as expected for heat resistant polymers, all other properties such as crystallinity, specimen modulus, etc. of these polymers were approximately the same as those of conventional polymers. Crystallite sizes along the chain axis were small and were only several times longer than the fibre identity periods.

As shown in Figure 1, X-ray fibre photographs of PEEK, PEK and PPS resemble one another. All the polymers belong to an orthorhombic unit cell with the space group of Pbcn-D21h\textsuperscript{4}, and the a, b and c dimensions...
of one of the polymers are approximately equal to those of others (see Table 1). Though the crystallographic repeat period must be about 30 Å for PEEK, and 20 Å for PEK with two monomers, the fibre identity periods were ca. 10 Å without appearance of the diffraction peak corresponding to 15 Å or 30 Å for PEEK, and 20 Å for PEK. This means that the molecular chains of PEEK and PEK are packed in the unit cell without distinguishing their ether and ketone groups. The bond angles at hetero-atoms which link the para-positions of phenyl rings are 126.5° for PEEK and PEK. On the other hand, the bond angle of PPS is somewhat small (110°). These unit cell parameters are in accordance with those previously reported.

**Elastic modulus $E_t$ of crystalline regions**

Figure 3 shows the stress–strain curves for the (008) plane of PEEK, PEK and PPS at room temperature. All the strains were reversible. The initial slopes of the curves increased in this order. This indicates that the molecules of PPS in the crystalline regions are the easiest to elongate. From these slopes, the $E_t$ values of 71 GPa, 57 GPa and 28 GPa were obtained for PEEK, PEK and PPS, respectively. The $f$-values, the force required to stretch a molecule by 1%, calculated from both the $E_t$ value and the cross-sectional area of one molecule in a crystal lattice, were 1.61 x 10$^{-5}$ dyn, 1.27 x 10$^{-5}$ dyn and 0.69 x 10$^{-5}$ dyn for PEEK, PEK and PPS, respectively. The observed $E_t$ values were smaller than for other rigid polymers such as aromatic polyamides and aromatic polyesters. Accordingly, these polymers in question can be used as the matrix resins of high performance composite materials with their high heat resistances; however, high modulus materials cannot be obtained from them because their $E_t$ values, i.e. the maximum attainable moduli, are relatively small.

Table 2  Stretching and bending force constants

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond distance (Å)</th>
<th>Force constant $k_1$ (N m$^{-1}$)</th>
<th>Angle</th>
<th>Bond angle (degree)</th>
<th>Force constant $k_p$ (N m$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–O</td>
<td>1.47$^{10}$</td>
<td>4.54$^{20}$</td>
<td>C–O–C</td>
<td>126.5$^{10}$</td>
<td>0.54$^{23}$</td>
</tr>
<tr>
<td>C–C</td>
<td>1.47$^{10}$</td>
<td>3.70$^{22}$</td>
<td>C–C(O)–C</td>
<td>126.5$^{10}$</td>
<td>0.15$^{22}$</td>
</tr>
<tr>
<td>C–S</td>
<td>1.74</td>
<td>2.43$^{12}$</td>
<td>C–S–C</td>
<td>110.0$^{18}$</td>
<td>0.157$^{22}$</td>
</tr>
<tr>
<td>C$<em>{ax}$–C$</em>{ax}$</td>
<td>1.39$^{32}$</td>
<td>7.62$^{21}$</td>
<td>C$<em>{ax}$–C$</em>{ax}$–C$_{ax}$</td>
<td>–</td>
<td>0.661$^{22}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C$<em>{ax}$–C$</em>{ax}$–C$_{ax}$</td>
<td>–</td>
<td>1.06$^{20}$</td>
</tr>
</tbody>
</table>
Crystal modulus of PEEK, PEK and PPS: T. Nishino et al.

The deformation through bond angle bending at hetero-atoms plays an important contribution to the extension of the chain. The bending force constant for the ketone group is one-third of that for the ether group. This is the reason the $E_t$ value of PEK, whose ketone content is larger than for PEEK, is smaller than that of PEEK. For PPS, both the small bending force constant for sulphide and the small bond angle bring the much smaller $E_t$ value. Garbarczyk reported the bond angle of sulphide from 103° to 107° instead of 110° based on the potential energy calculation. So $E_t$ was calculated for these bond angles under the restriction of the fibre identity period being fixed at the observed value (10.27 Å).

Table 3 shows the change in the calculated $E_t$ value with the bond angle. It is evident that the bond angle greatly affects the $E_t$ value. A small bond angle gave a small $E_t$ value and diverged from the observed $E_t$ value. As a result, the calculated $E_t$ value for the bond angle of 110° fits the observed $E_t$ value. Thus, the bond angle of PPS seems to be near 110° from the mechanical point of view, too.

Macroscopic specimen moduli $Y_t$ are relatively small for these polymers. For example, Kunugi et al. reported a $Y_t$ value of PEEK up to 13.3 GPa by zone-drawing, which corresponds to 19% of $E_t$.24 As far as we know, this is the maximum attained $Y_t$ for PEEK. As described before, $E_t$ values, which are the maximum attainable moduli, were relatively small and this limited $Y_t$ values for the polymers mentioned here. Thus these small $Y_t$ seem to be ascribed partly to the small $E_t$ values.

Recently, Ward et al. reported the value of $E_t$ for PPS by X-ray diffraction.25 They obtained 38 GPa and 43 GPa for the observed and calculated $E_t$ values, respectively. They employed the (114) plane for the measurement of $E_t$, though the normal of this plane is inclined at 28.3° to the fibre axis and there are meridional reflections. They corrected the measured strain by considering this inclination of the plane, and the Poisson's ratio of the crystal lattice. Though full details are not known, the observed strain was multiplied by 0.7 in order to convert it to the value in the chain direction. We here measured the $E_t$ value for the (114) plane, and 32 GPa was obtained. By correcting the stress and strain simply with the inclination for the (114) plane, in this study, an $E_t$ value of 28 GPa was estimated for PPS. This value agrees with the $E_t$ value for the (008) plane. Thus, the correction method employed by Ward et al. seems not to be adequate.

As shown in Figure 2, there are some equivalent meridional reflections other than the 008 reflection. We then measured the $E_t$ value by using these planes in the same way.

Figures 6 and 7 show the $\sigma$- $e$ curves for the (002) and (006) planes of PEEK and PEK, respectively. Figure 8...
shows the $\sigma$–$\varepsilon$ curves for the (002), (004) and (006) planes of PPS. In all figures, the broken lines indicate the $\sigma$–$\varepsilon$ curves for the (008) plane. The $\sigma$–$\varepsilon$ curves for the (002), (004) and (006) planes differed from that for the (008) plane. The initial slope increased with a decrease in the order of reflections. This means that the $E_I$ value changed depending only on the order of reflection.

Table 4 shows the $E_I$ values obtained from the initial slopes of these curves and the fibre identity period measured for each meridional reflection of PEEK, PEK and PPS. Higher order reflections gave the higher $E_I$ values, though an inherent $E_I$ value should be obtained for each meridional reflection of PEEK, PEK and PPS. Higher order reflections gave the higher $E_I$ value, and PEK against one another, their ratio is 5.9: 10: 11. The $E_I$ values described before by more than one order. While polymer main chain atoms are linked with covalent bonds, the auxiliary valences such as van der Waals force and hydrogen bonding act in the direction perpendicular to the chain axis as intermolecular interaction. This leads to smaller values for $E_I$. These $E_I$ values are somewhat larger than that of PE (ca. 4 GPa)$^{23}$ at room temperature, but are smaller than those of nylon 6 $\gamma$-form in the hydrogen bonds direction (11.4 GPa)$^6$ and polyoxymethylene in which dipole–dipole interaction acts (7.8 GPa)$^8$. Thus strong intermolecular interaction was not considered to act in the polymers studied in this paper.

Figure 9 shows the anisotropies of $E_I$, in the ab plane of PEEK and PEK superposed on the crystal structure of PEEK. In order to draw the curves fitted to the observed values, the elastic modulus $E_I$ in the $\theta$ direction from the a axis was calculated as follows$^{31}$:

$$
1/E_\theta = (\cos^4 \theta/E_{0a}) + (\sin^4 \theta/E_{0b}) + \left\{ (1/G_{ab}) - 2(v_{ab}/E_{a}) \right\} \sin^2 \theta \cos^2 \theta
$$

where $\theta$ is the angle from the a axis, $E_\theta$ and $E_0$ represent the $E_I$ values for the (200) and (020) planes, respectively, $G_{ab}$ and $v_{ab}$ are the shear modulus and Poisson's ratio of the crystal lattice when stress is applied in the direction of the a axis. We here assumed $v_{ab}$ to be 1/3. The area surrounded by the closed curve can be said to correspond to the integral of the intermolecular interaction in the direction perpendicular to the chain axis. This thus may be regarded as one parameter for the intermolecular cohesive energy. Comparing these areas for PE$^{30}$, PEEK and PEK against one another, their ratio is 5.9: 10: 11.

The melting point of a polymer is defined as the ratio of the change in enthalpy to that in entropy on fusion

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_I$ (GPa)</th>
<th>$d$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEEK</td>
<td>5.9</td>
<td>9.93</td>
</tr>
<tr>
<td>PEK</td>
<td>5.4</td>
<td>9.91</td>
</tr>
<tr>
<td>PPS</td>
<td>5.7</td>
<td>9.91</td>
</tr>
</tbody>
</table>

$^{*}$ (004) reflections were not observed for poly(ether ketone) and poly(ether ketone)
Crystal modulus of PEEK, PEK and PPS: T. Nishino et al.

Figure 9 Stress–strain curves for the equatorial reflections of poly(ether ether ketone) and poly(ether ketone)

Figure 10 Anisotropies of elastic modulus $E_t$ in the ab plane of poly(ether ether ketone) and poly(ether ketone)

and all these polymers have a zigzag skeletal conformation. In other words, $T_m$ is considered to become the same parameter for the intermolecular cohesive energy in these cases. Considering the ratio for $T_m$ of these polymers (PE, 418 K; PEEK, 621 K; PEK, 646 K) is 6.4:10:10.4, this ratio is nearly in accordance with that of the area surrounded by the closed curves in Figure 10. Thus this resemblance indicates that $T_m$ for these polymers is governed by the intermolecular cohesive energy. Accordingly, isotropic large intermolecular interaction (though there is no special strong interaction) is the reason why poly(aryl ether ketone)s have higher melting temperatures and are known as heat resistant polymers. Conversely, $E_t$ values can provide important information on the heat resistivity of polymers.

The macroscopic specimen modulus $Y$, in the direction perpendicular to the chain axis was 3.1 GPa for PEEK and 3.4 GPa for PEK. The ratios of the $Y$ value to the $E_t$ value, $Y/E_t$, are 0.53–0.74. These values are relatively large compared with other common polymers, where $Y/E_t$ is usually less than 0.5. This indicates that the mechanical properties of these polymers are strongly controlled by that of crystalline regions in the normal direction.

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