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# Temperature dependence of the elastic modulus of the crystalline regions of poly(ethylene 2,6-naphthalate)*

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The temperature dependence of the elastic modulus $E_l$ of the crystalline regions of poly(ethylene 2,6-naphthalate) (PEN-2,6) in the direction parallel to the chain axis has been investigated up to 228°C by X-ray diffraction. The $E_l$ value of PEN-2,6 was 145 GPa at room temperature, which is about 40% greater than that of poly(ethylene terephthalate) ($E_l = 108$ GPa). The axial chain contraction coefficient was constant from 22 to 228°C, and correspondingly the value of $E_l$ remained unchanged up to 228°C. The deformation mechanism is considered to remain unchanged up to 228°C and the skeletal conformation of PEN-2,6 in the crystalline regions is stable against heat. It is reasonable to conclude that stress is homogeneous throughout the sample.

**(Keywords: poly(ethylene 2,6-naphthalate); elastic modulus; skeletal structure)**

## INTRODUCTION

The elastic modulus $E_l$ of the crystalline regions of polymers in the direction parallel to the chain axis provides important information on the molecular conformation and its relation to the mechanical properties of polymers[1–3]. We have been engaged in measuring $E_l$ values by an X-ray diffraction method and were able to relate the $E_l$ value, i.e. the extensivity of a molecule, to the molecular conformation and the deformation mechanism in the crystal lattice. Generally, a molecular chain with a fully extended planar zig-zag conformation has a larger $E_l$ value. On the contrary, the $E_l$ values for polymers having contracted or helical conformations are smaller, because it is easier to deform these chains than to deform the extended chain. For example, we have measured the $E_l$ values for some aromatic polyesters. Poly(ethylene terephthalate) (PET) has almost planar conformation and the $E_l$ value is 108 GPa (refs 4, 5). On the other hand, the $E_l$ values of poly(butylene terephthalate) (PBT) $\alpha$-form and poly(trimethylene terephthalate) (PTT) are 13.5 GPa and 2.6 GPa, respectively[6,7]. The molecules of PBT $\alpha$-form and PTT are much more contracted (12% and 25%, respectively) from the planar extended conformation in the crystalline regions than those of PET (2%). These contracted chain molecules deform through an internal rotation around the C–C single bond, whose force constant is much smaller than those of bond stretching and bond angle bending. This is the reason for the small $E_l$ values of PBT $\alpha$-form and PTT. From another point of view, knowledge of the elastic modulus $E_l$ is of interest in connection with the mechanical properties of polymers, because $E_l$ signifies the maximum value for the specimen modulus of a polymer.

We have also investigated the temperature dependence of $E_l$ for various polymers and discussed it in terms of the thermal expansion and stability of the crystalline regions for each polymer[5,8,9]. With regard to aromatic polyesters, we have already reported the temperature dependence of $E_l$ for PET, PBT $\alpha$-form[10], poly(ethylene oxybenzoate) $\alpha$-form[11] and liquid crystalline polyesters (Rodrun, Vectran)[12,13].

Poly(ethylene 2,6-naphthalate) (PEN-2,6) is an aromatic polyester in which the benzene ring of PET is replaced by a naphthalene ring. Recently, increasing use has been made of PEN-2,6 because of its good physical properties[14]. For instance, PEN-2,6 is used as the base film of long-playing videotapes and as an insulating material in the electronics industry instead of PET. It has been shown that PEN-2,6 is superior to PET in heat resistance (PEN-2,6: $T_g = 117$°C (ref. 15), $T_m = 272$°C; PET: $T_g = 69$°C, $T_m = 265$°C), Young's modulus and tensile strength. Ito *et al.*[16] and Ghanem and Porter[17] attempted to obtain high modulus and high strength PEN-2,6 by two-stage drawing, and reported that good mechanical properties are achieved for PEN-2,6. PEN-2,6 is also expected to be used for applications under various environmental conditions. This suggests the need to clarify the relationships between mechanical properties and temperature.

In this study, we have measured the temperature dependence of $E_l$ for PEN-2,6 at high temperature, and

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investigated the molecular motions in the crystalline regions, comparing them with those of PET.

## EXPERIMENTAL

### *Samples*

PEN-2,6 film (Teonex, Teijin Co. Ltd), in the form of an amorphous film, was used as a starting material in this study. A rectangular film (thickness ~140 μm) was drawn to five times its original length at 125°C, and then annealed at 250°C for 2 h at constant length.

*Figure 1* shows the X-ray fibre photograph of drawn and annealed PEN-2,6 films at room temperature. It showed a high crystallinity and a high degree of orientation of the crystallites. Two crystal modifications have been reported for PEN-2,6, α-form and β-form[18,19]. The unit cell parameters of PEN-2,6 α-form, determined by Mencik[18], are $a = 6.51$ Å, $b = 5.75$ Å, $c = 13.2$ Å (fibre axis), $\alpha = 81.3°$, $\beta = 144°$, $\gamma = 100°$. All the reflections in *Figure 1* could be indexed with the unit cell of PEN-2,6 α-form.

The degree of crystallite orientation $\pi$ was 0.97, determined from the equation:

$$\pi = (180° - H°)/180° \qquad (1)$$

where $H°$ is the half-width of the intensity distribution curve for the $\bar{4}110$ reflection of PEN-2,6 along the Debye–Scherrer ring.

The density $d$ of the specimen obtained by a flotation method (benzene–carbon tetrachloride system at 30°C) was 1.366 g cm$^{-3}$. The degree of crystallinity $X_c$ was 0.51, as calculated by the following equation:

$$1/d = X_c/d_c + (1 - X_c)/d_a \qquad (2)$$

where $d_c$ is the crystal density (1.407 g cm$^{-3}$) (ref. 18) and $d_a$ is the amorphous density (1.325 g cm$^{-3}$) (ref. 20).

The melting point $T_m$ and the heat of fusion $\Delta H$ of this sample were 272°C and 69.9 J g$^{-1}$, respectively, and were measured using a differential scanning calorimeter (Daini Seikosha SSC-560S) at a heating rate of 10°C min$^{-1}$ and sample weight of 5 mg. $T_m$ and $\Delta H$ were calibrated with tin.

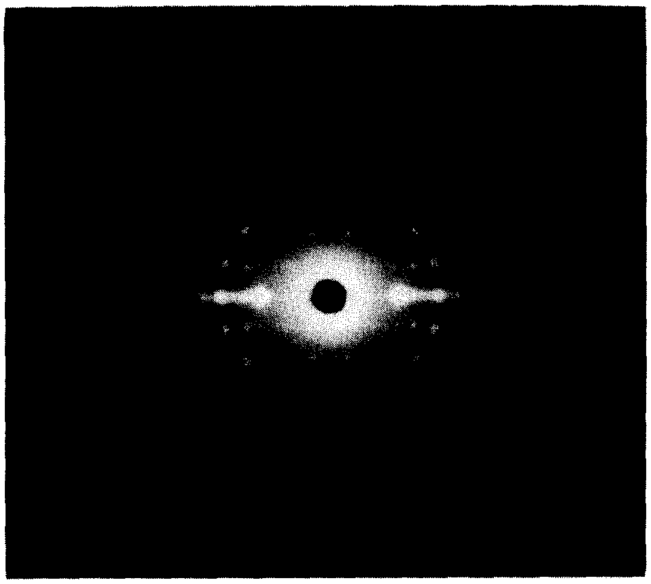

**Figure 1** X-ray fibre photograph of poly(ethylene 2,6-naphthalate)

The mechanical tan $\delta$ values of drawn and annealed PEN-2,6 were measured using a dynamic mechanical thermal analyser (Rheometrics RSA II) in a stretching mode (parallel to the drawn direction) with a frequency of 10 Hz and a heating rate of 2°C min$^{-1}$.

Stress–strain curves for the macroscopic specimen were measured with a tensile tester (Shimadzu, Autograph SD-100) at various temperatures. The initial length of the specimen was 20 mm and the extension rate was 2 mm min$^{-1}$.

The crystallite size $D$ in the direction perpendicular to the ($\bar{4}$110) plane was 122 Å, which was determined by measuring the profile followed by correcting for both the instrumental and CuKα broadening, and then applying Scherrer's equation.

### *Measurement of the elastic modulus of the crystalline regions*

The lattice extension under a constant load was measured by means of an X-ray diffractometer (Rigaku Denki RAD-B System) equipped with both a stretching device and a load cell.

There is no meridional reflection for PEN-2,6 α-form, so that two off-meridional reflections $\bar{4}$1 10 (reflection angle $2\theta = 71.72°$ for CuKα radiation) and $\bar{2}$05 ($2\theta = 34.28°$) were employed for the measurement of $E_l$. The normals of these lattice planes are inclined at angles of 4.6° and 8.7°, respectively, to the fibre axis. Stresses and strains were not corrected for the inclination of the lattice planes, because these angles are relatively small as for the ($\bar{1}$05) plane of PET[5].

Values of $E_l$ at high temperature were measured using the electric heating cell with a temperature controller. The temperature was detected with a thermocouple, and it could be maintained to within an accuracy of ±1°C during the measurements.

The strain $\varepsilon$ in the crystalline regions was estimated by use of the relation $\varepsilon = \Delta d/d_0$, where $d_0$ denotes the initial lattice spacing for the ($\bar{4}$1 10) or ($\bar{2}$05) planes, and $\Delta d$ is the change in lattice spacing induced by the applied constant stress. The change of these spacings was measured by eye from the shift of peak positions. The experimental error in measuring the peak shift due to the lattice extension was evaluated to be generally less than ±0.01° in $2\theta$.

The stress $\sigma$ in the crystalline regions was assumed to be equal to the macroscopic stress applied to the sample. This assumption of a homogeneous stress distribution has been proven experimentally for many polymers including cellulose[1], polyethylene[8] and poly(vinyl alcohol)[9].

The elastic modulus $E_l$ was calculated by using the equation:

$$E_l = \sigma/\varepsilon \qquad (3)$$

A more detailed description of the measurement was given in earlier papers[1–13].

## RESULTS AND DISCUSSION

*Figure 2* shows the stress–strain curve for the ($\bar{4}$1 10) plane and ($\bar{2}$05) plane of PEN-2,6 crystal at 22°C. Plots for the ($\bar{2}$05) and ($\bar{4}$1 10) planes coincide within experimental error. Although the stresses and strains should be corrected for the inclinations of these lattice planes, results in *Figure 2* confirm that small inclinations of lattice planes need not be corrected for. All the data points could be expressed with a straight line through the origin, and the lattice extensions were always reversible. The slope of the stress–strain curve yields an $E_{\mathrm{l}}$ value of 145 GPa as the crystal modulus of PEN-2,6 α-form. The $f$ value, defined as the force required to stretch a molecule by 1%, is calculated from both $E_{\mathrm{l}}$ and the cross-sectional area (21.8 $\text{Å}^2$) of one molecule in a crystal lattice of PEN to be $3.16 \times 10^{-10}$ N. The $E_{\mathrm{l}}$ and $f$ values of PET are 108 GPa and $2.24 \times 10^{-10}$ N, respectively. Both the $E_{\mathrm{l}}$ anf $f$ values of PEN-2,6 are about 40% larger than those of PET. This indicates that it is difficult to elongate the molecule of PEN-2,6 along the chain axis because of the rigidity of the naphthalene ring and the fully extended structure. These $E_{\mathrm{l}}$ and $f$ values are consistent with those previously reported for solid-state coextruded PEN-2,6 and the value (144 GPa) calculated by Treloar's method[21]. Detailed arguments on the relationship between the skeletal structure and $E_{\mathrm{l}}$ value of PEN-2,6 were given in an earlier paper[21]. The accordance of the $E_{\mathrm{l}}$ values for these two kinds of PEN-2,6 samples, despite their differences in microstructure and specimen modulus, indicates that the assumption of a homogeneous stress distribution is also valid for PEN-2,6.

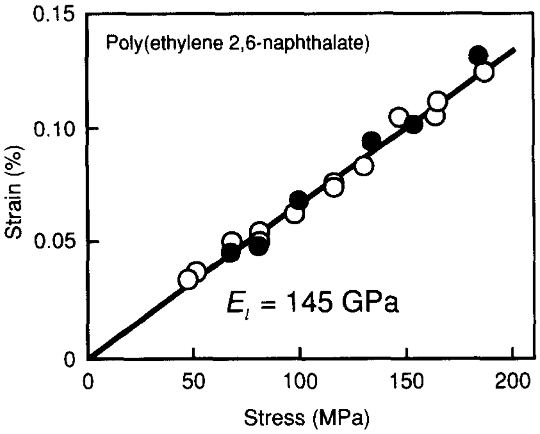

**Figure 2** Stress–strain curves for the $(\bar{4}110)$ (○) and the $(\bar{2}05)$ (●) planes of poly(ethylene 2,6-naphthalate) at 22°C

*Figure 3* shows the stress–strain curves for the $(\bar{4}110)$ and $(\bar{2}05)$ planes of PEN-2,6 at high temperatures. Again, each plot could be expressed with a straight line through the origin, and lattice extensions were always reversible. Although the maximum stress that could be applied to the sample was reduced at high temperatures, the slopes of all the curves at various high temperatures were in good agreement with that at room temperature, within experimental error.

*Figure 4* shows the $E_{\mathrm{l}}$ values of PEN-2,6 as a function of temperature. The $E_{\mathrm{l}}$ value of PEN-2,6 is constant at 145 GPa from 22 to 228°C. The $E_{\mathrm{l}}$ value depends on the deformation mechanism of chain molecules in the crystalline regions, so that it is clear that the deformation mechanism remains unchanged up to 228°C.

The mechanical tan $\delta$ values of macroscopic specimens of drawn and annealed PEN-2,6 are also superimposed on *Figure 4*. Tan $\delta$ has two major dispersions, the main relaxation peak at around 175°C, and the sub-relaxation peak at lower temperature. The former is considered to

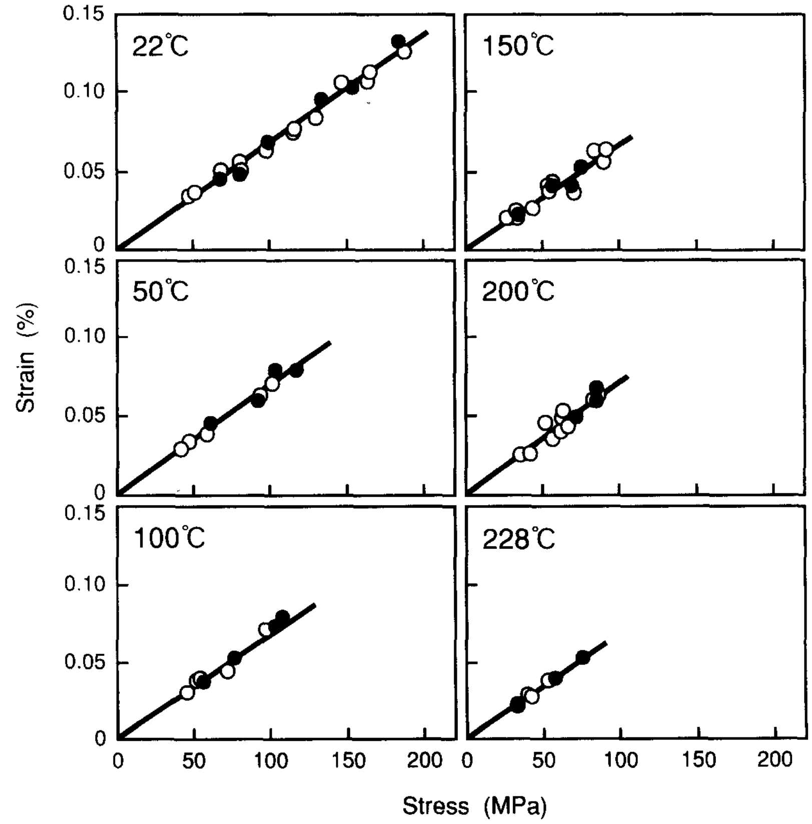

**Figure 3** Stress–strain curves for the $(\bar{4}110)$ (○) and the $(\bar{2}05)$ (●) planes of poly(ethylene 2,6-naphthalate) at various temperatures

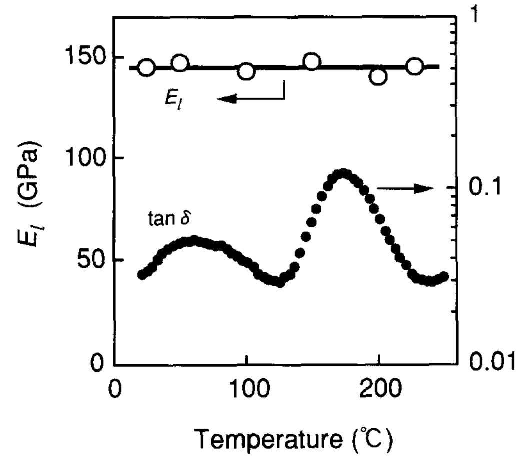

**Figure 4** Relationships of elastic modulus $E_l$ and mechanical tan δ of poly(ethylene 2,6-naphthalate) with temperature

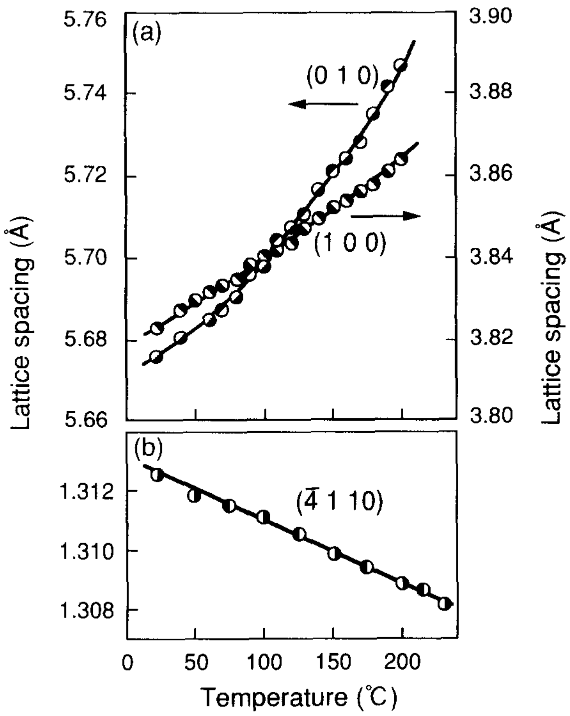

**Figure 5** Effect of temperature on the lattice spacings of (a) (100) and (010) planes, and (b) ($\bar{4}$110) plane of poly(ethylene 2,6-naphthalate). ◑, ◒, ◓, heating process; ◐, ◔, ◕, cooling process

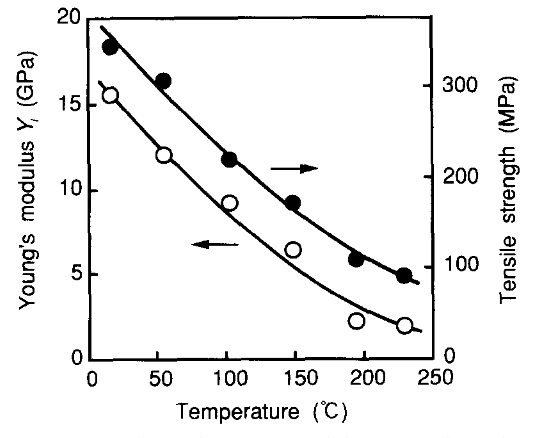

**Figure 6** Relationships of Young's modulus (○) and tensile strength (●) of poly(ethylene 2,6-naphthalate) with temperature

correspond to the glass transition (α-relaxation), while the cause of the latter (β-relaxation) is not clear. However, judging from the constancy of $E_l$ at high temperatures, there is no crystalline relaxation, at least in the chain direction, in the temperature range studied. We have investigated the temperature dependence of $E_l$ for more than 30 species of polymers, and found that the $E_l$ value decreases above a certain temperature, except for PET[5], isotactic poly(4-methyl-1-pentene)[22], cellulose[23] and Rodrun[12]. Corresponding to the decrease of $E_l$, some discontinuous change was also observed in the axial thermal expansion coefficient[8,9]. These phenomena show that local shortening of molecules due to some conformational change, such as kink, may occur beyond that temperature. We next measured the thermal expansion of a PEN-2,6 crystal in order to clarify the effect of temperature on the crystal lattice.

*Figure 5* shows the temperature dependence of the lattice spacings of (100), (010), and ($\bar{4}$110) planes for the α-form of PEN-2,6. The changes in spacings of crystal lattices were reversible at both heating and cooling processes. The lattice spacing of ($\bar{4}$110) decreases linearly without indicating an inflection point as temperature rises. The inclination gives a thermal expansion coefficient $\alpha_{\bar{4}110}$ of $-1.56 \times 10^{-5}\,K^{-1}$ within a temperature range of room temperature to 228°C. This indicates that conformational changes which cause a decrease of $E_l$ did not take place in the crystalline regions for PEN-2,6.

These results make it clear that the skeletal conformation of PEN-2,6 in the crystalline regions is stable against heat, and the force constants of bond stretching and bond angle bending remain constant over both the temperature and the stress ranges studied.

*Figure 6* shows the macroscopic specimen modulus ($Y_l$) and tensile strength as a function of temperature. The value of $Y_l$ is 15.6 GPa at room temperature, and decreases with increasing temperature to become 2.0 GPa at 228°C. The tensile strength also falls with increasing temperature, from 345 MPa at 22°C to 92 MPa at 228°C. Judging from the constancy of the $E_l$ value with temperature, it is considered that the decrease of specimen modulus $Y_l$ at high temperatures may be due mainly to the decrease of the elastic modulus ($E_a$) of the amorphous regions. If stress distribution is heterogeneous within a sample, for example some parts of the crystalline regions are mechanically parallel with the amorphous regions, the decrease of $E_a$ would lead to stress concentration on the crystalline regions, and consequently $E_l$ should decrease with increasing temperature. However, the $E_l$ value of PEN-2,6 did not decrease with increasing temperature up to 228°C as we have shown. Therefore, it is reasonable to conclude that the homogeneous stress model is valid for PEN-2,6 as well as for other polymers.

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