Neutron Structure Analysis of Poly(*p*-phenylenebenzobisthiazole)

Yasuhiro Takahashi

Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

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Poly(*p*-phenylenebenzobisthiazole) (PBZT) is known to be a strong polymer and the polymer with the highest modulus,[1,2] as is frequently discussed in comparison with poly(*p*-phenylenebenzobisoxazole) (PBO).[3] PBZT is a rigid rodlike polymer, consisting of benzobisthiazole and phenyl rings (Figure 1), and is of much interest in its excellent properties, high modulus, high strength and high heat resistance. The X-ray study of PBZT was first reported by Adams at al.[4] Thereafter, Fratini et al.[5] proposed the crystal structure. In a previous paper,[6] the crystal structure and structural disorder were analyzed by X-ray diffraction. Two molecular chains pack in the monoclinic unit cell with parameters, $a = 11.60$ Å, $b = 3.588$ Å, $\gamma = 92.0°$, and the plane group $p2$. Although the space group cannot be defined because of the diffuse streak layer lines, $P2_1$ or $P2$ are considered to be possible from the plane group. The fiber identity period could be estimated as 12.51 Å.[6] The PBZT crystal includes disorder with respect to the molecular height: on the *ac* plane, the molecular heights are disordered by $^1/_2$, and on the *bc* plane, the molecular heights are disordered by every $^1/_5$ of the fiber identity period.[6]

Neutron diffraction has several advantages in comparison with X-ray diffraction as described before.[3,7−9] New information about crystal structure could be obtained differing from the X-ray work. The scattering length of an atom is independent of the atomic number. Accordingly, the hydrogen and deuterium atoms have different scattering lengths for neutron diffraction, although they have the same scattering length for X-ray diffraction. The scattering lengths of hydrogen (−3.74) and deuterium (6.67) located on the outer shell of the molecule are comparable to the scattering lengths of carbon (6.65) and oxygen (5.80). Furthermore, the scattering lengths by neutron diffraction are independent of the scattering angle θ. The intensities of the reflections with large θ values can be observed strongly and can be measured accurately. This is especially an advantage for crystalline polymers, in which the reflection intensities become rapidly weak with the angle θ because of the disorder in crystalline region and the low degree of orientation. Accordingly, it can be said that neutron structure analysis gives more accurate crystal structure than X-ray structure analysis. Absorption of neutrons by most elements, for example, aluminum, is very small. Therefore, an apparatus for low- and high-temperature measurements can be easily designed, and measurements at low and high temperature are easy.

The purpose of the present study is to determine the crystal structure of PBZT more accurately than X-ray structure analysis[6] and to obtain the temperature dependence of the crystal structure.

The fiber sample of PBZT was kindly supplied by Dr. Chyi-Shan Wang of University of Dayton Research Institute.

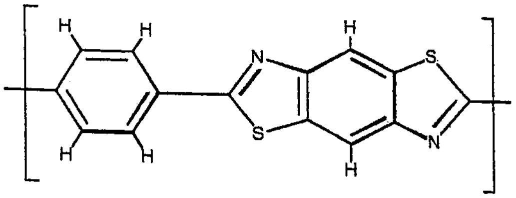

Figure 1. Chemical structure of PBZT.

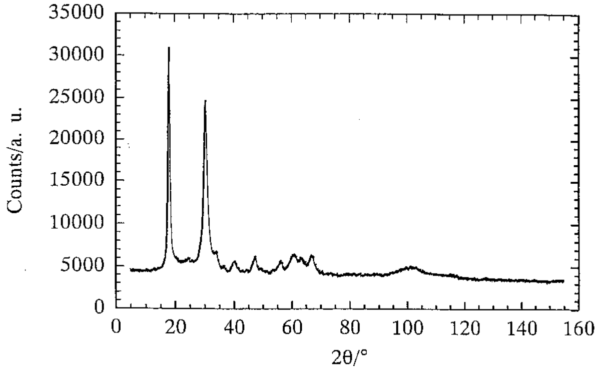

Figure 2. Neutron diffraction pattern of the equator of PBZT at 17 K.

Neutron diffraction measurements were carried out by a powder diffractometer (HERMES)[10] equipped with an atomic reactor JRR-3M installed by Japan Atomic Energy Research Institute (JAERI) using $\lambda = 1.8196$ Å. The specimen was made by arranging the fibers in a cylindrical bundle about 10 mm in diameter, covered by vanadium foil, and set into the aluminum sample tube with 6.5 cm diameter. Intensity distributions in the range $5° \leq 2\theta \leq 150°$ on the equator were measured at 17, 60, 120, 180, 240, and 295K. Thirteen reflections could be observed. In Figure 2, the intensity distribution measured at 17 K is shown.

Neutron diffraction in the region of $2\theta = 24{-}31°$ are shown in Figure 3, where the curve separation was carried out by using a program Winfit,[11] where the intensity profile is approximated by a Pearson VII function. The overlapping of $hk0$ and $-hk0$ reflections could not be separated on all the intensity distributions. Therefore, the unit cell parameters could not be determined only from the neutron data. In Figure 4, the temperature dependence of the *d* spacings of the 200 reflection and the overlapped reflection of 010, 110, and 110 are shown. The temperature dependence is very small in comparison with the flexible polymers, polyethylene-d_4[9] and poly(vinyl alcohol).[8] The value 0.05 Å is generally accepted to be within the accuracy of the standard deviations. Therefore, the constant unit cell parameters $a = 11.60$ Å, $b = 3.588$ Å, and $\gamma = 92.0°$, which were determined by X-ray diffraction, were used for the structures of PBZT at every temperature.

The structure refinement was carried out by using the constrained least-squares method,[12] where the values proposed by Fratini et al.[5] were used for bond lengths and bond angles. The values for bond lengths and bond angles are shown in Figure 5. Furthermore, an overall isotropic temperature parameter was adopted. The carbon atom C5 of the phenyl ring is chosen as the origin of the molecule (Figure 5). The variable parameters to be refined are the scale factor, the coordinates

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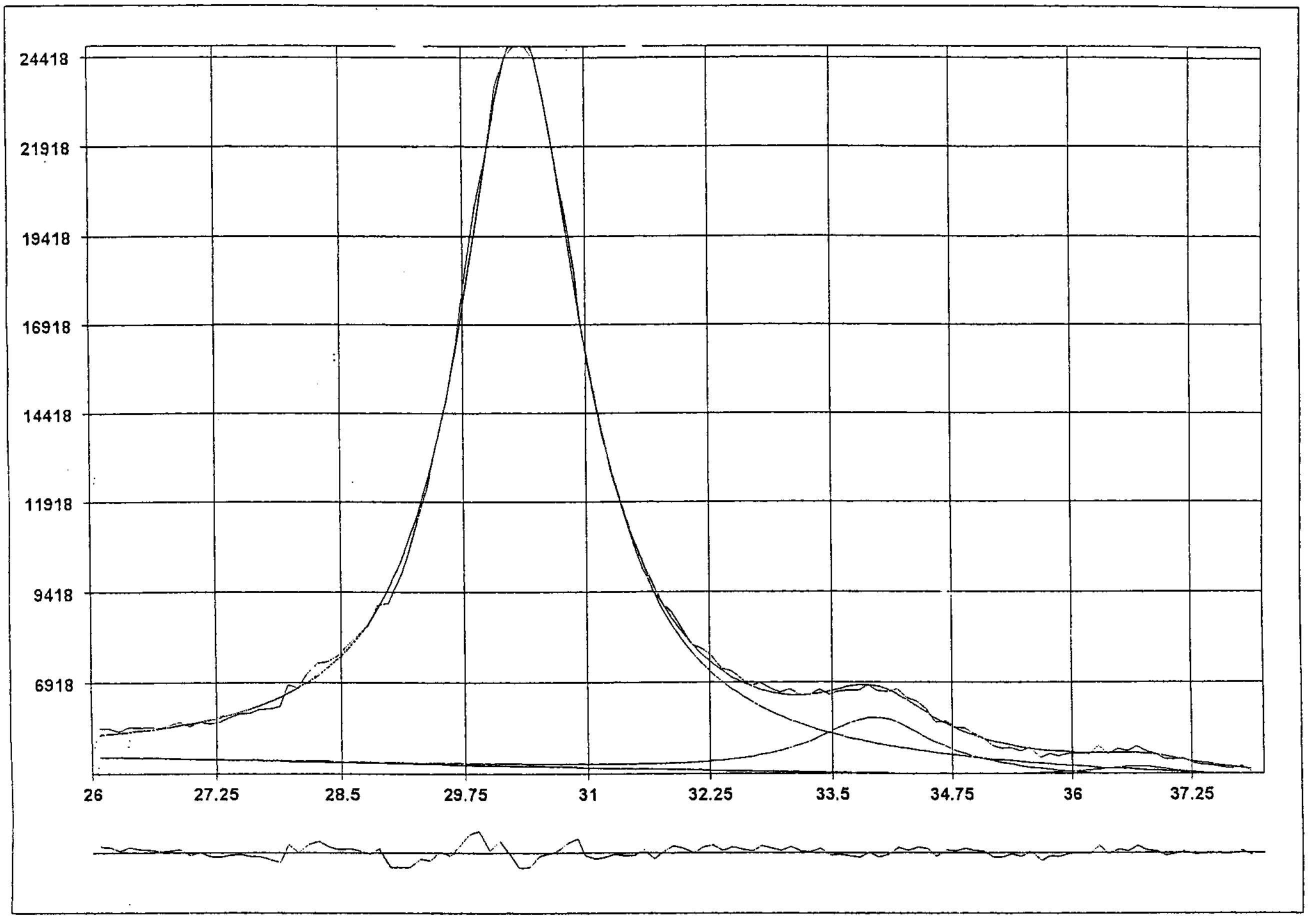

Figure 3. Neutron intensity profile and curve separation of the region 26−38° at 17 K.

Table 1. Atomic Parameters Finally Obtained by the Constrained Least-Squares Refinement.

	17 K	60 K	120 K	180 K	240 K	295 K
fractional coordinates of the origin atom C5						
x	0.240 (0.006)	0.236 (0.006)	0.238 (0.007)	0.239 (0.007)	0.237 (0.005)	0.238 (0.005)
y	0.191 (0.024)	0.200 (0.028)	0.195 (0.032)	0.196 (0.028)	0.207 (0.026)	0.205 (0.025)
Eulerian angle,[b] ϕ (deg)	−7.3 (5.3)	−8.7 (6.0)	−7.8 (7.1)	−7.3 (5.8)	−9.0 (6.2)	−7.3 (4.7)
angle between phenyl and benzobisthiazole rings, τ (deg)	208.4 (3.8)	207.9 (3.2)	209.1 (4.9)	206.8 (3.8)	208.2 (3.0)	205.7 (3.1)
overall isotropic temp factor, B (Å^2)	1.66 (0.85)	1.91 (0.79)	1.97 (1.08)	2.42 (0.92)	2.46 (0.73)	3.13 (0.77)
reliability factor, R (%)	8.84	9.79	11.26	10.94	9.30	9.09

[a] Parentheses show the standard deviations. [b] The values of θ and χ are fixed on −87.329° and 0.0°, respectively.

of the origin atom, x and y, the azimuthal angle of the benzobisthiazole ring with respect to the line perpendicular to the b axis, ϕ, the internal rotation angle N′−C4′−C8−C7, τ, which defines the angle between phenyl and benzobisthiazole rings, and the overall isotropic temperature parameter B (Table 1). After the refinements, the R factors converged to 8.84, 9.79, 11.26, 10.94, 9.30, and 9.09% for the intensity data at 17, 60, 120, 180, 240, and 295 K, respectively. The parameters finally obtained by the constrained least-squares refinements are given in Table 1. The crystal structure at 295 K is shown in Figure 6.

As shown in Figure 6, the crystal structure obtained in the present study is somewhat different from the structure obtained by X-ray structure analysis.[6] In the present neutron study, the benzobisthiazole ring is rather parallel to the *ac* plane and the phenyl ring is perpendicular to the *bc* plane, but, in the X-ray structure analysis,[6] the phenyl ring is parallel to the *ac* plane. In the neutron diffraction, the hydrogen atoms in the outer shell of the molecule contributes to the intensity more than in X-ray diffraction, and therefore, the present neutron diffraction gives more accurate structure than X-ray diffraction. This arrangement is consistent with the disorder better than the X-ray structure. In the *bc* plane, the molecular heights are disordered by $^1/_5$ of the fiber identity period. This shows that the molecular packing is governed by the sulfur atoms with the largest van der Waals radii, the height difference of which is $^2/_5c$ of the fiber identity period. On the other hand, in the *ac* plane, the molecular heights are disordered by $^1/_2$ of the fiber identity period in the same way as the case of poly(*p*-phenylenebenzobisoxazole), in the both cases of which the molecular packings are governed by the hydrogen atoms located on the outer shell of the molecule. In the X-ray structure analysis,[6] the overlapped reflections in the ranges of 24−31° and 46−60° are separated into five and four reflections, respectively, under the assumption of the Gauss−Cauchy function. The curve separations may reproduce the accurate 2θ angles but may not necessarily reproduce the accurate intensities. The molecular chain locates on the general

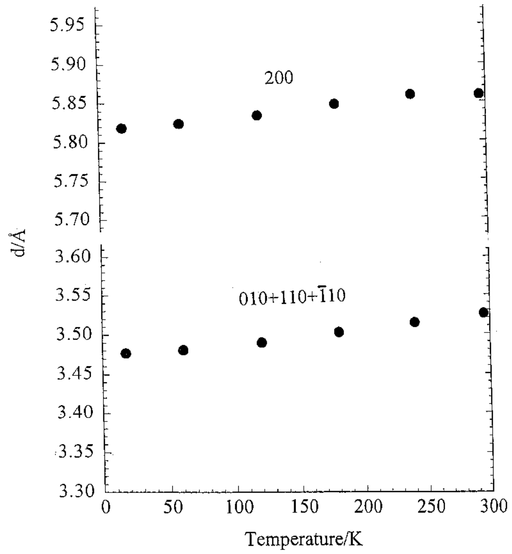

Figure 4. Temperature dependences of d_{200} and $d_{010+110+110}$.

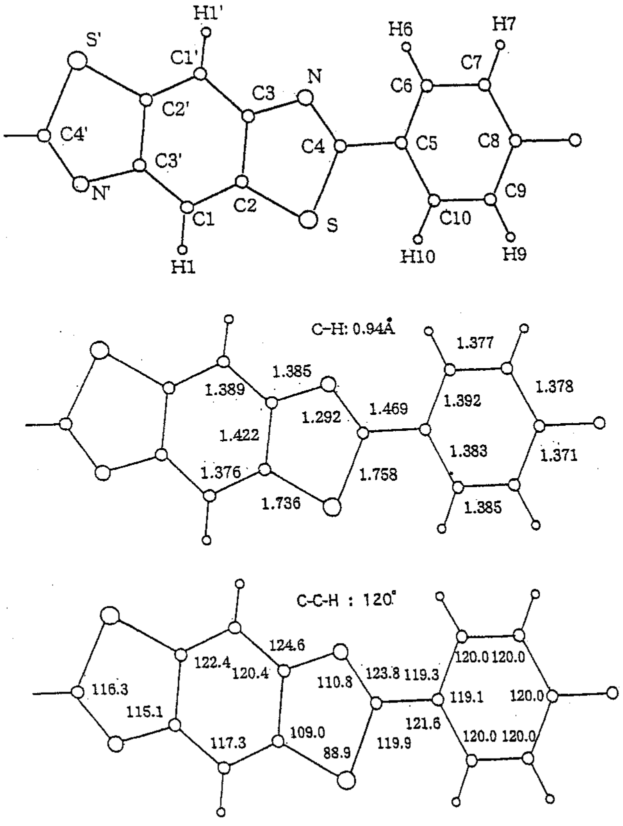

Figure 5. Values of bond lengths and bond angles.

position of the plane group $p2$, and therefore, two molecular chains in the unit cell are related by a 2-fold rotation axis. This is different from the structure reported by Fratini et al.,[5] in which the molecular chains locate on the corner and center of the unit cell and are related by a simple translation. The azimuthal angle of the molecule with respect to the lattice ϕ is independent of temperature within the accuracy of the standard deviation and is estimated as the average −7.9°. The angle between the phenyl and benzobisthiazole rings is also independent of temperature and is estimated as 27.7°, which corresponds well to the value of the X-ray structure analysis,[6] 20.5° and is far from the value 46° reported by Fratini et al.[5] The value 27.7° also corresponds well to the calculated values, 27,[13,14] 20,[15] 21,[16] and 29°,[17] although the value 55° was reported.[18] The structure change dependent on temperature is not so large as those in the flexible polymers, polyethylene[9] and poly(vinyl alcohol).[8] The smaller dependency on temperature can be seen in the case of PBO,[3] and is attributed to the rigidity of the molecular structure.

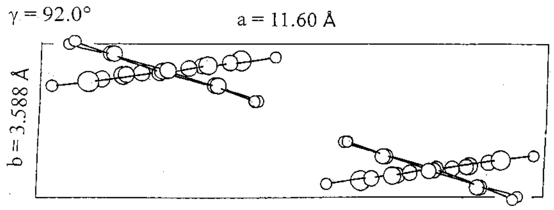

Figure 6. Crystal structure of PBZT at 295 K.

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