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Microstructure of a thermotropic random copolymer of hydroxybenzoic acid, isophthalic acid and hydroquinone (HBA–IA–HQ)

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Transmission electron microscopy has been used to study microstructural features in a thermotropic copolyester composed of 4-hydroxybenzoic acid, isophthalic acid and hydroquinone residues. Selected-area electron diffraction patterns indicate that thin sheared samples of the pure copolymer, and of an analogue containing glass filler, exhibit a dual molecular orientation in which the meridional maxima are closely periodic in scattering angle. Dark-field (DF) imaging in one set of the diffuse equatorial reflections reveals "bands" which have an average period of 200 nm. Annealing the material in the solid state at 250 °C leads eventually to a change in the structure in which the banded texture is replaced by regions of uniform orientation within which the molecules are aligned with the shear axis. Needle-like diffracting crystalline entities, measuring approximately 80 nm long, in the direction of the molecular chain axis, and 5–8 nm thick, have been imaged in DF using the first meridional reflection as the source of diffraction contrast.

1. Introduction

The principal objective of some recent research [1, 2] has been to use dark-field (DF) imaging in transmission electron microscopy (TEM) to characterize the crystalline entities which occur in a thermotropic copolymer composed of 4-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) residues. This class of polymer, abbreviated B–N, exhibits liquid-crystalline characteristics at elevated temperatures and over a broad composition range. That the chains contain random molecular sequences is confirmed by the aperiodic meridional maxima in both X-ray [3–7] and electron [1, 2] diffraction patterns. The crystalline entities, first observed by Donald and Windle [8], are the consequence of similar but non-periodic sequences of monomer units on neighbouring molecules coming into register [9, 10] and have been referred to as non-periodic layer (NPL) crystallites.

Investigations of thin films by TEM [1] and chemically etched samples with scanning electron microscopy (SEM) [7] have indicated that the NPL crystallites in B–N copolymers are no more than about 20 nm thick in the direction of the molecular chain axis and up to 300 nm long, the latter dimension depending on the degree of polymerization. Recent results [2] have shown that a very similar crystallization phenomenon occurs in a co-polyester–amide, denoted N–AT.

The objective of this study is to use TEM to characterize the microstructural features in a chemically-related thermotropic copolyester containing hydroxybenzoic acid (HBA), isophthalic acid (IA) and hydroquinone (HQ) residues, and which is designated here as B–IQ.

2. Experimental procedure

2.1. Polymerization methods

The copolymer used throughout this work was manufactured by ICI (Wilton, UK) and is composed of 36% HBA, 32% IA and 32% HQ units:

4-Acetoxybenzoic acid and hydroquinone diacetate were obtained by conventional acetylation of hydroxybenzoic acid and hydroquinone with acetic anhydride in acetic acid at 120 to 140 °C. The reaction was catalysed with sulphuric acid. The copolymers were prepared by two different routes: a non-aqueous route involving a clay dispersant and a melt-acidolysis route. The clay particles remained in the final polymer, and except where specifically noted, all the microscopy presented here was carried out on the melt-acidolysis material.

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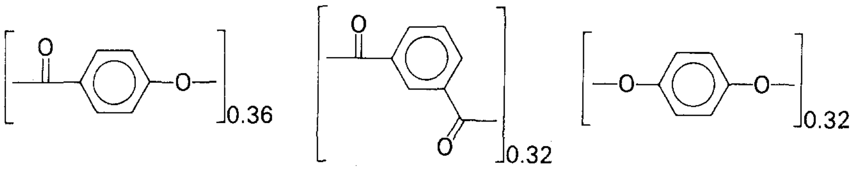


2.1.1. *Non-aqueous dispersion route*

The copolymer was prepared by the general procedure described in detail elsewhere [11]. The reaction vessel was charged with the relevant stoichiometric quantities of 4-acetoxybenzoic acid, hydroquinone diacetate and isophthalic acid, together with liquid paraffin and a catalyst. The mixture was heated to 230 °C while being slowly stirred in a nitrogen atmosphere to the point where acetic acid was beginning to be evolved. Hydrophobisized clay dispersed in liquid paraffin was added to the reaction mixture, whereupon the stirrer speed was increased to disperse the monomer melt in the heat-transfer medium. Polymerization was induced by increasing the temperature to 300 °C over 60–70 min, and the evolved acetic acid collected. The dispersion was held at 300 °C for a further 80 min under an increased nitrogen flow.

2.1.2. *Melt-acidolysis route*

The copolymer was prepared by the general process outlined by Jackson and Kuhfuss [12]. The reaction vessel was charged with the relevant stoichiometric quantities of 4-acetobenzoic acid, hydroquinone diacetate, isophthalic acid, potassium acetate (130 p.p.m.) and acetic anhydride (2.4%). The flask was heated in a metal bath at 200 °C under a nitrogen atmosphere and the contents stirred until the monomers melted, after which the bath temperature was raised stepwise according to the following scheme:

(i) held at 260 °C until 55–60% of the distillate was evolved;
(ii) held at 280 °C until 85–90% of the distillate was evolved;
(iii) held at 320 °C for 40 min;
(iv) held at 340 °C for 40 min.

A vacuum was applied to the vessel and increased gradually down to 1 torr or better, and the polymerization was allowed to continue until the material was too viscous to stir. The copolymer was then cooled under vacuum.

2.2. Electron microscopy

To obtain electron-transparent ultrathin films suitable for TEM, a melt-shearing technique discussed elsewhere [1, 2, 8] was used. Small blocks were cut from bulk B–IQ extrudates and pellets, and each block was placed on a slab of freshly-cleaved rocksalt and heated to 340 °C, which is above the temperature at which the material enters its fluid mesophase (290–300 °C). The molten copolymers were then sheared with a razor blade, and the resultant films quenched to 0 °C on an aluminium block. Following dissolution of the substrate in distilled water, the films were picked up on folding copper TEM grids. Some of the samples were annealed at 250 °C for 30 min. It should be borne in mind that the films were annealed without a substrate, in contrast to the samples prepared by Donald and Windle [8, 13]. All of the specimens were carbon-coated to improve stability under the electron beam.

Electron micrographs and selected-area diffraction (SAED) patterns were obtained with a Jeol JEM 2000-EX electron microscope, fitted with an LaB_6 filament and high-resolution polepiece and operated at 200 kV. Optimum operating magnifications, limited by the radiation sensitivity of the material, were 5000–10000×. In all the micrographs and diffraction patterns presented in this paper, the shear direction used in sample preparation corresponds to the vertical on the page.

3. Results

3.1. Modes of imaging

A typical SAED pattern of the sheared polymer, obtained from a region approximately 2.5 μm in diameter, is shown in Fig. 1. There is a clearly defined bimodal distribution of molecular orientations about the vertical shear axis. The components of this dual orientation are separated by 62°. The first meridional reflections, corresponding to repeat units along the

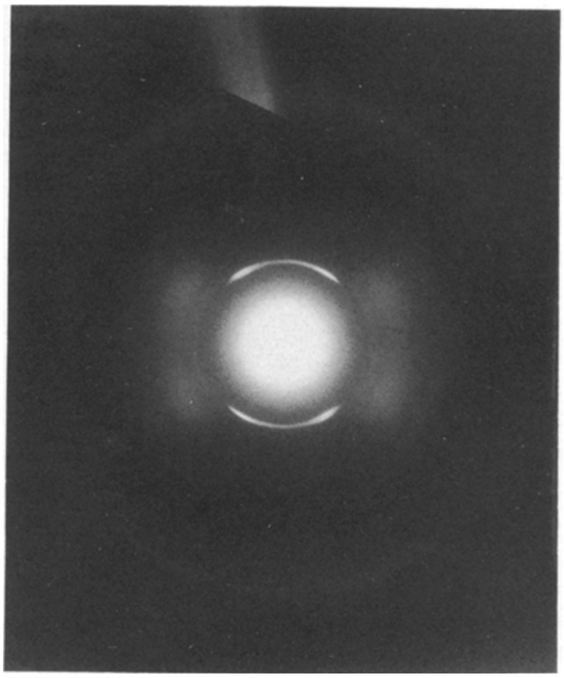


Figure 1 Selected-area diffraction pattern for the standard B–IQ copolymer showing sharp meridional reflections, diffuse equatorial ones and a bimodal orientation distribution in which the two orientations are separated by about 62°. As with all the figures presented here, the shear direction is vertical.

molecular axes, are sharply defined in terms of the scattering vector. The ratio of the lengths of these vectors for the first- and third-order peaks (which are of significant intensity in the diffraction pattern) is exactly 3. The periodicity of these maxima is in marked contrast to the distinctly aperiodic ones obtained from related random copolyesters such as B–N and N–AT, both of which contain the longer naphthoic unit. By way of contrast, the equatorial maxima in Fig. 1 are particularly diffuse in comparison with the related copolymers those seen for ([1, 2, 8] and Fig. 10 below). The sample made by the dispersion route showed similar, bimodal diffraction patterns.

The bright-field image of the polymer (Fig. 2) exhibits little contrast. However, tilting the beam to obtain a dark-field image in one of the equatorial reflections reveals, as shown in Fig. 3, the familiar banded microstructure in which the two orientations of material seen in the diffraction pattern correspond to each of the alternating bright and dark bands normal to the shear direction. The mean period of the bands is about 200 nm. It should be noted that the positioning of the objective aperture to include one of the equatorial maxima does not necessarily exclude the meridional reflection from the other, differently oriented, component.

Fig. 4 is a DF micrograph of the copolymer made by the alternative route, again imaged in one of the equatorial reflections. Although exhibiting bands as in the pure material, there are regions in Fig. 4 where the bands run in different directions. These regions are often observed to lie close to holes which are believed to be associated with the inorganic particles in the material which pulled out of the thin film on shearing.

3.2. Annealing of thin samples on a copper grid (30 min at 250 °C)

The effect of this treatment on the banded texture depends on whether the local area under observation is remote from or close to a grid bar. In the former case the microstructure does not change significantly on annealing (Fig. 5a), although there is some evidence that the bimodal orientation distribution becomes more sharply defined. Nearer to a grid bar the bands appear to break up into shorter segments, and in some regions the specimen has a uniform orientation, as shown in Fig. 5b. Corresponding SAED patterns from these regions exhibit a relatively narrow single molecular orientation distribution centred on the shear direction (Fig. 6).

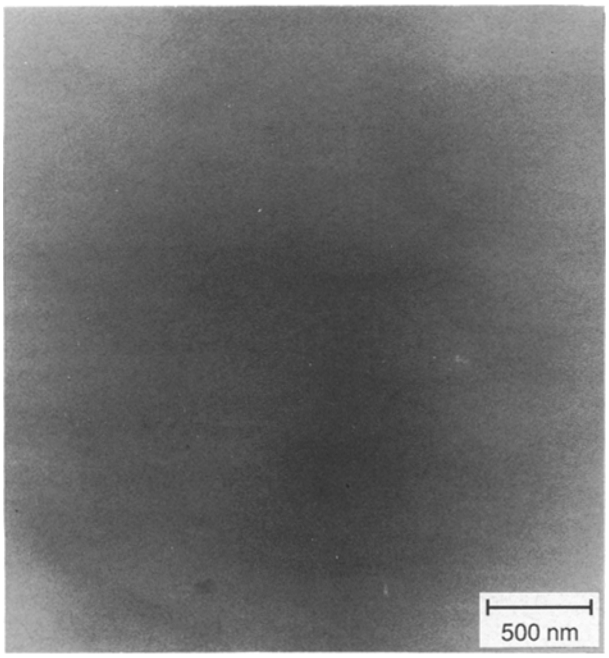


Figure 2 Bright-field electron micrograph of B–IQ polymerized by the melt-acidolysis route. The absence of contrast implies that the sample is of uniform thickness.

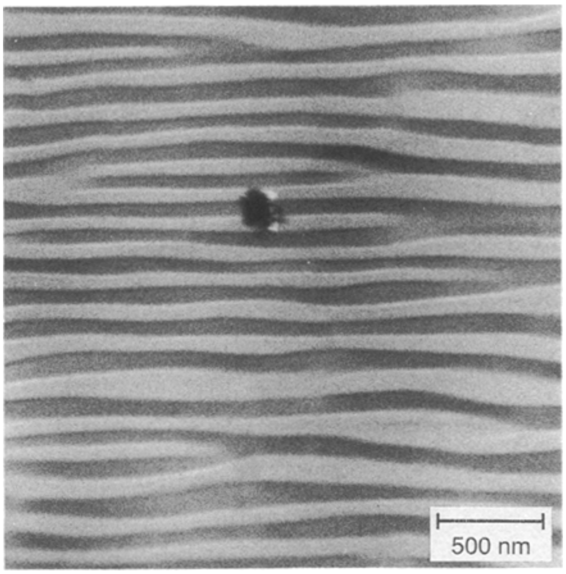


Figure 3 Dark-field micrograph imaged in one of the equatorial maxima of Fig. 2, showing the banded texture.

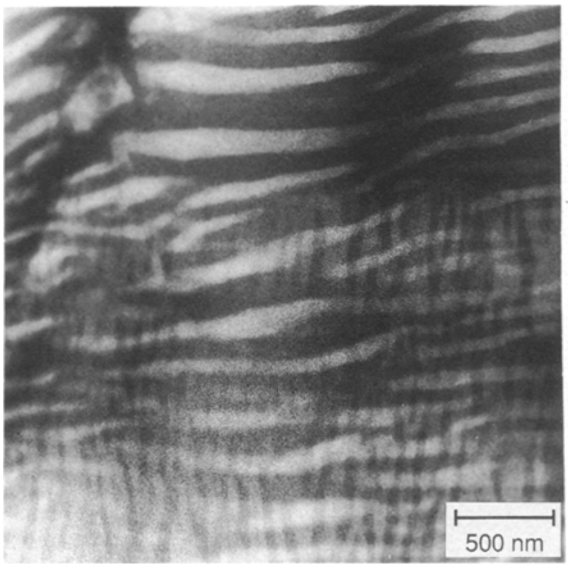


Figure 4 Bands observed in a dark-field micrograph of material polymerized using the non-aqueous dispersion route which contains traces of inorganic clay (not seen in any of the micrographs). The bands here, possessing a similar width as those in the previous figure, are observed to change direction entirely in some regions.

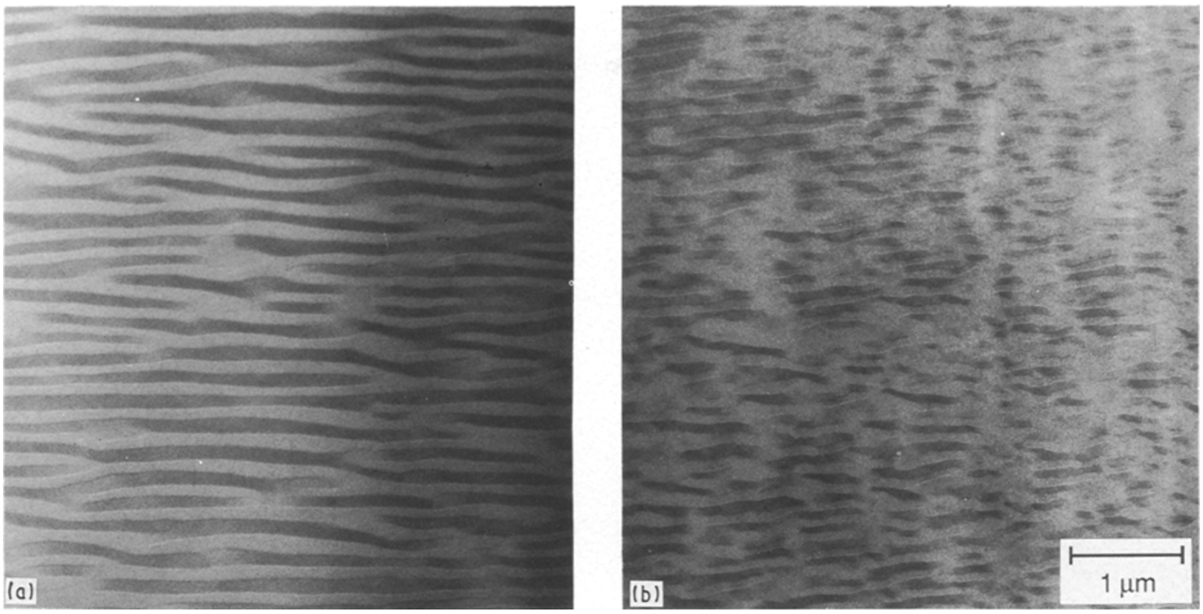


Figure 5 (a, b) Dark-field electron micrographs of the banded texture in B–IQ (melt-acidolysis) annealed at 250 °C for 30 min. The bands in (a) are near the centre of a TEM grid and resemble those in Fig. 3 (unannealed), whereas imaging near the copper grid bars (b) results in the bands dividing into small isolated regions. Regions are also observed to develop in which the bimodal distribution is replaced by a single one in which the molecules align with the shear axis.

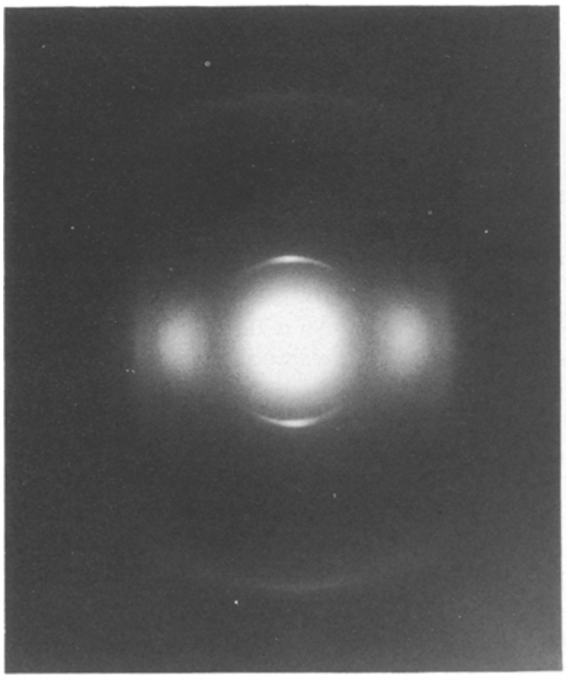


Figure 6 Selected-area diffraction pattern from a region which does not show any bands (as in Fig. 5b).

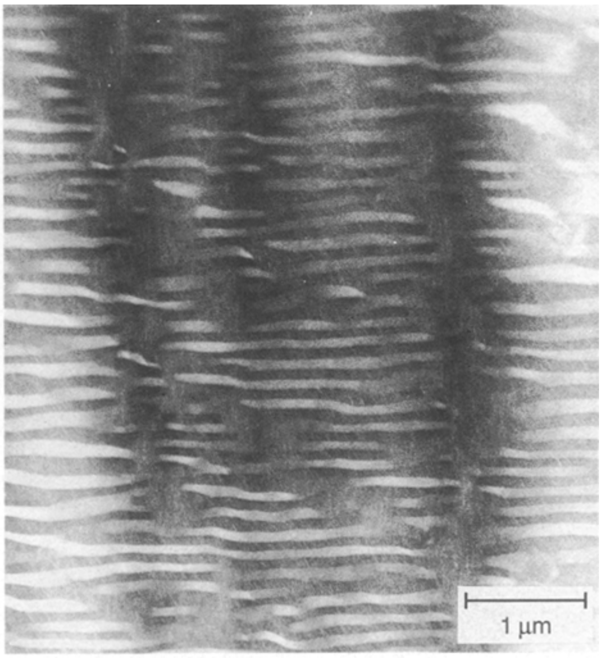


Figure 7 Low-dose dark-field image with the aperture including the first meridional reflection of the bimodal pattern. A fine acicular structure is visible in the dark bands where there is no contribution from the equatorial reflection.

3.3. Crystallites

The dark-field micrographs presented so far were produced by carefully focusing on the feature of interest (i.e. the bands) and then recording the image. DF images of samples annealed for 30 min at 250 °C obtained by "shooting blind", in which regions of interest are only subjected to the electron beam during the photographic exposure itself, show a rather different microstructure. Within the dark bands, there is an intricate fine acicular structure as can be seen in Fig. 7, and in the close-up in Fig. 8. The diffracting needle-like entities are approximately 8 nm thick and 80 nm long and appear to be oriented with their long axes parallel to the local molecular chain axes, both within the bands and in regions where the molecular orientation is more uniform. The reason why these diffracting entities do not appear in the bright bands is discussed below.

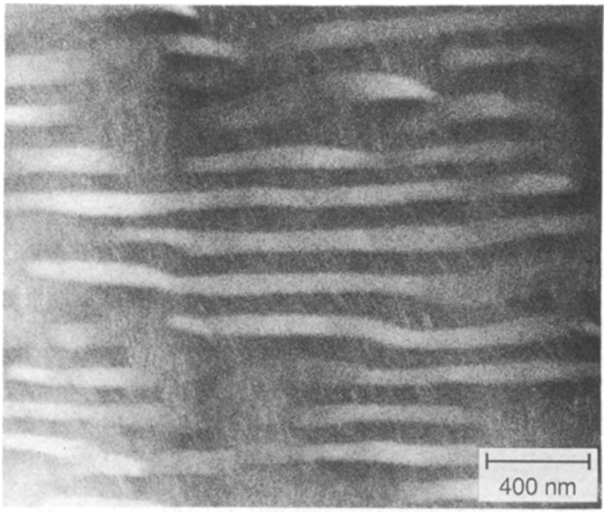


Figure 8 Close-up of Fig. 7. The diffracting entities are of the order of 8 nm thick and 80 nm long in the direction of the molecular chain axis.

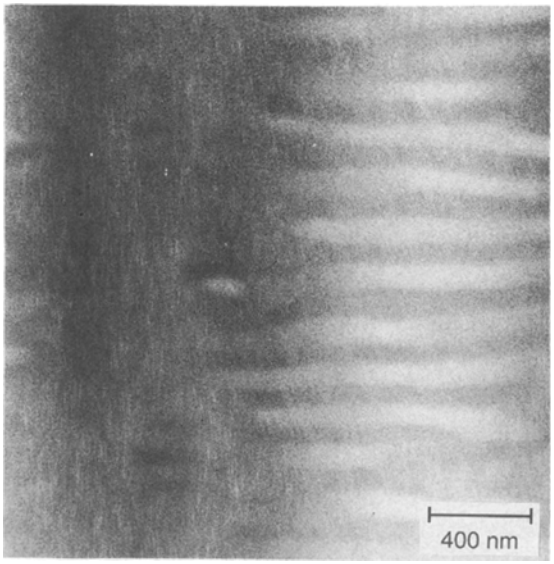


Figure 9 A dark-field micrograph of an annealed sample showing one region with the banded texture (right) and another in which the direction is aligned more exactly with the shear axis (left). Note that the acicular crystallites are oriented along the molecular direction.

Fig. 9 is a dark-field micrograph imaged in the first meridional reflection of an SAED pattern and illustrates a combination of Fig. 1 (banded texture) and Fig. 6 (uniform orientation). The electron beam was tilted so that one of the meridional components of the banded texture, as well as at least part of the meridional of the single texture, was permitted to pass through the objective aperture. This micrograph confirms that the light bands correspond to equatorial imaging, while the crystallites against a dark background correspond to meridional imaging.

4. Discussion

4.1. Banded textures

The banded textures seen in this copolymer (B–IQ) are markedly different from those previously observed in B–N and B–ET (hydroxybenzoic acid, ethylene glycol and terephthalic acid). They are much more sharply defined, and the clearly bimodal orientation distribution shown by the diffraction patterns confirms that the trajectory of the molecular chain axis forms a zigzag about the shear axis. The banded texture also appears more stable on annealing than in the case of B–N [1].

It is tempting to associate the uniquely sharp change in molecular orientation at the boundaries between the bands with the fact that the isophthalic acid disrupting unit in the B–IQ polymer is itself a kink. The molecule can thus turn through 60° with little if any cost in conformational energy. In this context, it is sufficient to note that the measured angular deviation of the molecular axes between successive bands is 62°. Such a picture does however assume that the deviation between bands is in the plane of the specimen.

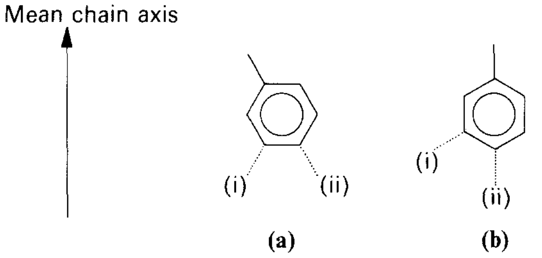
The loss of the banded texture on annealing at 250 °C for 30 min occurs only in regions of the sample close to a copper grid bar. It is possible that internal stresses occur on annealing which are unable to relax fully because of the constraint of the adjacent metal to which the sample adheres. The role of stresses of this nature in removing the banded texture is not really clear, but will not be pursued further here.

4.2. Crystallites

The presence of crystallites in this material has been proposed by Erdemir *et al.* [14, 15] on the basis of X-ray diffraction data. However, the morphology of the crystallites, as revealed here by microscopy, is in total contrast to that seen in some other thermotropic random copolyesters. For purposes of comparison, an SAED pattern and a DF image of B–N are shown in Figs 10 and 11, respectively. It should also be kept in mind that the meridional maxima in the B–IQ material are, as accurately as can be measured, periodic even though it is a random copolymer. There is thus no evidence that the crystallites are of the NPL type (based on matching of aperiodic chain sequences and shown in B–N in Fig. 11). Indeed, their radically different morphology would indicate that they are not of this special form. In many ways they are reminiscent of crystallites observed in lyotropic aromatic homopolymers such as poly(*p*-phenylene terephthalamide) (PPTA) [16] and poly(*p*-phenylene benzobisthiazole) (PPTZ) [17]. The issue is whether the isophthalic unit is in a conformation which gives a comparatively straight molecule and has a length sufficiently similar to that of the other aromatic units, so that the polymer is able to organize itself as a homopolymer, at least within the very localized regions which appear as the acicular entities.

Johnson *et al.* [18] have demonstrated a scheme in which, for a conformational model with the aromatic rings and ester groups lying in the same plane, all the units, whether HBA, IA or HQ, provide the same advance along the mean chain axis of about 0.6 nm. The key to achieving the same axial repeat irrespective of whether a unit is *para* or *meta* is to orient the benzene rings as shown in (a) below rather than (b).

Attachments in (i) *meta* and (ii) *para* are equivalent in terms of axial advancement.



The evidence of the electron diffraction patterns is that the (approximately) 0.6 nm repeats, as projected on to the mean chain axis, are in longitudinal register with each other over significant distances of the order of 80 nm in the chain direction. Longitudinal register is thus able to occur even though the polymers are random copolymers, and without the need for sequence matching which is the basis of non-periodic layer crystallization. The order in the lateral direction, however, is not as well developed. This is because the maintenance of a periodic axial repeat in a random chain based on *meta* and *para* linkages can only be achieved at the expense of the chain zig-zagging from side to side at random on a molecular scale; clearly not conducive to crystalline packing. It is also apparent that the register between the 0.6 nm axial repeats is lost after about 8 nm lateral displacement. It is a moot point as to whether it is helpful to refer to the observed order as smectic, although diffraction patterns which show sharp meridional reflections, but diffuse equatorial ones, are generally characteristic of this mesophase in small-molecule materials.

It is established by Johnson, Tomka and co-workers [14, 15] that more extensive annealing of these polymers in the range 240 to 300 °C leads to the development of a very clearly defined crystal phase which indexes as poly(IA–HQ). The effect of these crystallites on the meridional distribution of diffraction intensity is now well understood. However, they are based on homopolymer sequences which must physically segregate to be opposite each other, or be generated in the right place as the result of transesterification. In either case the requirement of appropriately positioned lengths of homopolymer sequences will tend to severely limit the crystal thickness in the chain direction. Further studies on more extensively annealed samples are expected to reveal lamellar crystallites in this material.

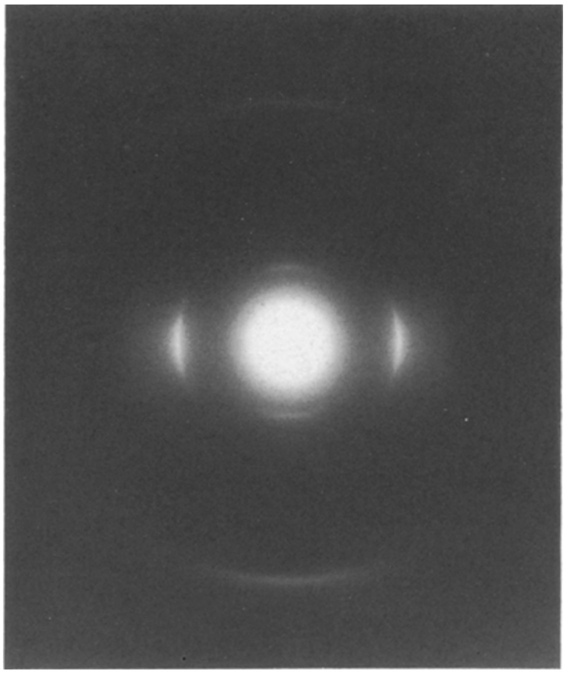


Figure 10 Selected-area diffraction pattern from an annealed sample of random copolyester of hydroxybenzoic and hydroxynaphthoic acids (B–N), showing a narrow range of molecular orientations. In the diffraction patterns from these samples the meridional maxima are aperiodic, and the equatorial reflections are sharply defined.

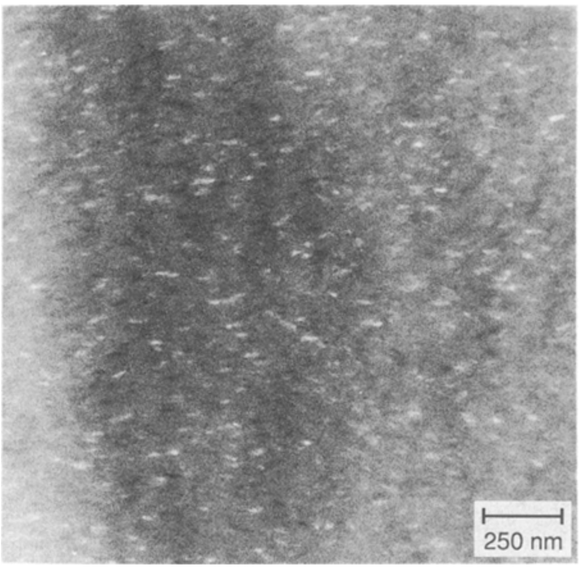


Figure 11 Dark-field image of NPL crystallites in a B–N material (the polymer composition is 75/25 (B/N) and the DP is about 150). Diffraction contrast is provided by the sharp equatorial reflections. Unlike the crystallites in B–IQ, the NPL crystallites in this B–N material are platelets oriented normal to the molecular chain axis.

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