PII: S0032-3861(96)00998-6

Polymer Vol. 38 No. 16, pp. 4241–4245, 1997
© 1997 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/97/$17.00 + 0.00

Preparation of rigid-rod poly(*p*-phenylene benzobisthiazole) films of single crystalline texture

Hyun Hoon Song*
Department of Macromolecular Science, Hannam University, Taejon, Korea

and Sung-Kwon Hong
Department of Polymer Science and Engineering, Chungnam National University, Taejon, Korea

(Received 12 June 1996; revised 20 August 1996)

Thin films of rigid-rod poly(*p*-phenylene benzobisthiazole) having single crystalline texture were prepared. An above critical concentration polymer solution of 6 wt% in methane sulfonic acid was sheared to orient the chains (*c*-axis) along the shear axis in the solution state. The sheared solution was then solidified into thin films via coagulation in the water. Self-assembling phenomenon, previously found in rigid-rod PBZT polymer molecules during the coagulation process, was utilized as the driving mechanism for the alignment of crystallographic *a* and *b*-axes in the process. WAXS and *FT*i.r. spectroscopy with the polarized radiation confirmed the presence of single crystal-like orientation in the film specimen with the crystallographic *c*-axis preferentially oriented parallel to the shear direction, *b*-axis to the transverse direction, and *a*-axis normal to the film surface. © 1997 Elsevier Science Ltd.

(Keywords: poly(*p*-phenylene benzobisthiazole); thin film; self-assembling phenomenon; single crystalline texture)

INTRODUCTION

Many bulk properties of polymers are highly dependent on the orientation of the chains and hence the properties can often be tailored by controlling the orientation of the polymer chains. A variety of processing techniques to control orientations in the bulk polymer samples have been developed. Extrusion of polymer melts or solution into fibres and films is the best known method for uniaxial orientation. Solid state extrusion is also used and is far more effective in orienting the molecules. Biaxial orientation in films has two principal directions against the machine direction and the film properties can be varied by balancing the two principal directions[1]. Roll-mill[2] or channel-die compression[3,4] are other very useful techniques for texturing solid polymers. In particular, these methods have proven effective in generating bulk specimens of single crystalline texture, where three crystallographic axes can be defined against the bulk specimen axes. The practical importance of specimens having such macroscopic three-dimensional orientations is that they can be utilized to determine various directional properties along the crystallographic axes and also to examine the mechanisms of physical phenomena taking place in polymeric materials[5,6].

Poly(*p*-phenylene benzobisthiazole) (PBZT)[7] is a rigid-rod polymer composed of heterocyclic and aromatic compounds in the backbone. Its chemical structure shown in *Figure 1* suggests a fully extended chain conformation. High mechanical strength and modulus[8], thermal and chemical stability[9], and notable optoelectronic properties[10,11] of the PBZT polymer apparently originate from the unique rod-like polymer structure. However, the polymer is intractable and soluble only in strong acid such as methanesulfonic acid (MSA) through protonation[12]. The polymer solution exhibits phase transition from an optically isotropic phase to an anisotropic liquid crystalline phase at about 5 wt% in MSA[7]. Highly ordered fibres and films are processed from the acidic polymer solutions of the anisotropic state. Similar to many other stiff polymers[13,14], the PBZT films made from polymer solution exhibit a planar isotropic packing state such that the chain axis is lying in the plane of the film surface. Recently, an interesting structural feature in the coagulated PBZT film was reported by the authors. It was found that the polymer chains tend to orientate spontaneously with their molecular planes (heterocycles and aromatic ring plane) lying perpendicular to the plane of the film surface[15]. The unique structural formation was attributed to the row nucleation of the rod molecules[16] and preferred growth in the direction of molecular plane during the coagulation process. More recently, a similar structural feature in thin films of poly[7-oxo-7H-benz(*d,e*)imidazo(4′,5′:5,6)benzimidazo(2,1-*a*)isoquinoline-3,4:10,11-tetryl)-10-carbonyl] (BBL) polymer having a ladder-like backbone, was observed[17].

The two self-assembling behaviours observed during the coagulation of the rigid-rod PBZT solution suggest that PBZT films having a single crystalline orientation can be made simply by orientating the chains in one direction before coagulating the solution. In the present

---

* To whom correspondence should be addressed

study, preparation of rigid-rod polymer thin films of single crystalline texture was examined. Orientations of the crystallographic planes in the prepared films were then characterized by wide angle X-ray scattering (WAXS). *FT*i.r. spectroscopy with polarized radiation was also used to confirm the chain orientations relative to the film axes.

EXPERIMENTAL

Materials and sample preparation

PBZT polymer used was obtained from the Materials Laboratory, Wright Patterson Air Force Base. The polymer has an intrinsic viscosity of 16 dl g^{-1} in methane sulfonic acid (MSA) at 30°C, corresponding to a weight average molecular weight of 27 000 g mol^{-1}.

Polymer solution was prepared by mixing the polymer in MSA at room temperature. The polymer solution was then poured on a glass surface, where several layers of Scotch tapes were pasted to control the solution thickness. The solution was slowly sheared using a smooth surfaced bar at a shear rate of approximately 0.5 s^{-1}. The shear rate was controlled in order not to induce shear band formation which results in the rotation of the a–b plane along the shear axis. The films were then prepared through the coagulation, i.e. dipping the sheared solution on the glass slide into water, followed by drying in a vacuum oven either as a free standing film or on the glass substrate. The solution concentrations were initially chosen as 1, 4 and 6 wt%. At concentrations of 1 and 4 wt%, which are below the critical concentration, the molecules did not align themselves under the shear flow. On the other hand, in the case of 6 wt% solution, being above the critical concentration, the molecules were easily aligned even by moderate shearing. The film thickness thus obtained ranged from 20 to 50 μm.

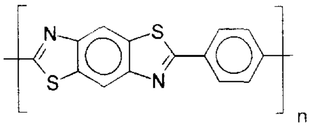

Figure 1 Chemical structure of PBZT

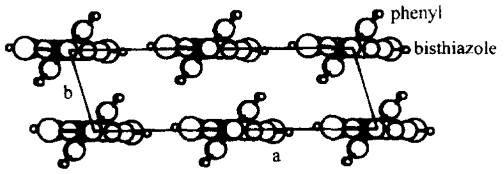

Figure 2 c-axis view of PBZT unit cell proposed by Fratini *et al.*[18]

X-ray scattering and i.r. spectroscopy

X-ray scattering intensities were measured from a flat film camera and a wide angle X-ray goniometer. Both camera units were coupled to a Rigaku sealed tube X-ray generator. The generator was operated at 45 kV and 30 mA and CuK_α radiation was monochromated by the nickel filter.

I.r. spectra were measured by a Nicolet 520 Fourier transform infrared spectrometer with a gold wire grid polarizer. A ZnSe (50 × 10 × 3 mm^3) crystal was used for the attenuated total reflection (ATR) measurements with an incidence angle of 45° to the plane of the film surface. All i.r. spectra were collected at a resolution of 4 cm^{-1}.

RESULTS AND DISCUSSION

WAXS

Before discussing the results, the crystal structure of PBZT proposed by Fratini *et al.*[18] and an equatorial X-ray diffraction scan from the PBZT fibre are first examined. As depicted in *Figure 2*, the polymer forms a non-primitive monoclinic cell with lattice parameters of $a = 1.179$ nm, $b = 0.354$ nm, $c = 1.251$ nm and $\gamma = 94°$. The unit cell suggests a non-planar conformation of the polymer chains. Only the bisthiazole plane lies in the ac-plane with a torsion angle of 46° relative to the phenyl ring plane, which is somewhat larger than the result of 30° estimated by semi-empirical calculations[19,20]. The fibre X-ray pattern, plotted in *Figure 3*, reveals two main

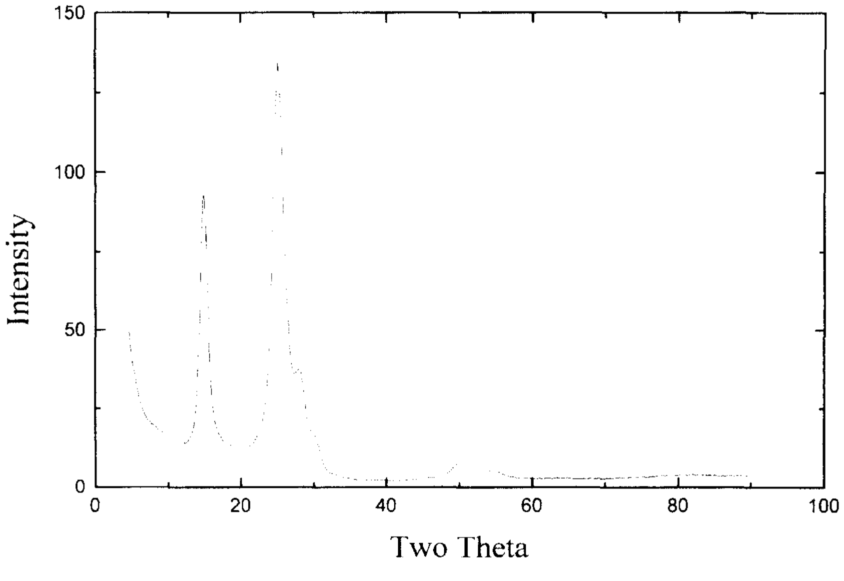

Figure 3 Equatorial X-ray diffraction pattern from PBZT fibre

peaks at 15° and 25°. The former peak at 15° and the latter peak at 25° can be assigned to (200) planes of the side-to-side inter chain packing and (010) planes of face-to-face packing, respectively. It is noted that the intensity ratio between the two peaks $I(200)/I(010)$ is about 80/135, suggesting a larger structure factor for the (010) plane than the (200) plane.

As discussed in the Experimental section, the films obtained from below critical concentration solutions (1 and 4 wt%) do not show any axial orientation of the chains even under a high shear. Hence, the following discussion of the results is limited to those films obtained from 6 wt% solution. X-ray patterns of the PBZT film from the 6 wt% concentration are shown in *Figure 4*. Pattern (a) was measured with incident X-ray beam perpendicular to the film surface and (b) parallel to the film surface. Both patterns (a) and (b) exhibit an axial orientation that the chains are well aligned along the shear direction. It should be also noted, in pattern (a), that only (010) reflection at $2\theta = 25°$ is visible in the absence of the (200) reflection at 15°. On the other hand, both reflection peaks are rather strong in pattern (b). X-ray diffraction from a set of crystal planes occurs when the Bragg condition, $\lambda = 2d \sin\theta$, is satisfied. Here λ, 2θ and d denote X-ray wavelength, diffraction angle, and d-spacing, respectively. The geometry of the Bragg condition, as illustrated in *Figure 5*, shows that the X-ray beam must intersect the crystal planes at an angle of θ which is 1/2 the diffraction angle 2θ. Thus, for the crystal planes (200) and (010) of PBZT unit cell to satisfy the Bragg condition, the intersect angles must be 7.5° and 12.5°, respectively. The appearance of a strong (010) peak in the absence of a (200) peak in pattern (a) with the X-ray beam parallel to the plane of the film surface suggests that the (010) reflection planes are preferentially lying perpendicular to the film surface. The two structural packing modes revealed by the pattern (a) demonstrate that the three crystallographic axes a, b, and c of the PBZT unit cell can be uniquely defined relative to the macroscopic film axes, as depicted in *Figure 6*. In pattern (b) of *Figure 4*, where the X-ray beam is parallel to the film surface, both the (010) and (200) peak appear to be quite strong, which contradicts the results of pattern (a). Complete or near absence of the (010) peak is expected from the geometry of the PBZT unit cell and the Bragg diffraction condition. The appearance of a rather marked (010) peak could be attributed to somewhat broad distributions of the planes and also to a greater structure factor of the (010) reflection, as was noted in the fibre pattern. Diffractometer scans of the films from 6 wt% solution were measured at various angles of the X-ray beam relative to the film surface. Here all the intensities were collected under the θ–2θ decoupled mode such that the angles initially set between the incoming X-ray beam and the film surface are maintained constant during the scan. Some of the intensities curves are plotted in *Figure 7* and the intensity curve (a) obtained with the X-ray beam normal to the film surface, therefore, corresponds to the flat film pattern (a) of *Figure 4*. The curve (d) with the beam 2° to the plane of the film surface also conforms to pattern (b) of *Figure 4*. The changes in the relative two peak intensities with respect to the incident X-ray direction clearly manifest the orientation of the (200) and (010) planes along the film thickness. The complete absence of the (200) peak in pattern (a) but the still discernible (010) peak in pattern (d) are consistent with the results of flat film patterns of *Figure 4*.

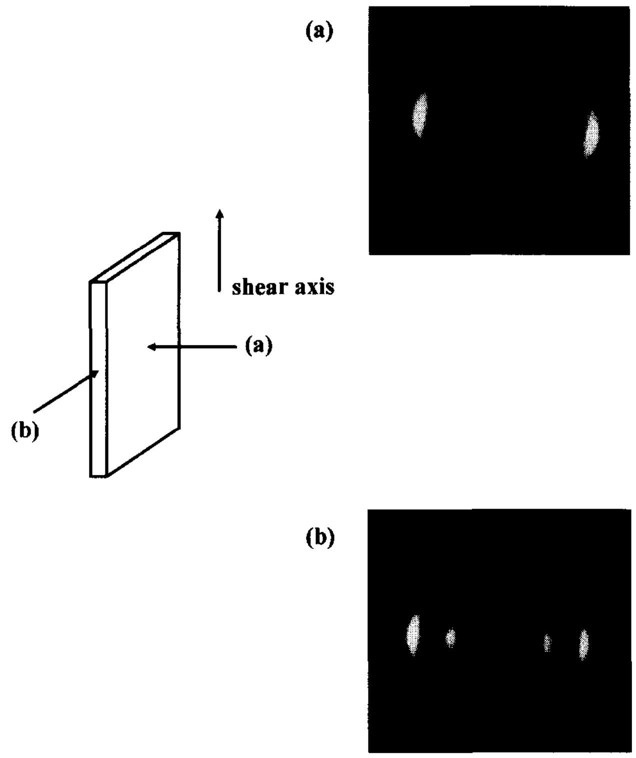

Figure 4 Flat film X-ray patterns: (a) with incident X-ray normal to plane of film surface; (b) with the beam parallel to the plane of film surface

FT *i.r. spectroscopy*

Determination of the three-dimensional orientation of polymers by a polarizing i.r. spectroscopy has been successfully demonstrated[21–24]. The measurements are done by changing the polarization direction of i.r. radiation relative to the film axes and comparing the

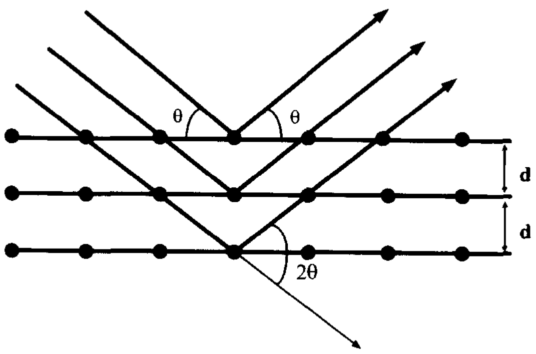

Figure 5 Geometry of Bragg diffraction condition

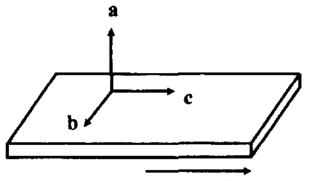

Figure 6 Orientations of crystallographic axes a, b, and c relative to the film axes

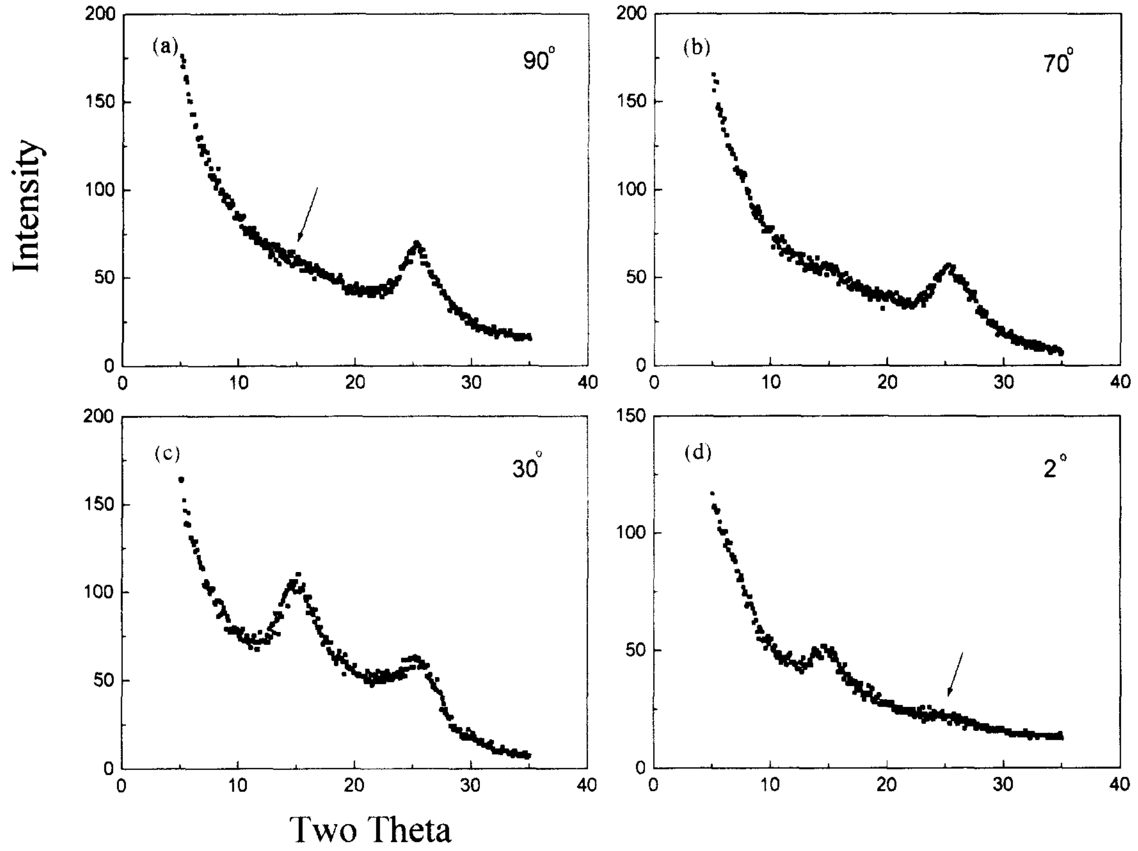

Figure 7 Diffractometer scans of PBZT film. The numbers denote angles between the X-ray beam and the film surface

relative strength of absorption bands. In the present study this technique was utilized to confirm the three-dimensional orientations of the rigid-rod PBZT chains in prepared films. The polarization spectra of the PBZT films are shown in *Figure 8*. The (a) and (b) spectra are the transmission data obtained with the polarization direction parallel to and transverse to the shear axis, respectively. Spectrum (c) was obtained by the attenuated total reflectance (ATR) technique with the radiation propagating along the shear axis. In this ATR measurement the radiation was polarized in the direction of film thickness with an incidence angle of 45° relative to the normal film surface. Assignments of prominent i.r. absorption bands of PBZT and their directions suggested by Shen and Hsu[24] are listed in *Table 1*. The three directions, x, y and z, given in *Table 1*, are defined such that y is the out-of-plane direction (normal to the heterocyclic or aromatic plane) and z is the direction parallel to the chain axis. x is normal to both y and z directions. The z transition moments are then associated with the chain stretching vibration and y moments are associated with the out-of-plane vibration of heterocycles or aromatic ring. Comparison of the three spectra reveals notable differences in the relative strengths of the z stretching bands and y out-of-plane bending bands. The orientation effects on i.r. absorption bands become much clearer, when comparing the quotient values of the spectra shown in *Figure 9*. Data points of curve (1) in *Figure 9* represent the quotients at each frequency, obtained by dividing spectrum (b) with spectrum (a). It is noted that the transition moments in the y direction (out-of-plane direction) show several maxima, while the z transition moments result in several minima, indicating an axial orientation of the polymer chains along the

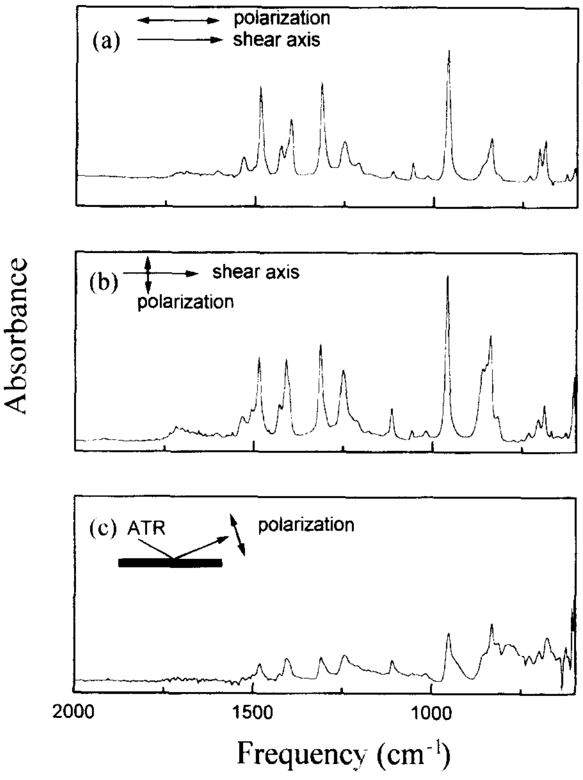

Figure 8 I.r. spectra of PBZT film: (a) transmission data obtained with the beam polarized parallel to the shear axis; (b) transmission data with the polarization perpendicular to the shear axis; (c) ATR spectrum with the polarization direction 45° to film surface normal

Table 1 I.r. bands of PBZT film and their assignment[24]

Frequency (cm^{-1})	Polarization directions	Assignment
1605	*z*	1,4-C_6H_4, 1,2,4,5-C_6H_2
1532	*z*	1,4-C_6H_4
1485	*z*	hetero ring stretch
1428	*z*	1,2,4,5-C_6H_2
1410	*y*	1,4-C_6H_4
1401	*z*	hetero ring stretch
1314	*z*	hetero ring stretch
1252	*y*	crystalline band
1211	*z*	C–C stretch
1113	*y*	1,4-C_6H_4
1056	*z*	1,4-C_6H_4
1017	*x*	1,2,4,5-C_6H_2
960	*z*	hetero ring 'breathing'
860	*y*	1,2,4,5-C_6H_2
837	*x*	1,4-C_6H_4
732	*z*	hetero in-plane ring deformation
705	*z*	1,4-C_6H_4
689	*z*	hetero ring stretch
627	*z*	1,4-C_6H_4
605	*y*	hetero out-of-plane ring deformation

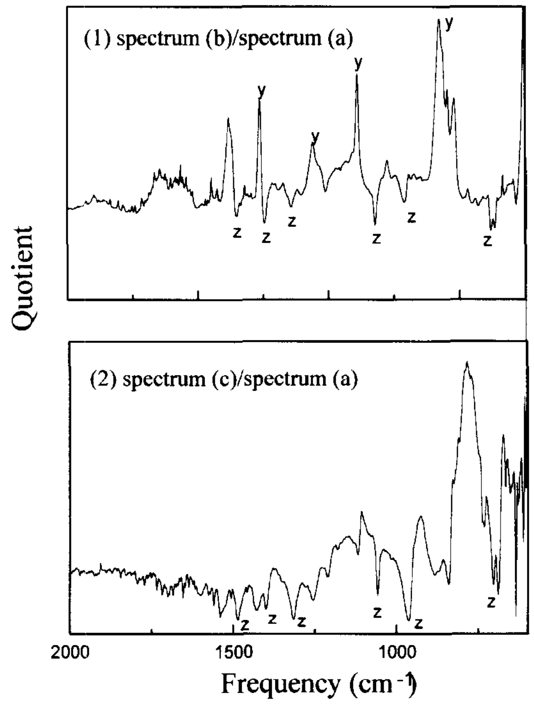

Figure 9 Quotients obtained by dividing the spectra (b) and (c) with the spectrum (a) of *Figure 8*: curves (1) and (2) correspond to spectra (b) and (c), respectively

shear axis. The orientation of molecular planes relative to the film axes can also be demonstrated by the quotient values of curve (2), which was obtained by dividing the ATR spectrum (c) with spectrum (a) of *Figure 8*. The quotient curve shows several minima in *z* transition moments without the presence of *y* maxima, confirming that on the average the heterocyclic planes and the aromatic ring planes of the PBZT are preferentially oriented normal to the plane of the film surface.

SUMMARY

For the first time rigid-rod PBZT films of single crystalline texture were prepared from polymer solution in MSA. The results of WAXS scattering and *FT*i.r. spectroscopy with a polarized radiation on the rigid-rod polymer films prepared, confirmed the presence of a three-dimensionally oriented structure so that the three crystallographic axes *a*, *b*, and *c* of the PBZT unit cell can be defined over the macroscopic film axes. In the process of making such single crystalline films, the *c*-axis orientation was induced by shearing the polymer solution, and *a*- and *b*-axis orientations were driven by the self-assembling nature of the rigid-rod polymer molecules during coagulation of the sheared solution. To achieve effective alignment of chains by the shear flow, the polymer solution had to be above the critical concentration.

ACKNOWLEDGEMENTS

This work was supported by Non Directed Research Fund, Korea Research Foundation. Professor Han-Sup Lee (Inha University) is thanked for help with *FT*i.r. spectroscopy.

REFERENCES

1. Lusinea, R. W., *Mater. Res. Soc. Symp. Proc.*, 1989, **134**, 265.
2. Pope, D. P. and Keller, A., *J. Mater. Sci.*, 1974, **9**, 920.
3. Gray, R. W. and Young, R. J., *J. Mater. Sci. Lett.*, 1974, **9**, 521.
4. Song, H. H., Argon, A. S. and Cohen, R. E., *Macromolecules*, 1990, **23**, 790.
5. Lin, L. and Argon, A. S., *Macromolecules*, 1992, **25**, 4011.
6. Bartczak, Z., Argon, A. S. and Cohen, R. E., *Macromolecules*, 1992, **25**, 5036.
7. Wolfe, J. F., Loo, B. H. and Arnold, F. E., *Macromolecules*, 1981, **14**, 909.
8. Allen, S. R., Fillipov, A. G., Farris, R. J., Thomas, E., Wong, L. C., Berry, G. C. and Chenevey, E. C., *Macromolecules*, 1981, **14**, 1135.
9. Denny, L. R., Goldfarb, I. J. and Soloski, E. J., *Mater. Res. Soc. Symp. Proc.*, 1989, **134**, 395.
10. Spry, R. J., Zelmon, D. E., Ramabadran, U. and Jackson, J., *J. Polym. Sci.: Part B: Polym. Phys. Edn*, 1992, **30**, 1507.
11. Rao, D. N., Swiatkiecz, J., Chopra, P., Ghoshal, S. K. and Prasad, P. N., *Appl. Phys. Lett.*, 1986, **48**, 1187.
12. Wong, C. P., Ohnuma, H. and Berry, G. C., *J. Polym. Sci. Polym. Symp.*, 1978, **65**, 173.
13. Berry, G. C., *J. Polym. Sci.: Polym. Phys. Edn*, 1976, **14**, 451.
14. Ree, M., Nunes, T. L. and Kirby, D. P., *Polym. Prepr.*, 1992, **33**, 309.
15. Song, H. H. and Wang, C.-S., *Polymer*, 1993, **34**, 4793.
16. Roche, E. J., *Mater. Res. Soc. Symp. Proc.*, 1989, **134**, 457.
17. Song, H. H., Fratini, A. V., Chabinyc, Price, G. E., Agrawal, A. K., Wang, C.-S., Bai, S. J., Burkette, J., Dudis, D. S. and Arnold, F. E., *Synth. Metals*, 1995, **69**, 533.
18. Fratini, A. V., Lenhert, P. G., Resch, T. J. and Adams, W. W., *Mater. Res. Soc. Symp. Proc.*, 1989, **134**, 431.
19. Farmer, B. L., Wierschke, S. G. and Adams, W. W., *Polymer*, 1990, **31**, 1637.
20. Yang, Y. and Welsh, W. J., *Macromolecules*, 1990, **23**, 2410.
21. Wolfram, L. E., Grasselli, J. G. and Koenig, J. L., *Appl. Spectrosc.*, 1970, **24**, 263.
22. Koenig, J. L. and Itoga, M., *Appl. Spectrosc.*, 1971, **25**, 355.
23. Shen, D. Y., Venkatesh, G. M., Burchell, D. J. and Hsu, S. L., *J. Polym. Sci. Polym. Phys. Edn*, 1981, **19**, 1475.
24. Shen, D. Y. and Hsu, S. L., *Polymer*, 1982, **23**, 969.