

# Elastic modulus of the crystalline regions of poly(ethylene-2,6-naphthalate)

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Elastic modulus  $E_1$  of the crystalline regions of poly(ethylene-2,6-naphthalate) (PEN-2,6) in the direction parallel to the chain axis was measured by X-ray diffraction. The  $E_1$  value for the  $(\bar{4}110)$  plane of PEN-2,6 was 145 GPa at room temperature, which coincided with the calculated value (144 GPa) obtained by Treloar's method. The  $E_1$  value of PEN-2,6 is larger than that of poly(ethylene terephthalate) (observed, 108 GPa; calculated, 122 GPa). This difference could be attributed to the difference of the deformability between naphthalene and phenyl rings.

(Keywords: elastic modulus; crystal modulus; poly(ethylene-2,6-naphthalate))

## Introduction

The elastic modulus of polymer crystals provides important information on the molecular conformation and intermolecular forces in the crystal lattice, and on the relation of these to mechanical properties of the polymers<sup>1-7</sup>. We have been engaged in measuring the elastic modulus  $E_1$  of the crystalline regions of various polymers, including polyesters, in the direction parallel to the chain axis by X-ray diffraction. Study of the data accumulated so far has enabled us to relate the  $E_1$  value — i.e. the extensivity of a polymer molecule — to the molecular conformation and the deformation mechanism of a polymer molecule in the crystal lattice. The  $E_1$  values for polymers with a planar zigzag conformation are 235 and 250 GPa for polyethylene and poly(vinyl alcohol), respectively, where the mechanisms of bond stretching and bond angle bending contribute to the chain extension<sup>1-4</sup>. On the other hand, the  $E_1$  values for polymers with a contracted or a helical conformation are smaller because simultaneous free rotation around the single bond of the chain, whose force constant is small, was involved in the chain extension. This is why the  $E_1$  value for poly(ethylene terephthalate) (PET) (108 GPa)<sup>8</sup> is larger than those of poly(butylene terephthalate) (PBT  $\alpha$ -form) (13.5 GPa)<sup>9</sup> and poly(trimethylene terephthalate) (2.6 GPa)<sup>10</sup>. Poly(ethylene-2,6-naphthalate) (PEN-2,6) is a polymer in which the phenyl ring of PET is replaced by a naphthalene ring. It has been shown that PEN-2,6 is superior to PET in some aspects, such as mechanical and thermal properties, radiation resistance, etc.<sup>11</sup>. Comparison of the  $E_1$  values should also provide information on the difference in deformability between naphthalene and phenyl rings. Recently, attempts have been made to obtain high modulus and high strength

PEN-2,6, and a specimen modulus of up to 30 GPa was attained<sup>12,13</sup>. In this respect, the  $E_1$  value is a monitor of practical achievement in processes aimed at obtaining high modulus oriented polymers<sup>1-7</sup>.

In this study, we measured the  $E_1$  value of PEN-2,6 by X-ray diffraction and compared it with that of PET.

## Experimental

PEN-2,6 (Teijin Co. Ltd) was solid-state co-extruded at 100°C followed by uniaxial drawing at 230°C. Total draw ratio was six times and the film thickness was 70  $\mu\text{m}$  (ref. 13).

Figure 1 shows the X-ray fibre photograph of the PEN-2,6 sample studied. It shows high crystallinity and a high degree of crystallite orientation. It has been reported that there are two crystal modifications for PEN-2,6. Judging from Figure 1, the PEN-2,6 sample studied here is a low-temperature modification reported by Zachmann *et al.*<sup>14</sup>.

The density  $d$  of this specimen obtained by a flotation method (benzene-carbon tetrachloride system at 30°C) is 1.362  $\text{g cm}^{-3}$ . This corresponds to a degree of crystallinity  $X_c$  of 47%, calculated by the equation:

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

where  $d_c$  is the crystal density ( $1.407 \text{ g cm}^{-3}$ )<sup>15</sup> and  $d_a$  is the amorphous density ( $1.325 \text{ g cm}^{-3}$ )<sup>16</sup>. The melting point,  $T_m$ , obtained by differential scanning calorimetry (Daini Seikosha SSC-560S) at a heating rate of  $10^\circ\text{C min}^{-1}$ , was 266°C, and the heat of fusion,  $\Delta H$ , was 56.5  $\text{J g}^{-1}$ .  $T_m$  and  $\Delta H$  were calibrated with tin.

The unit cell parameters<sup>15</sup> of PEN-2,6 are  $a = 6.51 \text{ \AA}$ ,  $b = 5.75 \text{ \AA}$ ,  $c = 13.2 \text{ \AA}$ ,  $\alpha = 81.3^\circ$ ,  $\beta = 144^\circ$  and  $\gamma = 100^\circ$ . The lattice plane of the PEN-2,6 crystal used for the measurement of  $E_1$  was  $(\bar{4}110)$ ;  $2\theta = 71.72^\circ$  for CuK $\alpha$  radiation (there is a near-meridional reflection at a higher  $2\theta$  value than for the  $(\bar{4}110)$  reflection, but it would overlap both  $(\bar{4}111)$  and  $(\bar{5}111)$  reflections).

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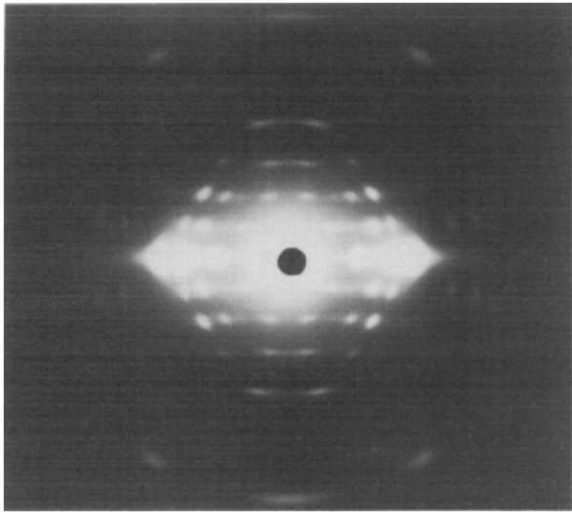


Figure 1 X-ray fibre photograph of poly(ethylene naphthalate)

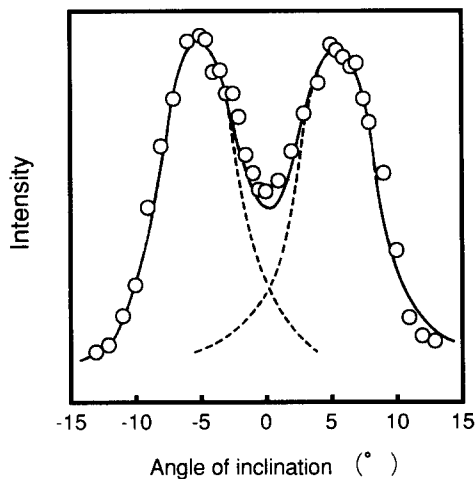


Figure 2 Diffraction intensity versus angle of inclination for the  $(\bar{4}110)$  plane of poly(ethylene naphthalate)

Figure 2 shows the diffraction intensity of the  $(\bar{4}110)$  reflection as a function of the inclination angle of the incident X-ray beam to the fibre axis. The broken lines indicate the result of resolving the curves, assuming that they are Gaussian. From this figure, it can be concluded that the normal of this plane is inclined at an angle of  $5.1^\circ$  to the fibre axis. This angle coincides with the angle expected from the crystal structure. This means that the tilting phenomenon, which is often seen for PET<sup>17</sup> and PBT<sup>18</sup>, did not occur in this sample. The degree of crystallite orientation  $\pi$ , defined by:

$$\pi = (180 - H^\circ)/180$$

was 0.96. In this equation  $H^\circ$  is the half-width of the intensity distribution curve along the Debye-Scherrer ring shown in Figure 2.

The crystallite size for the  $(\bar{4}110)$  was  $90 \text{ \AA}$ , obtained by measuring the profile followed by correcting for both the instrumental and  $\text{CuK}\alpha$  broadenings.

The elastic modulus  $E_1$  of the crystalline regions was measured by an X-ray diffractometer (Rigaku Denki RAD-B System) equipped with a stretching device and a load cell. The X-ray beam was incident to the specimen, at an angle of  $84.9^\circ$  to the fibre axis, that is, at the point of maximum intensity in Figure 2.

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  $(\bar{4}110)$  plane and  $\Delta d$  is the change in lattice spacing induced by the uniaxial constant stress applied. The experimental error in measuring the peak shift due to lattice extension was evaluated ordinarily to be less than  $\pm 1/100^\circ$  in an angle  $2\theta$ .

The stress  $\sigma$  in the crystalline regions was assumed to be equal to the stress applied to the sample. This assumption of a homogeneous stress distribution has been proven experimentally for many polymers, including PET<sup>1-10,19</sup>.

The elastic modulus  $E_1$  was calculated as:

$$E_1 = \sigma/\varepsilon$$

A more detailed description of the measurement has been given in previous papers.  $\sigma$  and  $\varepsilon$  were not corrected for the inclination of the lattice plane, because it is negligibly small<sup>8</sup>.

### Results and discussion

Figure 3 shows the stress  $\sigma$  versus strain  $\varepsilon$  curve for the  $(\bar{4}110)$  plane of PEN-2,6 at room temperature. All the plots could be expressed with a straight line through zero, and the lattice extensions were always reversible. The initial slope yields an  $E_1$  value of 145 GPa. The  $f$ -value, the force required to stretch one molecule by 1%, calculated from both the  $E_1$  value and the cross-sectional area  $(21.8 \text{ \AA}^2)^{15}$  of one molecule in the crystal lattice, is  $3.16 \times 10^{-10} \text{ N}$  for PEN-2,6. This  $E_1$  and  $f$ -value are larger than those of PET (108 GPa,  $2.24 \times 10^{-10} \text{ N}$ ). This indicates that it is harder to elongate the PEN-2,6 molecule to its chain axis than it is the PET molecule. In order to confirm this relationship, the  $E_1$  value of PEN-2,6 is calculated by Treloar's method<sup>20</sup>. This is the simplest method to investigate the effect on chain deformability of the change from phenyl ring (PET) to naphthalene ring (PEN-2,6). The bond lengths, bond angles and the force constants employed here are those used for PET by Treloar<sup>20</sup>, except for those concerning the naphthalene ring: it is assumed that the naphthalene ring behaves as though two phenyl rings are linked together, and that the deformation mechanism for bond angle bending is 1.5 times larger than that for the phenyl ring<sup>21</sup>.

Table 1 summarizes the observed and calculated  $E_1$  values of both PEN-2,6 and PET. In both cases, the calculated  $E_1$  values coincide with the observed values. Further, the  $E_1$  values for PEN-2,6 are somewhat larger

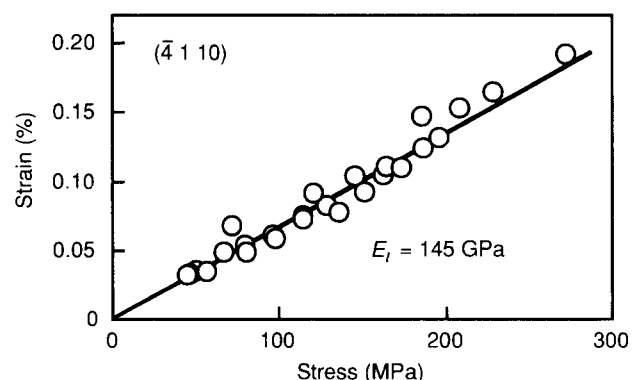


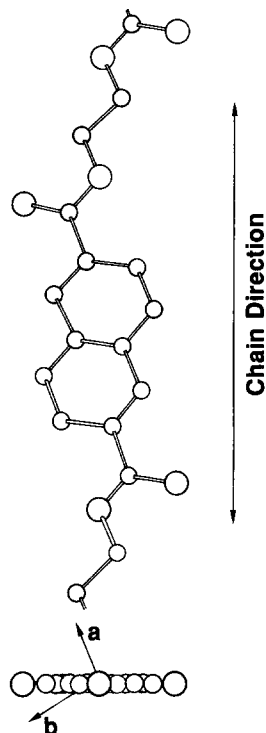
Figure 3 Stress versus strain curve for the  $(\bar{4}110)$  plane of poly(ethylene naphthalate)

**Table 1** Observed and calculated  $E_1$  values of poly(ethylene naphthalate) and poly(ethylene terephthalate)

	$E_1$ (GPa)	
	Observed	Calculated
Poly(ethylene naphthalate)	145	144
Poly(ethylene terephthalate)	108	122 <sup>a</sup> , 95 <sup>b</sup>

<sup>a</sup> Ref. 20

<sup>b</sup> Ref. 22



**Figure 4** Skeletal conformation of poly(ethylene naphthalate) after Menčík<sup>15</sup>

than those of PET. Thus, the incorporation of the naphthalene ring contributes to the high  $E_1$  and  $f$ -value of PEN-2,6 because of its rigidity, though the cross-sectional area of one molecule increased. The calculated  $E_1$  value coincides well with the observed value for PEN-2,6. The PET molecule is known to contract from

the fully extended chain by internal rotation around the O-CH<sub>2</sub> bonds<sup>17</sup>. In contrast to the conformation of PET, all the atoms of the PEN-2,6 chain, including O-CH<sub>2</sub>, are coplanar as shown in Figure 4<sup>15</sup>. The fibre identity period of fully extended PEN-2,6 is calculated to be 13.38 Å, which nearly coincides with the observed value (13.16 Å, measured by the lattice spacing for (4 1 1 0), (1 0 0), (0 1 0) planes). This may be the reason for the better agreement of observed and calculated  $E_1$  values for PEN-2,6.

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