polymer communications

Novel anisotropic texture of rigid-rod poly(*p*-phenylene benzobisthiazole) film

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Poly(*p*-phenylene benzobisthiazole) (PBZT) polymer film, prepared by a doctor-blading technique, was studied by wide-angle X-ray scattering. Emphasis was placed on the anisotropic arrangement of the extended rigid-rod chains against the macroscopic axes. Two X-ray patterns, one measured with the X-ray beam perpendicular to the plane of the film surface and the other with the beam parallel to the surface plane, revealed a unique morphological feature: the large molecular plane of the PBZT chain is lying perpendicular to the film surface plane with the long polymer axis being random but lying in the plane of the film surface.

(Keywords: PBZT film; wide-angle X-ray scattering; anisotropic texture)

Introduction

Rigid-rod poly(*p*-phenylene benzobisthiazole) (PBZT)[1] and poly(*p*-phenylene benzobisoxazole) (PBO)[2] have drawn strong attention for the last two decades because of their excellent thermal and mechanical properties as well as their respectable numbers in non-linear optical properties[3]. These polymers are usually processed from strong acidic polymer solutions (polyphosphoric acid or methane sulfonic acid) into highly ordered fibres or films with an extended chain conformation. In thin polymer films, the extended chain conformation results in an anisotropic packing of the polymer chains, where the long chain axes are lying parallel in the film surface plane. Such an anisotropic arrangement of the polymer molecules is extremely useful in understanding the optical responses of the polymer chains, which are highly dependent on the orientation of the molecules[4,5]. Another key structural anisotropy, associated with the optical responses of the polymer molecules, is the orientation of molecular planes (or faces of the molecules) against the film surface plane. Studies[6–8] on rigid-rod, ladder or semirigid polymers consisting of aromatic rings and/or heterocycles indicate that the polymer chains tend to orient with their molecular planes lying parallel in the film surface plane.

Recently, we investigated the morphology of PBZT polymer film, in particular the anisotropic structural order of the film, by wide-angle X-ray scattering. In the present communication, we report a novel macroscale anisotropic order found in the PBZT film.

Results and discussion

PBZT polymer films (see *Figure 1* for the chemical structure), prepared from 1% methane sulfonic acid solution by a doctor-blading technique, were used for the study. Several layers of PBZT films were stacked to increase the scattering volume. X-ray scattering was performed by using a Statton flat film camera coupled to a vertical graphite monochromator and a Rigaku rotating anode X-ray generator (Cu Kα).

Two X-ray patterns of PBZT film, pattern A, measured with the X-ray beam perpendicular to the film surface (flat view), and pattern B with the X-ray beam parallel to the film surface (edge view), are shown in *Figure 2*. The reflection rings shown in pattern A indicate that the

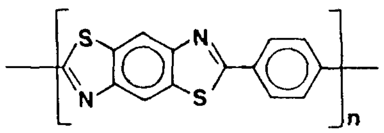

Figure 1 Chemical structure of PBZT molecule

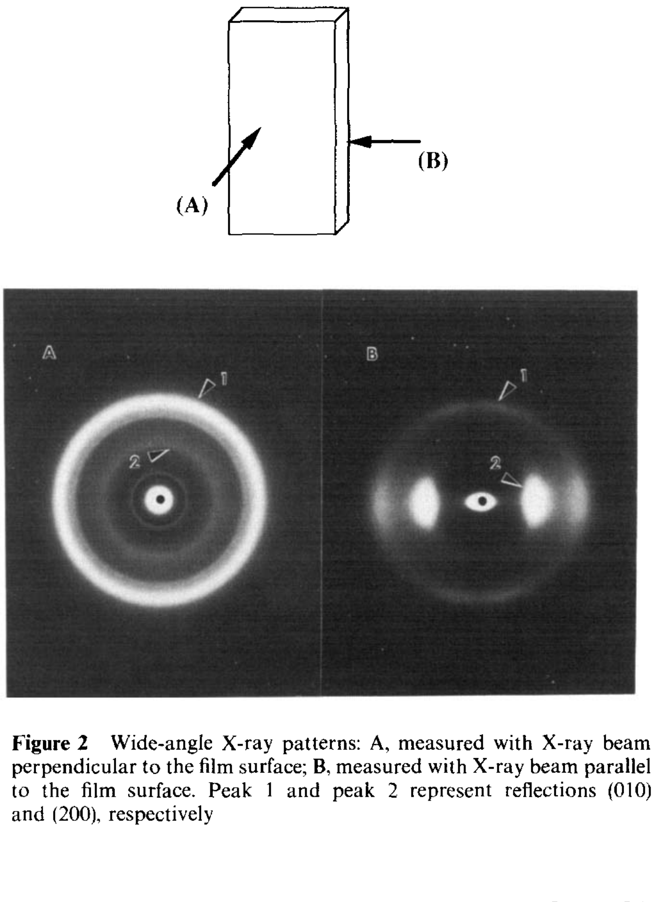

Figure 2 Wide-angle X-ray patterns: A, measured with X-ray beam perpendicular to the film surface; B, measured with X-ray beam parallel to the film surface. Peak 1 and peak 2 represent reflections (010) and (200), respectively

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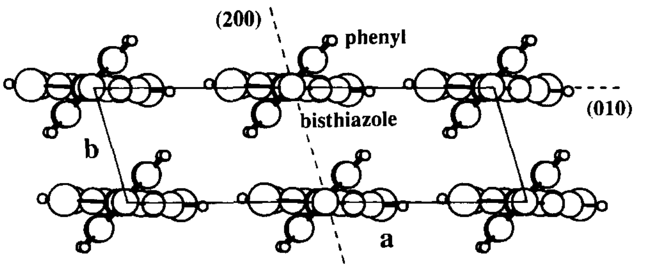

Figure 3 View of PBZT unit cell along the *c*-axis. The *a*-axis is horizontal

molecules or the stacks of molecules are randomly oriented in the film surface plane. Pattern B shows an anisotropic feature, indicative of a certain preferred orientation of the molecules along the film thickness.

Before analysing the results further, we begin with a unit cell of the PBZT polymer crystals proposed by Fratini *et al.*[9]. As depicted in *Figure 3*, the polymer forms a monoclinic unit cell with lattice parameters of $a = 11.79$ Å, $b = 3.539$ Å, $c = 12.514$ Å and $\gamma = 94.0°$. From the given unit cell geometry, the inner diffraction peak 2 at $2\theta = 15°$ in both X-ray patterns can be assigned to (200) planes formed by side-to-side interchain packing, while the outer diffraction peak 1 at $2\theta = 25°$ is assigned to the (010) planes of face-to-face interchain packing. The crystal structure also suggests that the PBZT forms a non-planar chain conformation. Only the bisthiazole plane is lying parallel in the *ac* plane of the unit cell. The torsion angle between the phenyl and bisthiazole is estimated as 46°, which is somewhat larger than the results (30°) of semiempirical calculations[10,11]. However, the small energy barrier of $0.1\ \mathrm{kcal\ mol^{-1}}$ at 0° ($1 \sim 2\ \mathrm{kcal\ mol^{-1}}$ at 90°), predicted by the semiempirical calculations[10,11], also suggests a variation towards the smaller torsion angles. Since the molecule is nearly planar, if not coplanar, with the large bisthiazole plane lying on the *ac* plane, hereafter we often use the term 'molecular plane' instead of the crystal *ac* plane (or (010) plane).

X-ray diffraction from a set of crystal planes can be treated as a reflection where the Bragg condition, $\lambda = 2d \sin \theta$, is satisfied only when the X-ray beam intersects the crystal plane at an angle θ. Here 2θ is the diffraction angle, λ is the X-ray wavelength, and d is the interplanar spacing. For the two main crystal planes, (200) and (010), of the PBZT polymer unit cell to satisfy the diffraction condition, the intersecting angles must be 7.5° and 12.5° for the (200) plane and (010) plane, respectively.

The (200) peak in the equator of pattern B (here the equator is a direction normal to the film surface) arises from the (200) planes whose normals are tilted at 7.5° to the film surface normal. Appearance of the (010) peak in the meridian, on the other hand, is from the (010) planes whose normals are parallel to the film surface. Much lower intensity of the (010) peak noticed in pattern B is due to the fact that only a small fraction of the (010) planes satisfies the Bragg condition, because the molecules are stacked randomly in the plane of the film surface, as discussed above. Only (010) planes tilted at 12.5° to the incoming X-ray beam contribute to the diffraction intensity. A very strong intensity of the (200) peak indicates that a large number of molecules are preferentially oriented along the thickness, such that the molecular planes are perpendicular to the film surface. Another reflection at $2\theta = 26°$ is also observed in the equator of pattern B. From the given cell parameters, the peak can be assigned to a (-110) reflection. It has not been observed in any of the X-ray patterns of PBZT fibres. Separation of (010) reflection at $2\theta = 25°$ in the meridian direction apparently resulted in a better peak resolution.

A completely different X-ray pattern is observed, as shown in pattern A, when the pattern is obtained with the X-ray beam perpendicular to the film surface. The intensity of the (010) reflection is very strong, whereas the (200) reflection is nearly absent. Again from the diffraction condition discussed above, the (010) peak in pattern A arises from the (010) planes tilted at 12.5° to the film surface normal direction. The strong intensity of the (010) peak, as noted in pattern A, confirms a consistent morphological feature that the molecular plane is perpendicular to the film surface. However, the appearance of the (200) peak in pattern A, although the intensity is very weak, suggests that misorientation of the (200) planes is large enough to result in the (200) reflection. In fact, the broad distribution of the (200) peak in the azimuthal direction, as noted in pattern B, is an indication that the misorientation of the molecular plane is quite extensive. Several satellite peaks (rings), in addition to the main (200) and (010) peaks, are also discernible in pattern A. The peaks arise from the structural order along the individual extended polymer chains. Only the chains whose chain axes are oriented perpendicular to the X-ray beam, i.e. lying parallel in the plane of the film surface, are responsible for the peak intensity shown in pattern A[12]. The misorientation (or the tilt) of the chain axis along the film thickness, as estimated from the azimuthal breadth of the layer lines in pattern B, appears not to be as extensive as that of the molecular planes.

In summary, the X-ray results of PBZT film provide evidence that the polymer chains form an anisotropic structure such that the molecular plane, thus the large bisthiazole plane of the PBZT molecule, is oriented perpendicular to the film surface with the long chain axis lying parallel in the plane of the film surface. The arrangement of molecules observed in the PBZT polymer film is a unique and extraordinary morphological feature, since most stiff polymers consisting of aromatic rings and/or heterocycles along the backbone are known to form a layered structure with the large molecular plane lying in the plane of the polymer film surface. We are not certain, at the present time, of the mechanisms that produce such a unique structure in the polymer film. It is, however, speculated that the structure formation is associated with a row nucleation[13] and preferred growth in the direction of face-to-face interchain interaction, which is apparently a stronger interaction than side-to-side interaction. Controlled precipitation of the crystal aggregates from the solution is also a key parameter for maintaining the macroscale anisotropy in the film. Other rigid-rod and ladder polymers are currently under investigation.

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References

1 Wolfe, J. F. and Arnold, F. E. *Macromolecules* 1981, **14**, 915
2 Wolfe, J. F., Loo, B. H. and Arnold, F. E. *Macromolecules* 1981, **14**, 909

3 Prasad, P. N. and Williams, D. J. 'Introduction to Nonlinear Optical Effects in Molecules and Polymers', Wiley-Interscience, New York, 1991, p. 241

4 Bai, S. J., Spry, R. J., Zelmon, D. E., Ramabadran, U. and Jackson, J. *J. Polym. Sci.: Part B: Polym. Phys. Edn* 1992, **30**, 1507

5 Rao, D. N., Swiatkiecz, J., Chopra, P., Ghoshal, S. K. and Prasad, P. N. *Appl. Phys. Lett.* 1986, **48**, 1187

6 Minter, J. R. Technical Report AFWAL-TR-82-4097, Vol. 1, 1982

7 Berry, G. C. *J. Polym. Sci.: Polym. Phys. Edn* 1976, **14**, 451

8 Ree, M., Nunes, T. L. and Kirby, D. P. *Polym. Prepr.* 1992, **33**, (1), 309

9 Fratini, A. V., Lenhert, P. G., Resch, T. J. and Adams, W. W. *Mater. Res. Soc. Symp. Proc.* 1989, **134**, 431

10 Farmer, B. L., Wierschke, S. G. and Adams, W. W. *Polymer* 1990, **31**, 1637

11 Yang, Y. and Welsh, W. J. *Macromolecules* 1990, **23**, 2410

12 Song, H. H., Dotrong, M. and Evers, R. C. *Polym. Mater. Sci. Eng.* 1993, **68**, 173

13 Roche, E. J. *Mater. Res. Soc. Symp. Proc.* 1989, **134**, 457