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# Neutron Structure Analyses and Structural Disorders of Poly(p-phenylenebenzobisoxazole) and Poly(p-phenylenebenzobisthiazole)

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Poly(p-phenylenebenzobisoxazole)(PBO) and poly(p-phenylenebenzobisthiazole)(PBZT) are disordered with respect to the molecular heights. The molecular heights of PBO are disordered by 1/2 along the molecular axis, while the molecular heights of PBZT are disordered by 1/2 on the *ac*-plane and by every 1/5 on the *bc*-plane. Neutron structure analyses of both polymers were carried out for the *c*-projected structure in the temperature range 17 - 295K. The molecular structures of both polymers deviate from the planar structure. The crystal structures are less dependent on the temperature than the flexible polymers, polyethylene and poly(vinyl alcohol).

KEYWORDS: poly(p-phenylenebenzobisoxazole), poly(p-phenylenebenzobisthiazole), neutron structure analysis, structural disorder, temperature dependence

## §1. Introduction

Poly(p-phenylenebenzobisoxazole) (PBO) and poly(p-phenylenebenzobisthiazole) (PBZT), whose structures are shown in Fig. 1, are well known to be the strongest polymers and polymers with the highest modulus. Their properties are mainly attributed to the molecular rigidity. X-ray studies on PBO and PBZT were reported by Fratini *et al.*[1] and by Takahashi and Sul.[2] Neutron diffraction has several advantages[3] in comparison with X-ray diffraction. Accordingly, new information about the crystal structure could be obtained that differs from the X-ray work. The scattering length of an atom is independent of the atomic number. That is scattering length of hydrogen (-3.74) (and deuterium (6.67)), which is generally located on the outer shell of the molecule, is comparable to the scattering lengths of carbon (6.65) and oxygen (5.80), although the scattering power of hydrogen (and deuterium (1.0)) is far less than those of carbon (6.0) and oxygen (8.0) in the case of X-ray diffraction. Accordingly, the molecular orientation can be determined more accurately with neutrons than with X-rays. Furthermore, the neutron scattering lengths are independent of the scattering angle $\theta$. The intensities of the reflections with large $\theta$ values can be observed strongly and can be observed accurately. This is especially advantageous for crystalline polymers, in which the reflection intensities become rapidly weak with the angle $\theta$ because of the disorder in the crystalline region and the low degree of orientation. Consequently, it can be said that neutron diffraction can give a more accurate polymer crystal structure than X-ray diffraction can give. Absorption of neutrons by most elements, for example, aluminum, is very small. Therefore, the apparatus for low- and high-temperature measurements can be easily designed and the measurements at low and high temperature are easier than X-ray diffraction. In the present study, the neutron structure analyses of PBO[4] and PBZT are carried out in the temperature region 17K - 295K. Together with the results of X-ray diffraction, the temperature dependence of the structure of these polymers determined in detail by neutron diffraction are shown. The structural disorders are also described.

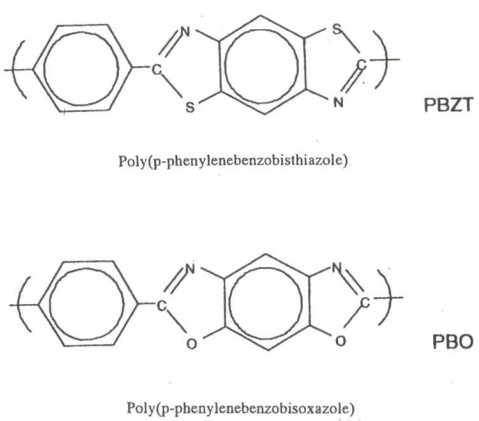


Fig. 1. Chemical structures of PBO and PBZT.

## §2. Experimental

The specimen for X-ray and neutron diffraction measurements was made by arranging the fibers in a cylindrical bundles about 0.5 mm and 10 mm in diameters. X-ray fiber photographs were taken by using a vacuum camera with 10 cm radius by CuK$\alpha$ radiation monochromatized by pyrolytic graphite. Neutron diffraction measurements using $\lambda = 1.8196$ Å were carried out by a powder diffractometer (HERMES) at the JRR-3M reactor istalled by the Japan Atomic Energy Research Institute (JAERI). Intensity distributions on the equators were

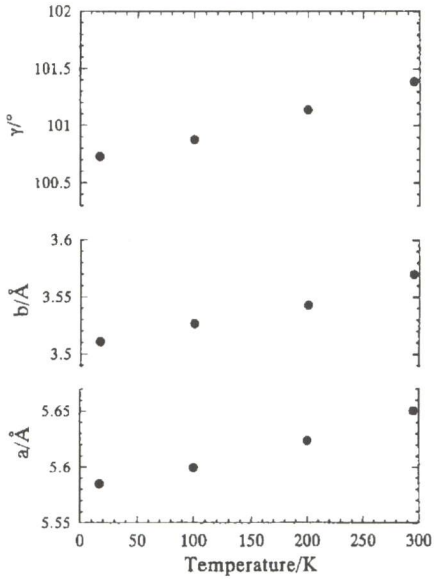


Fig. 2. Temperature dependences of unit cell parameters.

measured at 17K, 100K, 200K, and 295K for PBO and at 17K, 60K, 120K, 180K, 240K, and 295K for PBZT.

## §3. Results and Discussion

### *3.1 Unit cell parameters*

On the X-ray fiber diagrams of PBO, diffuse streak scatterings are observed along the first and third layer lines, and Laue spots can be observed on the equator, the second and fourth layer lines. All the observed diffraction spots can be indexed by a one-chain unit cell with parameters $a = 5.651$ Å, $b = 3.570$ Å, and $\gamma = 101.4$ ° (neutron at 295K), this $a$-parameter is half of that reported by Fratini *et al.*[1] Furthermore, the $c$-parameter should be reduced to a half, 6.03 Å, of the 12.05 Å reported by Fratini *et al.*[1] The space group is considered to be Pm from the symmetry of the molecule. Temperature dependences of the unit cell parameters a and b are shown in Fig. 2. These temperature dependences are much smaller than those of the flexible polymers, polyethylene[5] and poly(vinyl alcohol).[6] This may be attributed to the rigidity of the PBO molecule.

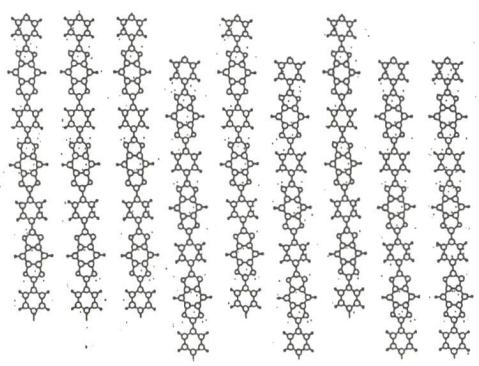

Fig. 3. Schematic representation of disorder in PBO.

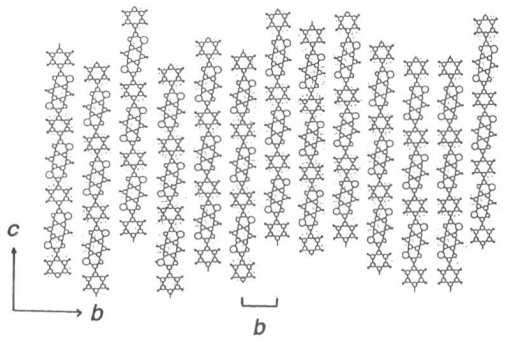


Fig. 4. Schematic representation of disorder on the $bc$-plane of PBZT.

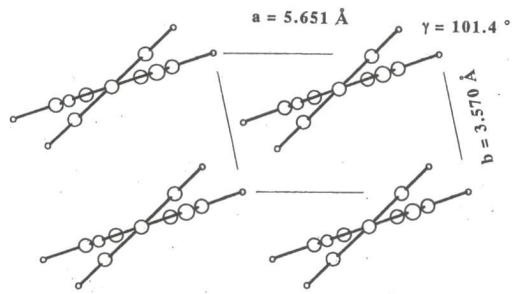


Fig. 5. Crystal structure of PBO.

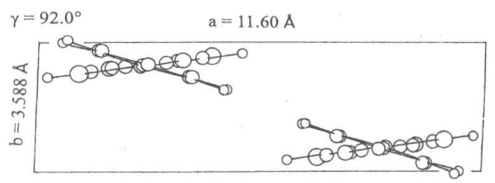


Fig. 6. Crystal structure of PBZT.

On the equator of the X-ray fiber diagram of PBZT, several reflections overlap on a few groups of reflections. In the previous paper,[2] the curve separation was successfully made for the equator of the X-ray pattern and the unit cell with parameters $a = 11.60$ Å, $b = 3.588$ Å, and $\gamma = 92.0$ ° were determined. But on the neutron diffraction, the curve separation did not succeed, especially for overlapped reflections of hkl and -hkl reflections, and temperature dependences of the spacings are so small that they are usually accepted to be within the accuracy of the standard deviation of polymer. And, therefore, during the neutron structure analyses, the unit cell parameters determined by X-ray diffraction are adopted.

### *3.2 Structural disorders*

Since, on the X-ray fiber diagram of PBO, the diffraction spots can be observed only on even numbers of layer lines, the molecular heights of PBO should be disordered by 1/2 along the molecular axis; the phenylene ring is substituted by the benzobisoxazole ring. The structural

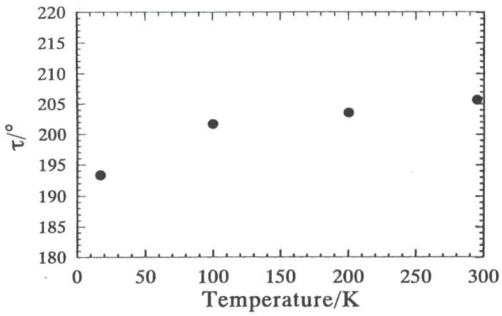


Fig. 7. Temperature dependence of the angle $\tau$ of PBO.

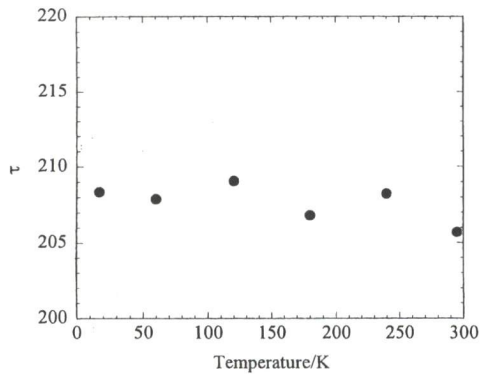


Fig. 8. Temperature dependence of the angle $\tau$ of PBZT.

disorder is shown in Fig. 3 schematically.

On the X-ray fiber diagram of PBZT, 102, 602, and 404 reflections can be observed, that is, only the h0l reflections with l = 2n can be observed. This shows that the molecular heights are disordered by 1/2 on the *ac*-plane in the same way as PBO. Furthermore, the 015 reflection can be observed. This suggests that the molecular heights are disordered by every 1/5 on the *bc*-plane (Fig. 4). This disorder is considered to be caused by large van der Waals radius of the sulfur atom, because the height between two sulfur atoms in a molecule corresponds just to 2/5c.

### *3.3 Neutron structure analyses*

The constrained least-squares method[7] was applied to the refinements of PBO and PBZT. In the case of PBO,the R-factors converged to 9.9, 9.5, 13.1, and 12.1 % for the intensity data at 17, 100, 200, and 295K, respectively. The numbers of reflections observed are 11 for 17K and 100K and 12 for 200K and 295K. In the case of PBZT, the R-factors converged to 8.8, 9.8, 11.3, 10.9, 9.3, and 9.1 % for 17, 60, 120, 180, 240, and 295K, respectively. Here, the number of the observed reflections is 13 for each data. In Figs. 5 and 6, the crystal structures of PBO and PBZT at 295K are shown, respectively. In Fig. 7, the temperature dependence of the angle $\tau$ between phenyl and benzobisoxazole rings is shown. Here, when $\tau$ is 180 °, the molecule is planar. The angle $\tau$ slightly decreases as temperature decreases. In Fig. 8, the temperature dependence of the angle $\tau$ between the phenyl and benzobisthiazole rings is shown. The angle $\tau$ of PBZT is constant within the accuracy of the standard deviation.

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