JOURNAL OF MATERIALS SCIENCE 16 (1981) 3303–3308

Microstructural study of as-extruded and heat-treated ribbons of poly(p-phenylene benzobisthiazole)

J. R. MINTER, K. SHIMAMURA*, E. L. THOMAS
Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003, USA

Ribbons of poly(p-phenylene benzobisthiazole) (PBT) prepared by extrusion from methane sulphonic acid solution into acid–water coagulation baths, were examined by electron microscopy, wide-angle X-ray scattering and small angle X-ray scattering. Electron diffraction patterns and corresponding dark-field images of as-extruded ribbons suggest that the chains are well oriented in the extrusion direction, with laterally-ordered regions averaging 2 nm in width. Upon heat treatment, the equatorial reflections sharpen and dark-field imaging indicates an increase in lateral order to about 15 nm. Small-angle X-ray scattering patterns show very little scattered intensity except for strong equatorial scattering attributed to voids elongated parallel to the extrusion direction. The absence of distinct crystalline images in 0 0 *l* dark-field is supporting evidence for axial shift of the molecules along the chain axis, as suggested by previous diffraction studies.

1. Introduction

Poly(p-phenylene benzobisthiazole) (PBT) a wholly aromatic, heterocyclic, rigid macromolecule, has been processed into high-modulus, high-strength fibres and films with good thermal stability [1]. Moduli of 110 GPa are typical for as-spun fibres with strengths around 1.1 GPa. Heat-treatment yields fibres with moduli as high as 280 GPa and strengths of 2.7 GPa [2, 3]. An initial electron microscopy study of PBT fibres spun from nematic solutions in methane sulphonic acid (MSA) has been reported by Roche *et al.* [4]. The molecular structure was suggested to be highly-aligned rods well packed in the lateral directions but with axial shift of the chains along the extension direction.

Mechanical properties of PBT ribbons are thus far substantially lower than those of the more well developed fibres. Because of voids and blisters in these preliminary materials, both as-extruded and heat-treated ribbons typically exhibit moduli of only 40 GPa with strengths of 0.5 GPa [5]. This paper reports the microstructure of as-extruded and tension heat-treated PBT ribbons prepared from nematic MSA solutions. Electron-beam damage and its effect on the dark-field (DF) images of PBT are also discussed.

2. Experimental procedure

PBT samples with an inherent viscosity (in MSA at 30° C) in the range of 14–18 were supplied by J. Wolfe of Stanford Research Institute [6]. These samples were processed into films by E. Chenevey of Celanese Research Corp. Ribbons were formed by extruding a 12 wt % PBT solution in MSA out of a rectangular die, through an air-gap into a MSA–H_2O coagulation bath followed by a water wash. Extrusion draw ratios ranged from 1.4 to 2.9 times. The final ribbon width averages 5 mm with final thickness of 0.025 mm. Ribbons were subsequently heat-treated at 475° C under slight tension with a 32 sec residence time.

A JEOL 100CX electron microscope operated at 100 kV was used. Images and electron diffraction patterns were recorded on Kodak 4463 and 4489

*Present address: Institute for Chemical Research, Kyoto University, Uji, Kyoto-611, Japan.

0022–2461/81/123303–06$02.60/0

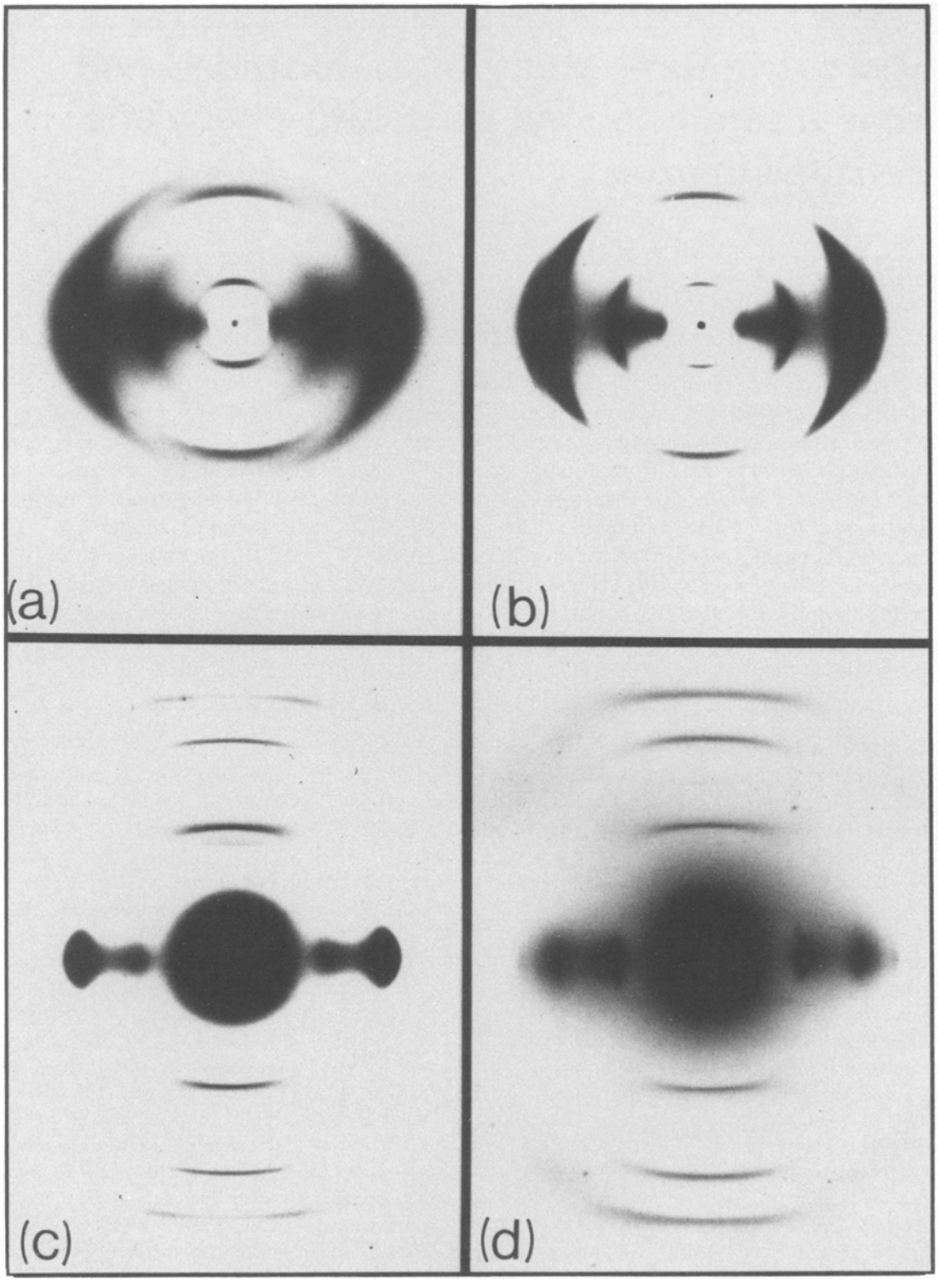

Figure 1 Wide-angle X-ray diffraction and selected-area electron diffraction of typical PBT films. The extrusion direction is vertical: (a) WAXD of as-extruded film, (b) WAXD of film continuously tension heat-treated at 475° C, (c) SAED of as-extruded film, and (d) SAED of heat-treated film.

film. Specimens thin enough for transmission electron microscopy were prepared by detachment replication [7]. Dark-field (DF) images were obtained by the tilted beam technique with objective aperture cut-offs of 0.8 and 2.3 nm^{-1}. Electron dose was determined by measuring the current on a calibrated phosphor observation screen using the method of Grubb and Groves [8].

3. Results and discussion

Examination with incident polarized-light microscopy revealed that the as-extruded ribbons are highly bi-refringent and contain elliptical voids which occur due to inhomogeneities during coagulation. Total extinction occurred when the ribbon axis was rotated into coincidence with the polarizer or analyser axis, suggesting that the ribbons are well oriented. In addition to the voids, large blisters were present in the heat-treated fibres due to the loss of residual water during annealing, as identified by mass spectroscopy/thermogravimetric analysis [2].

Selected-area electron diffraction (SAED) and wide-angle X-ray diffraction (WAXD) patterns from as-extruded and annealed films are shown in Fig. 1. WAXD patterns show that the as-extruded film sample is oriented in the draw direction (average azimuthal spread 30 to 39°). The equatorial reflections are, however, quite broad, indicating only relatively short-range lateral order. After annealing under slight tension, the equatorial reflections sharpen due to longer range lateral ordering while the molecular orientation in the extrusion direction remains essentially unchanged.

In contrast to the WAXD patterns, which come from a region of the films approximately 1 mm × 1 mm × 0.025 mm, the SAED patterns contain information from a region of the film approximately 1 μm × 1 μm × 50 nm. SAED patterns of as-extruded ribbons exhibit higher orientation (average azimuthal spread 10 to 12°) in the draw direction than for WAXD of the bulk ribbon due to misorientation from fibrillation and to possible higher orientation of the film surface selectively-sampled by the detachment replication. The breadth of the equatorial reflections in SAED patterns is consistent with that observed by WAXD. SAED from the tension heat-treated ribbons shows the increased perfection in lateral order with the high orientation in the extrusion direction remaining unchanged.

The diffracted intensity from heat-treated PBT

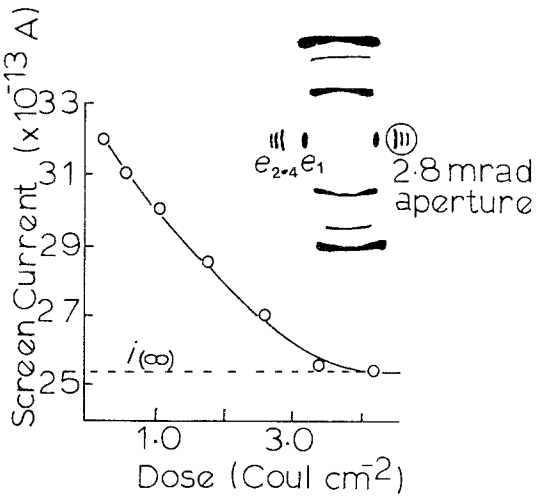

Figure 2 Decay of diffracted intensity of the Reflections e_2 to e_4 with increasing dose.

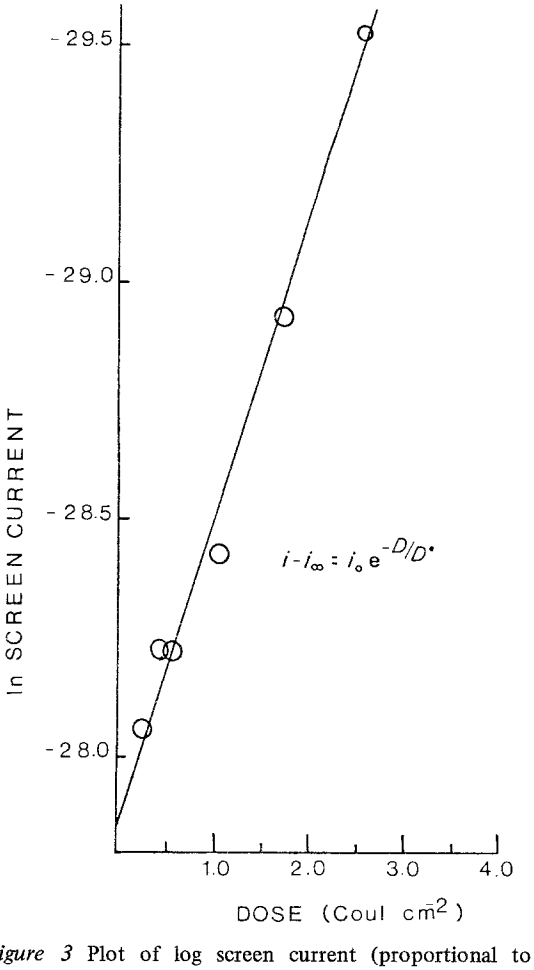

Figure 3 Plot of log screen current (proportional to diffracted intensity) against electron dose.

films decreases with increasing dose to a plateau value caused by scattering from the amorphous carbon support and radiation-damaged PBT. The decay of the diffracted intensity, $i(D)$, with increasing dose, D, is well modeled as

$$i(D) - i_\infty = i_0 \exp(-D/D^*), \quad (1)$$

where D^* represents the dose for the intensity to fall to $1/e$ of its initial value, and is a characteristic dose for the material (see Fig. 2), and i_0 is a constant. The main limitation to electron microscopy of polymers is radiation damage by the electron beam. From the aromatic nature of the PBT molecule good radiation stability is expected [9]. The radiation life-time of a material can be determined by monitoring the diffracted intensity as a function of specimen dose. D^* for the second, third and fourth, equatorial reflections (Reflections e_2 to e_4) was determined to be $1.6\,C\,cm^{-2}$ for annealed PBT (see Fig. 3). Dobb *et al.* [10] cite the total decay of the most stable 1 1 0 reflection as $0.2\,C\,cm^{-2}$ for PPTA. Literature values of $4 \times 10^{-3}\,C\,cm^{-2}$ are reported for both polyoxymethylene (POM) and polyethylene (PE) [8]. Thus PBT and PPTA are substantially more stable than POM or PE. This permits recording of more images at a given magnification or a single higher resolution image at a higher magnification.

DF images were examined as a function of electron dose and the laterally-ordered regions were found to remain constant in size but decreased in intensity with increased total dose. This suggests that the lateral packing persists upon irradiation, probably due to rigidity of the individual rod-like molecules but the lattice dimensions become less well defined. One can obtain useful equatorial DF images with a good signal-to-noise ratio up to a total dose of approximately D^*.

Bright-field (BF) (Fig. 4) micrographs of detached replicas from as-extruded and heat-treated PBT ribbons exhibit fibrillated sheet-like fragments.

Equatorial DF images from as-extruded films reveal an average bright speckle of 2 nm. The speckle is always less than 10 nm in size and is insensitive to the Airy-disc size of the objective aperture employed. Such small-scale image detail requires careful work to quantify since, at this level, the microscope optics strongly influence the image. Furthermore, images must be obtained

Figure 4 Bright-field/dark-field micrographs of detached fragment from a PBT film. Insert shows Reflections e_1 to e_4 used for the dark-field image.

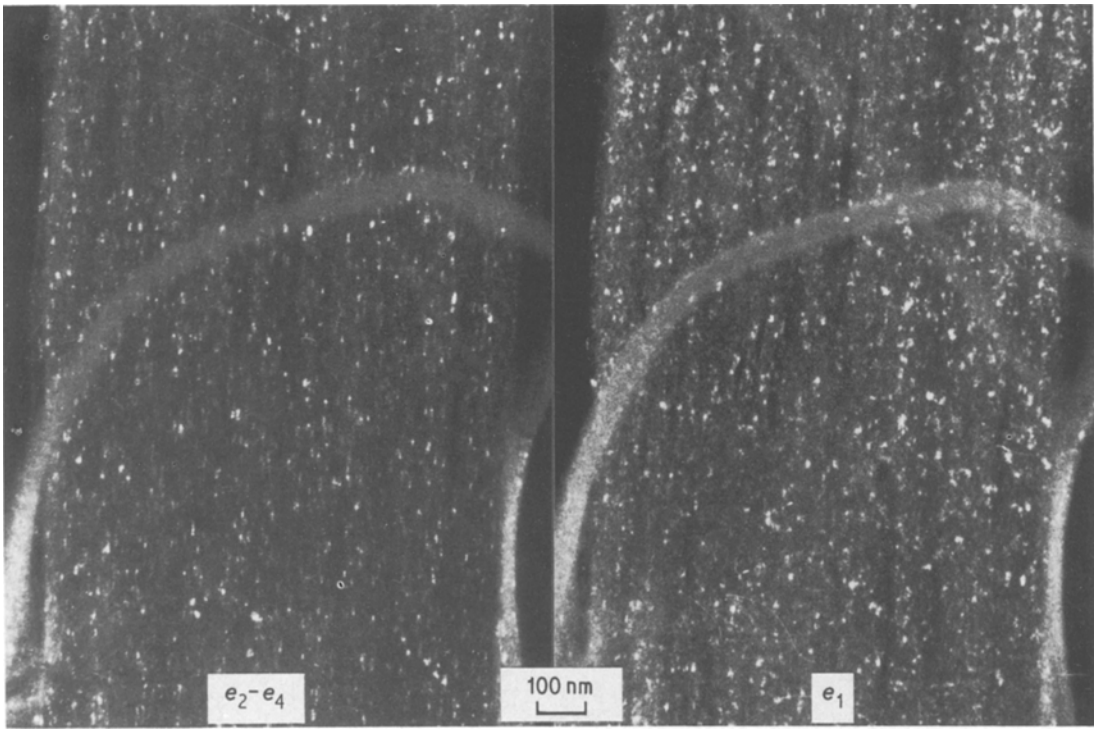

Figure 5 Successive equatorial dark-field micrographs of fragments from a heat-treated PBT film.

only from the thinnest areas of the fragments in order to satisfy the requirement that the thickness of the specimen be not much greater than the size of the projected object in order to avoid artefacts arising from a two-dimensional projection of a three-dimensional object. Recognizing these problems, it is estimated that the laterally-ordered regions in as-extruded PBT ribbons average 2 nm in size.

Fig. 5 shows DF images of Reflections e_1 and e_2 to e_4, from the same area of an annealed PBT film. The projection of the laterally-ordered regions in each image averages 10 nm wide by 16 nm long with no regions observed to be longer than 40 nm. The micrographs show a relatively uniform spatial distribution of laterally-ordered regions within the fragment. When the objective aperture is set to accept only the non-equatorial component of the Reflections e_2 to e_4, one still finds a uniform spatial distribution of laterally-ordered regions within the fragment. This shows that PBT ribbons do not possess periodic orientation fluctuations such as the "pleated sheet"-type structure proposed for PPTA by Dobb *et al.* [11].

Meridional DF images using various reflections from heat-treated PBT ribbons do not exhibit any prominent diffraction contrast. This is in agreement with the model proposed by Roche *et al.* [4] and Odell *et al.* [12] of laterally-ordered chains with molecular axial shift [13] along the fibre axis, since such structures are not three-dimensional crystals. Hence, the meridional reflections occur from intramolecular interferences and meridional DF microscopy images the individual molecules leading to a uniform spatial distribution of DF intensity.

SAXS from as-extruded and annealed PBT ribbons is dominated by micro-void scattering, i.e., a continuous, monotonic decrease in the equatorial scattered intensity, and no fibre long period is observed. This suggests that there are no periodic fluctuations in electron density. When the lack of an "amorphous halo" in the WAXD and SAED patterns is also considered, it is reasonable to conclude that the material is single-phase with laterally-ordered regions separated by defects from other laterally-ordered regions. The increase in the highly anisotropic SAXS intensity upon heat-treatment is probably due to the occurrence of thin, long, voids between fibrillar elements during the heat-treatment process.

4. Conclusions

Dark-field electron microscopy, SAED, WAXD and SAXS observations suggest that as-extruded ribbons of PBT are comprised of laterally-ordered regions, of the order of 2 nm in extent, which are highly-oriented in the draw direction. After heat-treatment at 475° C the lateral order increases to an average of 15 nm parallel to the draw direction and 10 nm perpendicular to the draw direction, with the high axial orientation remaining constant. Upon irradiation damage by the electron beam, these laterally-ordered regions become more disordered but remain essentially constant in size. Meridional dark-field images exhibit no prominent diffracting regions indicating a lack of well-defined three-dimensional crystalline order in the PBT films processed thus far.

Acknowledgements

The authors wish to thank A. K. Kulshreshtha of the University of Dayton Research Institute for supplying the wide-angle X-ray diffraction photographs. This work was supported by the Air Force Wright Aeronautical Laboratories/Materials Laboratory, Wright Patterson AFB under contract number F33615-78-C-5175 and the University of Massachusetts Materials Research Laboratory.

References

1. T. E. HELMINIAK, *Amer. Chem. Soc. Org. Coatings Plast. Prep.* **40** (1979).
2. S. R. ALLEN, A. G. FILIPPOV, R. J. FARRIS, E. L. THOMAS, C. P. WONG, G. C. BERRY and E. C. CHENEVEY, *Macromolecules*, to be published.
3. S. R. ALLEN, A. G. FILIPPOV, R. J. FARRIS and E. L. THOMAS, *J. Appl. Polymer. Sci.* **26** (1981) 291.
4. E. J. ROCHE, T. T. TAKAHASHI and E. L. THOMAS, "Fiber Diffraction Methods" American Chemical Society Symposium Series Vol. **141** (American Chemical Society, Washington D.C., 1980) p. 303.
5. E. C. CHENEVEY, private communication, 1980.
6. J. F. WOLFE, B. H. LOO and F. E. ARNOLD, *Polymer Prep.* **20** (1979) 82.
7. D. C. BASSETT, *Phil. Mag.* **6** (1961) 103.
8. D. T. GRUBB and G. W. GROVES, *ibid.* **24** (1971) 815.
9. V. E. COSSLET, *J. Microscopy*, **113 (2)** (1978) 113.
10. M. G. DOBB, D. J. JOHNSON and B. P. SAVILLE, *J. Polymer Sci. Polymer Symp.* **58** (1977) 237.
11. M. G. DOBB and D. J. JOHNSON, *Phil. Trans. Roy. Soc.* **A294**, (1979) 483.
12. J. A. ODELL, A. KELLER, E. D. T. ATKINS and M. J. MILES, *J. Mater. Sci.* **16** (1981) 3309.
13. B. K. VAINSHTEIN, "The Diffraction of X-rays by Chain Molecules" (Elsevier, Amsterdam and Oxford, 1966) p. 277.

Received 9 February and accepted 30 April 1981.