Lattice imaging of high modulus poly(p-phenylene benzobisthiazole) fibres

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

Ultrastructural research of materials has increasingly utilized high resolution electron microscopic techniques to obtain structural information at the molecular level. The use of electron microscopy for investigation of crystalline polymers has been limited due primarily to electron beam radiation damage of the specimen. Because of the low total useful electron dose, the attainable image resolution is low. Low magnification, diffraction contrast studies have nevertheless profitably studied dislocation networks between lamellar crystals [1, 2] macrosector and microsector fold and twin boundaries [3, 4] and crystallite size and orientation [5, 6]. Lattice imaging of synthetic polymers has only been achieved for poly(*p*-xylylene) (1.8 nm) [7], poly(*p*-phenylene terephthalamide) (PPTA, 0.64 nm and 0.43 nm) [8] and most recently poly[1.6-di)-N-carbazolyl)-2,4-hexadiyne) (1.2 nm) [9]. In this paper we report axial bright field lattice images utilizing the 0.59 nm and 1.24 nm reflections in poly (*p*-phenylene benzobisthiazole) (PBT).

PBT is a wholly aromatic, heterocyclic, rigid macromolecule and has been processed into high modulus, high strength fibres and films with good thermal stability [10]. 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 [11, 12]. For comparison, PPTA fibres have a modulus of 120 GPa and strength of 4.1 GPa while steel has a modulus of 200 GPa and strength of 3 GPa. An initial electron microscopy study of as-spun PBT fibres processed from nematic solutions in methane sulphonic acid (MSA) was reported by Roche *et al.* [13]. The molecular structure was suggested to be highly aligned rods packed well in the lateral directions but with translational disorder of the chains along the fibre axis.

Recent ($hk0$) wide angle X-ray line broadening and dark field electron microscopy studies of extruded PBT films showed an increase in the lateral crystallite size from about 2 nm in the as-spun film to 15 nm with heat treatment [14]. However, the absence of distinct crystallite images in ($00l$) dark field images of both as-spun and heat treated films suggested that the meridional reflections occur due to intramolecular interferences since the occurrence of axial shift in the molecular packing would lead to a uniform distribution of dark field image intensity [14].

While the tension heat treatment of PBT fibres and films results in significant improvements in axial tensile modulus over as-spun or annealed fibres [11] electron diffraction patterns still show no distinct hkl reflections. Preliminary molecular packing studies [15] suggest several favoured axial packing arrangements, so presumably with appropriate processing and tension heat treatment conditions, full three-dimensional crystalline order on a large scale will be achievable. In partially ordered systems high resolution electron microscopy has proved particularly valuable since, while the electron diffraction pattern is a composite average from a region of the fibre, imaging details of the structure locally can reveal minority regions of different degrees of order than the bulk average [16]. The electron beam radiation damage lifetime of PBT (defined as the dose required for the scattered intensity to decrease to $1/e$ of its original value) is approximately 1.6 C cm^{-2} for equatorial reflections at 100 keV and room temperature [14]. Since the radiation damage lifetime of PPTA is reported as 0.2 C cm^{-2} [8], the prospect of obtaining lattice images for sufficiently ordered PBT is quite good.

PBT of intrinsic viscosity 31 was supplied by J. Wolfe of Stanford Research Institute. The fibres

*Permanent address: Institute for Chemical Research, Kyoto University, Uji, Kyoto-611, Japan.
†Permanent address: Kodak Research Laboratories, Rochester, NY 14612, USA.

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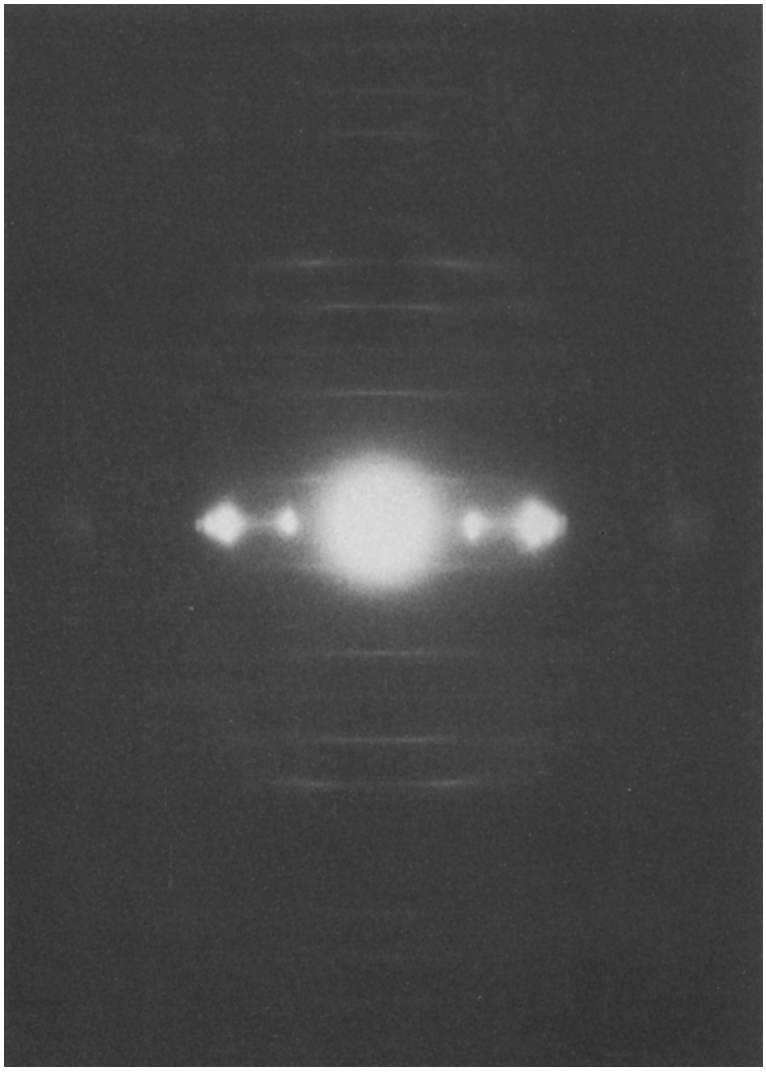

Figure 1 Electron diffraction pattern of PBT with axial disorder.

investigated here were spun by E. Chenevey of Celanese Research Corporation from a 5.6% solution in poly(phosphoric acid) using a 5 x 200 μm diameter spinneret maintained at 60° C. A spin draw ratio of 3.7 was obtained by use of a 7.5 cm air gap followed by coagulation in an aqueous bath containing 9% H_3PO_4 with final washing in pure water. The as-spun filament had a modulus of 70 GPa and a strength of 2.4 GPa. After drying, the filaments were tension heat treated by a continuous process through an oven maintained at 475° C with a nitrogen atmosphere. Residence time was 64 sec with a 4% applied stretch. A final modulus of 250 GPa and strength of 2.8 GPa was obtained.

Thin sections of fibre were prepared by detachment replication [14]. Regions of fibre suspended across holes in a perforated carbon support film were examined in axial bright field at 100 keV in a JEOL 100CX electron microscope with spherical aberration coefficient of 6.7 mm. Images were obtained at x100 000 with approximately Scherzer defocus conditions by minimizing granularity (phase contrast) in the carbon support film. For axial bright field this value of focus results in good transfer of diffracted beams over the spatial frequency range from about 0.7 to 2 nm^{-1} permitting equatorial and meridional lattice imaging to be simultaneously attempted. Once focus was obtained in a given area, an adjacent unirradiated area was quickly chosen and the 20 sec exposure corresponding to a dose of approximately 60% of the radiation damage lifetime was made. Both Kodak Electron Microscope Film 4489 and Kodak

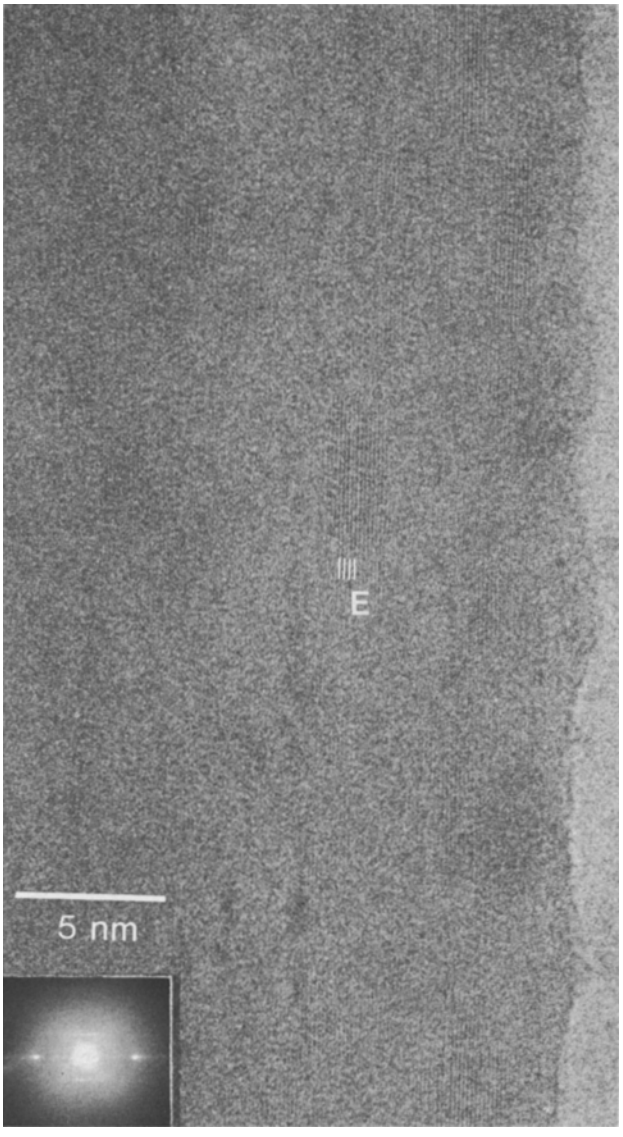

Figure 2 Axial bright field lattice image of tension heat treated fibre. Insert is optical transform showing sharp spots from the 0.59 nm equatorial fringes and diffuse streaks from the 1.24 nm meridional fringes.

Electron Image Film SO-163 were employed. Optical transforms of electron micrograph negatives were obtained on a Polaron optical diffractometer using Polaroid type 55 positive/negative film.

Fig. 1 shows an electron diffraction pattern typical of the heat treated PBT fibre. The axial molecular orientation is very high. The pattern is characterized by discrete equatorial reflections and diffuse, continuous layer lines (up to 20 orders being visible on the negative). This type of pattern can arise due to an axially disordered crystal structure [17–19]. There is good lateral packing of chains but along the fibre axis the chains are irregularly positioned. The unit cell based on the (ten) equatorial reflections is monoclinic with $a' = 0.597$ nm, $b' = 0.362$ nm, $\gamma' = 95.2°$ with fibre repeat of $c = 1.24$ nm [13]. The cylindrically averaged Fourier transform of a single (completely planar conformation) chain has been calculated [20, 21] and shows good agreement with the observed diffraction pattern confirming the basic two-dimensional order with high axial orientation.

Axial bright field images obtained using an $8\ \text{nm}^{-1}$ cutoff objective aperture are shown in Figs. 2 and 3. Distinct fringes (labelled E) are observed parallel to the fibre axis over regions 20 nm wide by 40 nm long with spacing of 0.59 nm corresponding to the first equatorial reflection (e_1). Less distinct, somewhat meandering fringes are also observed approximately normal

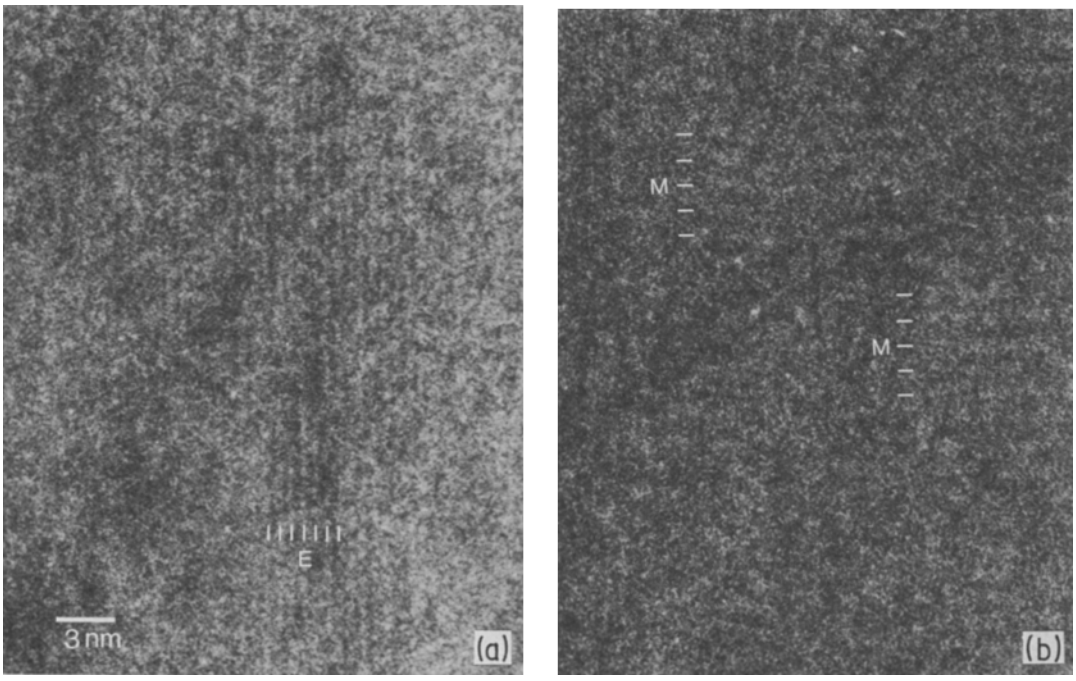

Figure 3 Axial bright field lattice images of tension heat treated fibre. (a) The 0.59 nm fringes from the e_1 reflection are labelled E. (b) The 1.24 nm fringes from the m_1 reflection are labelled M.

to the fibre axis (labelled M in Fig. 3b). These fringes have a constant spacing of 1.24 nm corresponding to the first layer line (m_1). They occur in groups of 3 to 10 fringes with their lateral extent limited to about 5 nm. An optical transform of the bright field micrograph used to print Fig. 2 is shown in the inset. A pair of sharp spots is seen normal to the fibre axis with a pair of streaks oriented 90° to the spots. The ratio of their reciprocal spacings is 2.1, corresponding well with the expected ratio of m_1/e_1 (i.e. 1.24/0.59 = 2.10). The intensity distributions in the optical transform also correspond well with the expected shape transforms of the large equatorial and small meridional fringe regions. The 1.24 nm lattice fringes are unequivocal evidence for the occurrence of true three-dimensional crystalline order in local regions of the fibre. The fringe regions thus so far observed while limited in extent, show no evidence of structural defects. This is similar to the perfection of order in lattice images of PPTA fibres [8]. On-going work is concerned with detailed correlation of the extent and orientation of the lattice image regions with improved fibre mechanical properties.

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