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Temperature dependence of the elastic modulus of the crystalline regions of poly(*p*-phenylene benzobisthiazole)

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Dedicated to Professor Ronald K. Eby on the occasion of his 70th birthday

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Abstract

Temperature dependence of the elastic modulus E_l of the crystalline regions of poly(*p*-phenylene benzobisthiazole) (PBZT) in the direction parallel to the chain axis was investigated by X-ray diffraction over a temperature range from − 180 to 400°C. The E_l value of PBZT was 372 GPa at room temperature, which was the highest E_l value ever investigated. This value coincided with that reported by Lenhert and Adams (395 GPa) [Lenhert PG, Adams WW, Mat. Res. Soc. Symp. Proc. 1989; 134: 329] within experimental error. The axial chain thermal expansion coefficient was constant at $-2.9 \times 10^{-6}\,K^{-1}$ from 20 to 445°C, and correspondingly the E_l value remained unchanged up to 400°C. Moreover, the E_l value at − 185°C also coincided with that at room temperature. It is considered that the deformation mechanism remains unchanged over a wide temperature range and the skeletal conformation of PBZT in the crystalline regions is stable against the heat. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(*p*-phenylene benzobisthiazole); Elastic modulus; Skeletal structure

1. 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. We have been engaged in measuring the E_l value for a variety of polymers by X-ray diffraction [1–3]. Studies of the data accumulated so far have enabled us 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. The E_l values for polymers with a fully extended planar zigzag conformation are 235 and 250 GPa for polyethylene (PE) and poly(vinyl alcohol) (PVA), respectively [1–3], where the mechanisms of bond stretching and bond angle bending contribute to the chain extension. The force constants of these deformation mechanisms are high, therefore these possess the highest E_l values among the flexible polymers. The E_l value also plays an important role in the attempt to obtain high modulus materials, because the E_l value represents the maximum specimen modulus of a polymer. Thus, in the case of high modulus polymers, the E_l value can be a monitor of practical achievement for obtaining a high modulus polymer.

Poly(*p*-phenylene benzobisthiazole) (PBZT) is one of the high performance polymers. PBZT, a rigid rod-like polymer, consists of thiazole and phenyl rings, which has been of considerable interest because of its excellent physical properties, e.g. especially high modulus, high strength, and high heat resistance in comparison with conventional polymers. For example, the macroscopic specimen modulus, Y_l, of PBZT is reported to be 330 GPa [4,5], which exceeds the E_l value of PE. On account of these outstanding properties, PBZT is expected to have various applications and uses in severe environmental conditions as advanced materials, such as a reinforcement fiber in high performance composites. A broad range of studies have been carried out to investigate the structural features, and the mechanical properties. Thus it is important to evaluate the mechanical and thermal properties of PBZT. Lenhert and Adams have reported the E_l value of PBZT as 395 GPa experimentally at room temperature [6]. Several calculated El values were also reported [7–9], however, they varied widely from 370 to 620 GPa as

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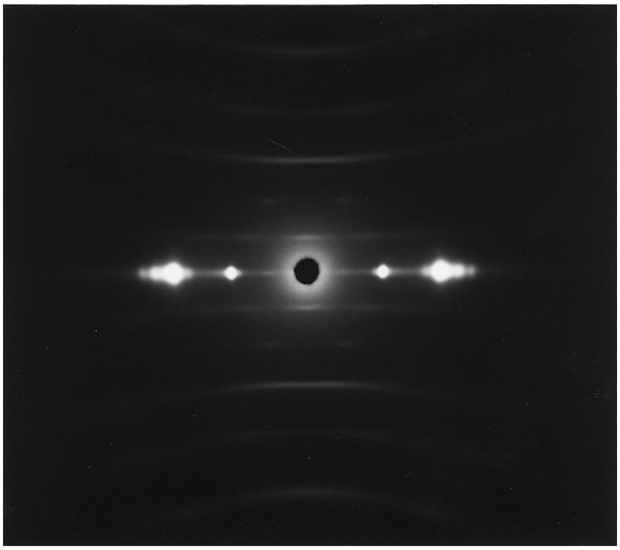

Fig. 1. The X-ray fiber photograph of PBZT.

described later, though the E_l value should be an inherent value for the polymer.

In this study, first the E_l value of PBZT measured by X-ray diffraction at room temperature, second the measured temperature dependence of the E_l value of PBZT was reported, and then relationships among the skeletal structure, mechanical property and heat resistance will be discussed.

2. Experimental

2.1. Sample and characteristics

PBZT fiber annealed at 650°C under constant length was used throughout this study.

Fig. 1 shows the X-ray fiber photograph of PBZT at room temperature. Spot-like equatorial reflections imply a high degree of the crystallite orientation and a good lateral packing of the PBZT molecules in the crystal lattice.

The degree of the crystallite orientation, f_c, in the direction of fiber axis was obtained by using 1 0 0 reflection and the following equations.

$$f_a, f_b = (3\langle\cos^2\phi\rangle - 1)/2,$$

where f_a,f_b show the degree of crystallite orientation for the *a*- and *b*-axis, respectively; and

$$\langle\cos^2\phi\rangle = \frac{\int I(\phi)\cos^2\phi \sin\phi \, d\phi}{\int I(\phi) \sin\phi \, d\phi},$$

where $I(\phi)$ shows an azimuthal intensity distribution, whose profile fits with a Pearson VII function [10]. As a result, $f_a = -0.497$, then $f_c(= 1 - f_a - f_b)$ of this sample was 0.994 by assuming $f_a = f_b$.

In order to determine the crystallite size *D* and the lattice distortion along the chain direction, the observed integral width of each meridional reflection was corrected for both the CuKα doublet broadening and the instrumental broadening. The integral width (δS) in the reciprocal lattice space was given as follows:

$$(\delta S) = \beta \cos\theta/\lambda,$$

where β, θ, and λ are the pure integral width, the Bragg angle, and the X-ray wave length, respectively. It has been said that there are two types of lattice distortion, that is, the microcrystalline type distortion (the first kind) and the paracrystalline type distortion (the second kind). In preliminary experiments, we confirmed that there exists paracrystalline type distortion in PBZT. Here the parameter of paracrystalline type distortion $g_{\|}$ was calculated as follows [11]:

$$(\delta S) = (1/D^2) + (\pi^4 g_{\|}^4 m^4/d^2),$$

where *m* is the order of reflections and *d*, the fiber repeat period. The observed *D* and $g_{\|}$ of PBZT were 178 Å and 0.77%, respectively.

The dynamic storage modulus (E'), and mechanical tan δ were measured using a dynamic viscoelastic analyzer (ITK Co., DVA-200) in a stretching mode (parallel to the fiber direction) with a frequency of 10 Hz and a heating rate of 6°C/min.

Macroscopic thermal expansion behavior of the fiber was measured using a thermo-mechanical analyzer (Seiko Instruments Co., TMA 120) with a stretching mode of the stress at 4 MPa, and a heating rate of 10°C/min.

The density of the specimen measured by a flotation method (carbon tetrachloride–bromoform system at 30°C) was 1.579 g/cm^3.

2.2. Measurement of the elastic modulus E_l of the crystalline regions

The lattice extension under a constant load was measured by an X-ray diffractometer (Rigaku Denki RAD-B System) equipped with a stretching device and a load cell. CuKα radiation was employed. The strain, ε, of the crystal lattice was calculated by the following equation,

$$\varepsilon = \Delta d/d_0,$$

where d_0 shows the initial lattice spacing for the meridional reflection determined by Bragg's equation, and Δd is the difference in the lattice spacing induced by a constant stress. The change of the spacing was measured by eye from the shift of peak position. The experimental error in measuring the peak shift due to the lattice extension was evaluated to be generally less than ± 1/100° in 2θ. The stress σ in the crystalline regions was assumed to be equal to the stress applied to the sample. The validity of this assumption of homogeneous stress distribution has been proven for various polymers in earlier studies [1–3,12–14].

The elastic modulus E_l was calculated by

$$E_l = \sigma/\varepsilon.$$

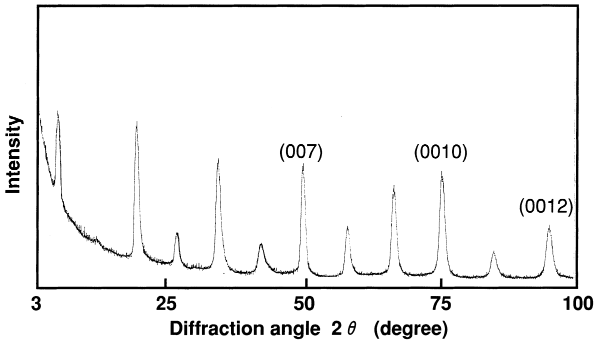

Fig. 2. The meridional diffraction profile of PBZT at room temperature.

Table 1
The observed and calculated E_l values and the maximum specimen modulus of PBZT reported in the literatures

Authors	E_l (GPa)	Ref. no.
Experimental		
In this study	372	
Adams et al.	395	[6]
Jiang et al.	450	[17]
Calculated		
Macturk et al.	370	[7]
Tashiro et al.	405	[8]
Wierschke et al.	620	[9]
Specimen	330	[4,5]

The E_l values at high and low temperatures were measured using the electric heating cell and the liquid nitrogen blowing cell with a temperature controller, respectively. The temperature was detected with a thermocouple, and it could be maintained within an accuracy of ± 1°C during the measurements.

A more detailed description of the measurement was given in earlier articles [1–3].

3. Results and discussion

3.1. Elastic modulus E_l at room temperature

Fig. 2 shows the meridional diffraction profile of PBZT at room temperature without any correction. More than 10 meridional reflections could be observed. In this study, we employed three reflections, i.e. 007, 0010 and 0012 reflections for the measurement of E_l, because they have relatively high intensity and high diffraction angle to minimize the experimental error.

Fig. 3 shows the stress(σ)–strain(ε) curves for these three reflections of the crystal lattice of PBZT at 20°C. All the plots could be expressed with a straight line through the origin, and the extensions of the crystal lattice were reversible. The inclination gave the E_l value of 372 GPa at 20°C. Thus, this shows that the E_l value is not influenced by the Laue lattice factor which causes the different E_l values among the reflection indices [15–17].

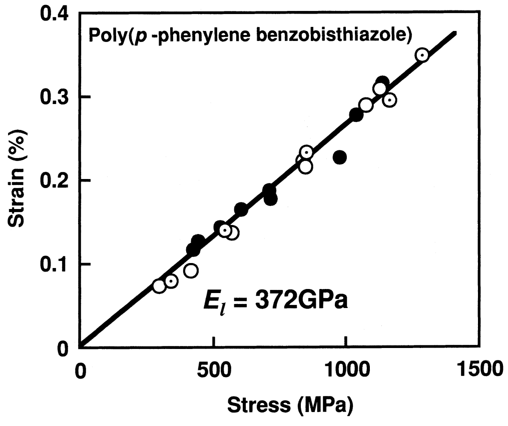

Fig. 3. The stress–strain curves for the meridional reflections of PBZT at 20°C. ○;(007) plane, ●;(0010) plane, ⊙;(0012) plane.

Table 1 summarizes the observed and the calculated elastic modulus E_l values of PBZT already reported, and a maximum specimen modulus [4–9,18]. Though the calculated values scattered widely from 370 to 620 GPa depending on the assumption of the calculation and the force constant employed, the value reported by Macturk et al. [7] is close to the experimental value. Lenhert and Adams reported 395 GPa as a E_l value for PBZT by X-ray diffraction [6], which is equivalent for that in this study within experimental error. The maximum specimen modulus [4,5] of PBZT reported so far shows about 90% of the E_l value, hence it seems reasonable to suppose that the attempt to obtain high modulus PBZT has almost reached the limit.

Table 2 shows the E_l value, the cross-sectional area (*S*) of one molecule in the crystal lattice [19] and the *f*-value (the force required to stretch a molecule by 1%, which is calculated from E_l and *S*) of several polymers together with those of PBZT. The E_l and *f*-values of PBZT are 1.5 times larger than those of PE and PVA, which are known to possess the highest modulus among the flexible polymers.

Remarkably high E_l values of PBZT is considered to be given mainly by the following three skeletal factors. First, PBZT skeleton is constructed from very rigid moieties, namely benzobisthiazole and phenyl rings. Secondly, the

Table 2
The E_l, cross-sectional area (*S*) and *f*-values of PBZT and some other polymers

Polymer	E_l (GPa)	*S* (Å^2)	*f*-value (10^{-5}dyne)	Ref. no.
PBZT	372	20.8	7.74	[18]
PE	235	18.2	4.28	[1,11]
PVA	250	21.6	5.40	[1,12]
Cellulose I	138	31.9	4.40	[27]
PPTA	156	20.2	3.16	[19]

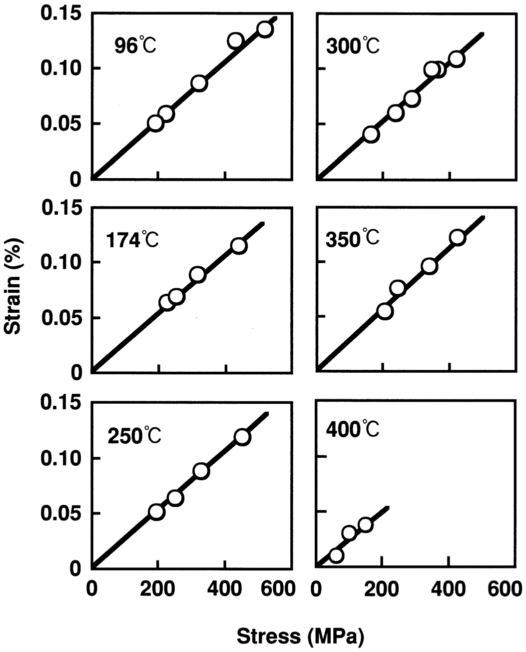

Fig. 4. The stress–strain curves for the (0010) plane of PBZT at various temperatures.

PBZT chain has an almost linear skeletal structure, though the benzobisthiazole ring tilts slightly from the chain axis. By these two factors, the deformation of the PBZT molecule is mostly through bond stretchings and bond angle bendings, which possess large force constants for the deformation. Finally, the cross-sectional area of one PBZT molecule in the crystalline region is relatively small, therefore, the applied load can be transmitted to more numerous molecules packed in a unit area than those with large cross-sectional area. The effect of the cross-sectional area on the E_l value is obvious from the comparison of the E_l values of PE and cellulose I, where the large difference in the E_l values could be observed in spite of the almost same rigidity (same *f*-value) of both polymers.

3.2. Elastic modulus E_l at high temperatures

Fig. 4 shows the stress(σ)–strain(ε) curves for the (0010) plane of PBZT at high temperatures up to 400°C. Every plot of each σ–ε curve fitted to a straight line through the origin, and the lattice extensions were always reversible as well as those at room temperature. All the inclinations of σ–ε curves were in good agreement with one another, which indicates that the E_l value is independent of temperature.

Fig. 5 shows the relationship between the temperature and the E_l value of PBZT together with the temperature dependence of the lattice spacing for the (0010) plane, and macroscopic fiber dimension. The E_l value of PBZT was constant at 372 GPa from 20 to 400°C. This indicates the high thermo-mechanical stability of the PBZT crystal. With respect of both heat resistance and high modulus, PBZT is found to be superior to other high performance polymers such as poly(*p*-phenylene terephthalamide) (PPTA) [20], Vectran [21] etc. The axial thermal expansion coefficient, α_c, for the (0010) plane was $-2.9 \times 10^{-6}\,\mathrm{K}^{-1}$ and it remained unchanged up to 445°C. We have been engaged in measuring the temperature dependence of the E_l value of a variety of polymers. It has been found that the E_l value decreased above a certain temperature [12,22,23] except for poly(ethylene terephthalate) [24], cellulose I [25], and isotactic poly(4-methyl-1-pentene) [26]. These characteristic temperatures are in accordance with the temperature range where the α_c value changed abruptly. This phenomenon shows that the mobility of chain molecules in the crystalline regions increases beyond that temperature, and the local shortening of molecules due to some conformational change, such as kink, may occur beyond that temperature. In contrast with these cases, the E_l value remained unchanged when α_c was constant, as for PBZT. Thus, this result makes it clear that the skeletal conformation of PBZT in the crystalline regions is stable against heat. The α_c value in this study is smaller than the macroscopic value, α, from -5.7×10^{-6} (around room

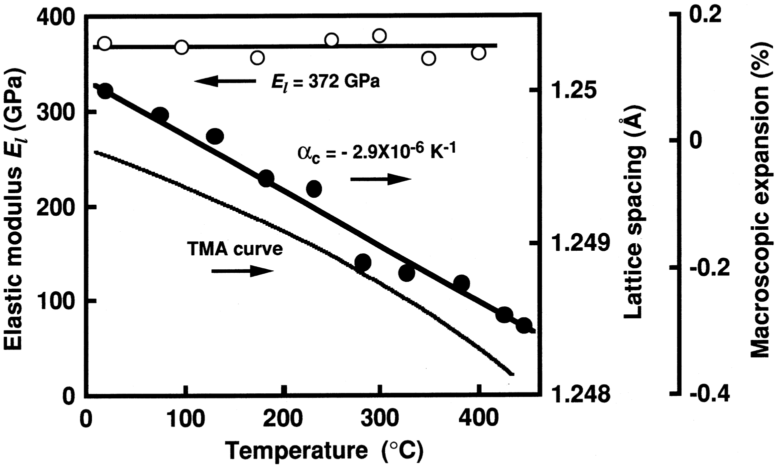

Fig. 5. Relationships among temperature, the elastic modulus E_l, the lattice spacing for the (0010) plane and the macroscopic dimension of PBZT.

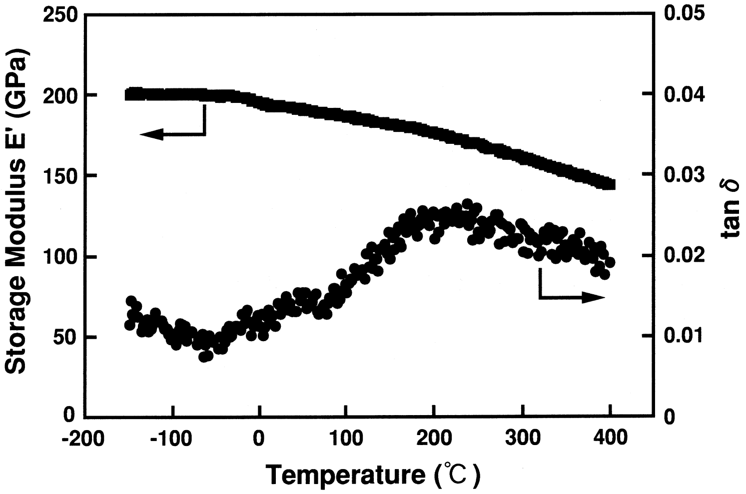

Fig. 6. Relationships between temperature and the storage modulus E' and mechanical tanδ of PBZT.

temperature) to $-11.8 \times 10^{-6}\ \mathrm{K}^{-1}$ (around 400°C) for the PBZT specimen. It seems that the macroscopic thermal contraction was mainly caused by an orientation relaxation of molecules in the noncrystalline regions, hence the difference between α_c and α reflects the difference in the chain mobility of the crystalline and non-crystalline regions, and clearly exhibits that the molecules in the crytalline regions are superior to those in the noncrystalline regions in the view point of heat resistance.

Jiang et al. reported the correlated relaxation around 300–400°C, both in the ultrasonic modulus, and in the *a*-, *b*-axis dimensions [18]. They attributed this phenomenon to a conformational oscillation around the single bond connecting the phenyl rings and the bisthiazole moieties. Macturk et al. observed a discontinuous increase in the X-ray diffraction intensity ratio (200)/(010) around 300–400°C, which can be explained by the same oscillation using molecular dynamics simulations [7]. The increase in a torsion angle was also reported to develop the translational molecular motions in the direction parallel to the chain axis, which brought the thermal contraction of the chain and the decrease of the sonic modulus of PBZT. However, as described earlier, the constancy of the E_l value up to 400°C indicates that this kind of molecular motion does not influence the chain rigidity along the chain in the crystalline regions.

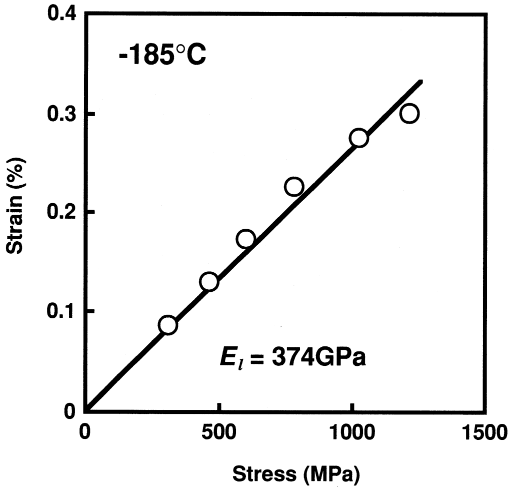

Fig. 7. The stress–strain curve for the (0010) plane of PBZT at $-185°$.

Fig. 6 shows the relationships between temperature and the storage modulus E' and mechanical tan δ of the PBZT fiber. E' slightly decreased from $-100°$, and finally E' became 110 GPa at 350°C. Judging from the constancy of the E_l value with temperature, it is considered that the decrement of E' value at high temperature should be due to the decrement of the elastic modulus E_a of the noncrystalline regions with temperature. If stress distribution is heterogeneous within a sample, the decrease of E_a will lead to the concentration of stress on the crystalline regions, consequently, the E_l value should apparently decrease with increasing temperature. However, the E_l value of PBZT did not show any decrease with temperature up to 400°C. Therefore, it is reasonable to conclude that the homogeneous stress distribution model is also proven on PBZT as well as other polymers. The broad tanδ peaks could be observed around room temperature and 200°C. Some relaxations seem to be take place over a wide range from -100°C to over 400°C, further investigations will be needed to clarify these origins. However, it is considered that the origin of these relaxations were not influenced by the mobility of chain in the direction parallel to the chain axis in the crystalline regions because of the constancy of the E_l value of PBZT.

3.3. Elastic modulus E_l at low temperatures

In order to make use of PBZT under various severe environments, it is necessary to investigate the mechanical property not only under high temperature, but also under low temperature.

Fig. 7 shows the stress–strain curve for the (0010) plane of PBZT at −185°C. The inclination of the σ–ε curve yields an E_l value of 374 GPa, which is completely coincident with that at room temperature. Accordingly, the E_l value of PBZT is constant from −185 to 400°C.

The results described lead to the conclusion that PBZT is the highest performance polymer that we have investigated from the viewpoint of high modulus and the thermal stability within the range of this study.

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