PII: S0032-3861(96)00904-4

polymer communications

Lattice imaging of HBA–HNA non-periodic layer crystals

C. J. G. Plummer* and H.-H. Kausch

Laboratoire de Polymères, École Polytechnique Fédérale de Lausanne, CH-1015, Switzerland
(Received 23 September 1996)

Solution cast thin films of the Vectra[RM] HBA–HNA thermotropic liquid crystalline random copolymer, annealed for 1 h at 240°C have been investigated by HREM. Non-periodic layer crystals were observed with the c^* direction lying in, or close to the plane of the films, with crystalline core widths of about 10 nm. Lattice fringes werre obtained from the 1 1 0 and 2 0 0 planes of the orthorhombic unit cell, and from the first of the non-periodic meridional maxima of the fibre diffraction pattern, these latter extending over the whole of the core widths. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: HREM; HBA–HNA; non-periodic layer crystals)

Introduction

The present work concerns the commercial thermotropic liquid crystalline copolymer Vectra[TM] A950 (Hoechst, A.G., Germany) which consists of random sequences of hydroxybenzoic acid (HBA) and hydroxynaphthoic acid (HNA) units in the ratio ~3 : 1. The promise of HBA–HNA for precision and high performance moulding is at least partly responsible for the current interest in its crystallization behaviour. That the HBA and HNA monomers are of different lengths (0.635 and 0.837 nm respectively[1,2]) also raises the fundamental question of how the chains are able to pack together to form the 3-D crystalline arrays with X-ray and electron diffraction show to exist in the solid polymer. The observed $h k 0$ reflections are generally indexed according to a two chain orthorhombic cell, with the chain axis along c, although there may be variation in the lattice parameters and chain conformations depending on the temperature and crystallization conditions[3]. The corresponding diffracting regions have been shown to be associated with lenticular extended chain nanocrystals growing perpendicular to the director[4,5]. Crystallization is no doubt facilitated by the similar conformations and packing of the HBA and HNA homopolymers, which are both highly crystalline and intractable, but the need to accommodate the axial aperiodicity in crystals of the homopolymer has provoked considerable discussion in the literature. Windle *et al.* coined the term 'non-periodic layer (NPL) crystals', which refers to the non-periodic layer line spacings observed in fibre diffraction patterns. They initially investigated the possibility of crystallization by long range segregation of matching monomer sequences[6]. However, other authors have suggested extensive sequence matching to be unnecessary to account for the observed X-ray structure factors in HBA–HNA[2,7], and to be inconsistent with the observed crystallite sizes and separations in high molecular weight materials[1,2].

To our knowledge, direct observation of NPL crystals in HNA–HBA has to date been restricted to investigations of the external morphology and dimensions by dark field transmission electron microscopy (TEM)[4,5] and by replication of permanganate etched surfaces[1,8] (the similar packing of the crystals and the nematic phase lead to minimal contrast in bright field). However, the high aromaticity of HBA–HNA should render it sufficiently insensitive to the electron beam for lattice imaging by high resolution TEM (HREM) to be relatively straightforward using a conventional microscope.

Experimental

To investigate the possibility of HREM imaging of NPL crystals we have cast approximately 50 nm thick films of Vectra A950 from 2,3,4,5,6-pentafluorophenol at 50°C onto glass slides. The films were floated onto distilled water, and picked up on 400-mesh copper grids. They were then carbon coated and annealed at 240°C for about 1 h under vacuum prior to examination in the TEM, conditions which resulted in a clear melting peak at about 300°C in d.s.c. scans of injection moulded bulk samples, with an associated enthalpy change of the order of $10 \, J \, g^{-1}$. The TEM was a Philips EM 430 ST at 300 kV (point resolution 2 Å). Magnifications of up to 81 000× were employed, with an objective aperture used only where referred to in the text, and exposure times limited to within the lifetime of the 0 0 2 diffraction spots. The total end point dose for these reflections was estimated from the screen current to be about 0.1 coulomb cm^{-2} for 300 kV electrons. Images were recorded on Kodak SO-163 films using standard low dose techniques, and developed in Kodak D19 for 12 min. Selected regions magnified optically and digitized as 768 × 512 arrays in order to obtain positive images and for digital fast Fourier transforms (FFT). Where image simulations are referred to these were Bloch wave calculations carried out using the EMS package[9].

Results and discussion

Electron diffraction patterns of the thin films showed a strong reflection at a lattice spacing of 0.45 nm, and weaker reflections at about 0.67 nm and 0.38 nm, which could be indexed at 1 1 0, 0 0 2 and 2 0 0 respectively using

---

* To whom correspondence should be addressed

an orthorhombic unit cell with $a = 0.76$ nm, $b = 0.56$ nm and $c = 1.34$ nm, consistent with values reported elsewhere for comparable annealing conditions[3]. A further meridional reflection was observed at a lattice spacing of 0.2 nm confirming the non-periodic nature of these crystals, corresponding roughly to the 3rd and 4th harmonics of the HBA and HNA spacings respectively[10], and which could not be indexed according to the above unit cell. This latter reflection remained visible well after the disappearance of the inner reflections at high doses.

Figure 1 shows an approximately lenticular NPL crystal imaged at 100 nm defocus with a 50 μm objective aperture, showing 1 1 0 lattice fringes with a spacing of 0.45 nm. The overall dimensions of the fringed region were roughly 50×10 nm^2, consistent with previously reported NPL crystal sizes in Vectra[1,6]. In parts of the sample containing distinct parallel fringed regions, these showed a lateral spacing of between 20 and 30 nm, again consistent with previously reported values of the long period[1]. There was nevertheless considerable superposition of the fringes in certain parts of the sample, indicating projections of individual crystals to overlap, so that these estimates of the long period should be treated with caution. The projection of the c^* and by implication the orientation of the local director field was perpendicular to the long axis of lenticular crystals such as in *Figure 1*, although irregularly shaped patches of fringes extending up to 25 nm in the c^* direction were also occasionally seen. In regions of the sample where the crystals did not show substantial superposition, the projection of the director field could be mapped over extended regions of sample by identifying and observing the local orientation of the lattice fringes. In the present case of unoriented films, the director generally lay in, or close to the plane of the film, but its orientation varied continuously within the plane of the film on a scale of the order of 1 μm to give the so-called 'tight texture', as observed by polarized light microscopy in thicker solution cast films[11]. Indeed the orientation of the lattice fringes is different in the two NPL crystals visible in *Figure 1*, indicating a slight rotation of the director. Over distances greater than about 1 μm the orientation of the lattice fringes appeared uncorrelated, the lack of long range alignment also being apparent from electron diffraction patterns.

Figure 2 shows fringes with spacing 0.67 nm, corresponding to the first aperiodic meridional reflection

(0 0 2), running parallel to the long axis of an NPL crystal, together with weak 1 1 0 fringes, indicating [1 $\bar{1}$ 0] to be approximately vertical. Although the contrast of the 0 0 2 fringes varied considerably, their form and spacing did not appear to change systematically across the width of the fringed regions. *Figure 3* shows 1 1 0, 0 0 2 and 2 0 0 fringes at a branch point between two NPL crystals, the one on the right of the picture being in the [1 $\bar{1}$ 0] orientation and the one on the left in the [0 1 0] orientation. Interestingly, although the director shows substantial splay, the 1 1 0 and 2 0 0 fringes are continuous and in the same orientation at the point of contact of the two crystals. The respective spacings are significantly different however, making twinning unlikely. This structure may therefore result from the presence of the pseudo hexagonal phase in the as-cast films[3,12], in which the 1 1 0 and 2 0 0 spacings are sufficiently close to be indistinguishable in electron diffraction patterns. Both sets of planes can therefore be approximately indexed at 1 0 $\bar{1}$ 0 planes in a hexagonal lattice. Since a given set of 1 0 $\bar{1}$ 0 planes in a hexagonal structure may transform either to 1 1 0 or to 2 0 0 planes on annealing to form the orthorhombic phase (assuming this to result from a simple distortion), it is possible that the two crystals in *Figure 3* had their origin in a branched pseudo-hexagonal crystal present prior to annealing.

Image simulations of poly(HBA) and poly(HNA) (using published structures[13,14]) suggested the projected charge density approximation to be valid up to thicknesses of the order of 30 nm. In other words, for reasonable crystal thicknesses and for periodic crystals, the dark regions of the lattice images should correspond to the projection of columns of monomers, and the light regions, to regions of low charge density. Under these conditions (i) phase contrast images at optimum defocus may be interpreted directly in terms of the molecular conformations and packing and (ii) the absence of contributions to the image from high order reflections owing to limitations imposed by the objective lens transfer function results in a loss of resolution. For the present non-periodic structures however, the absence of contributions from high order non-periodic reflections makes interpretation less straightforward (given the maximum resolution of the microscope and the less than ideal operating conditions, this must be assumed to be the case). Moreover, the widespread practice of extracting information from the noisy images typical of low dose HREM of partially crystalline polymers by

Figure 1   1 1 0 lattice fringes in an NPL crystal imaged at 100 nm defocus. Fringes from an adjacent crystal are also visible (bottom left)
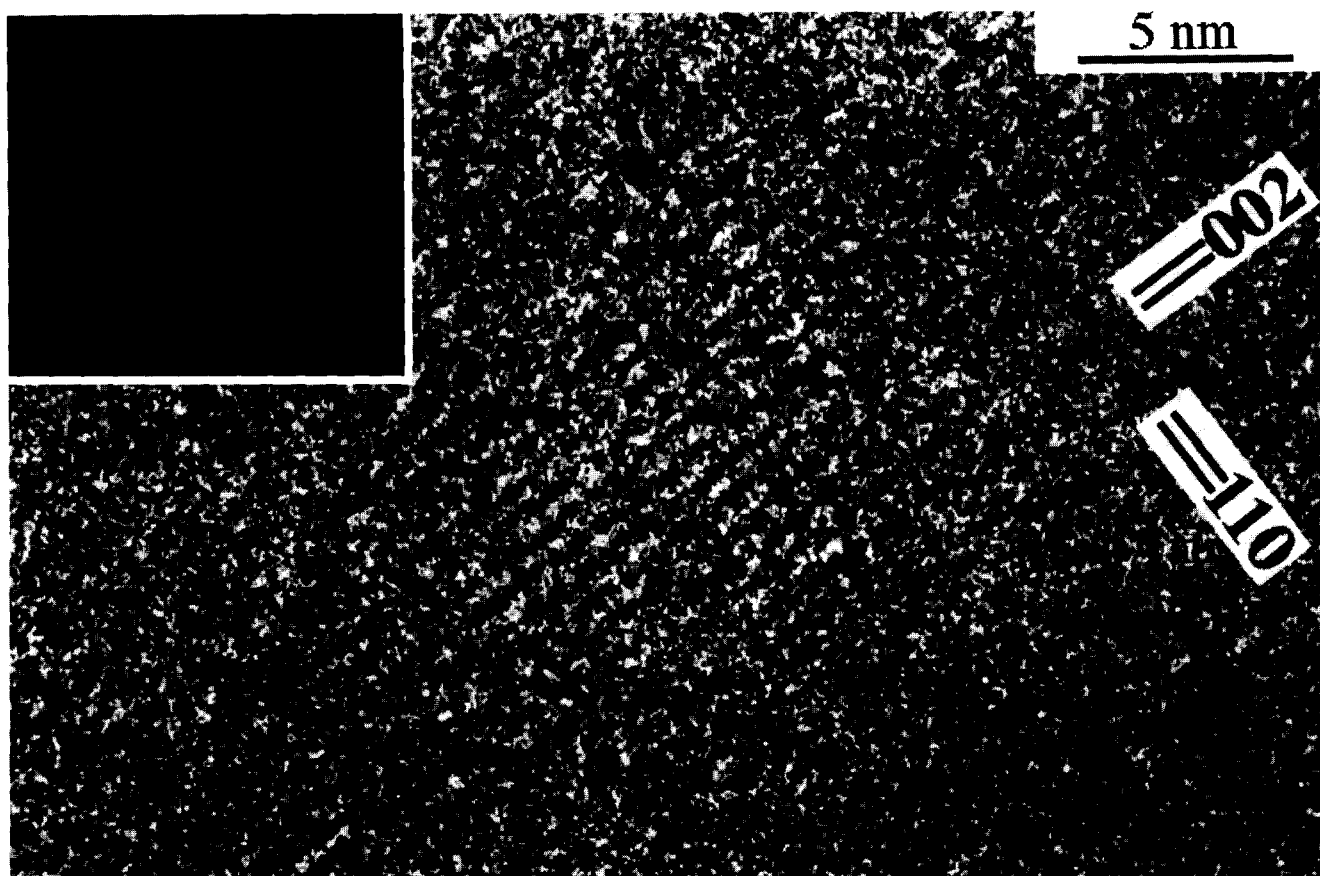
Figure 2 0 0 2 and 1 1 0 fringes in a lenticular NPL crystal, and the corresponding FFT

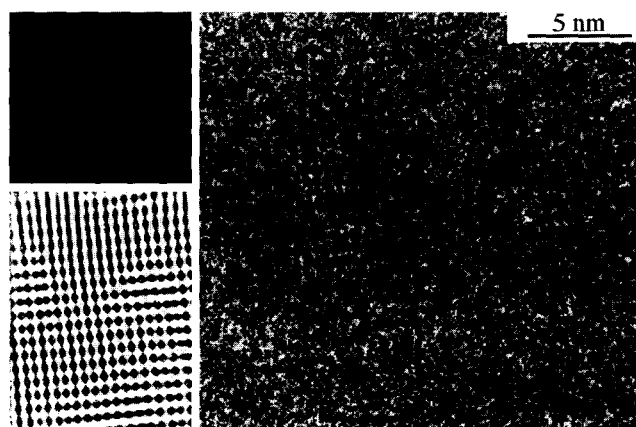**Figure 3** 0 0 2, 2 0 0 and 1 1 0 fringes at a branch point between two NPL crystals, and the corresponding FFT

Figure 4 An image of part of an NPL crystal in the [1 1 0] orientation along with the corresponding Fourier filtered image

Fourier filtering, is likely to reinforce the effect of the absence of contributions from high order reflections and hence be misleading. Thus the Fourier filtered image shown in *Figure 4*, of part of an irregularly shaped single crystal viewed along [1 10], is suggestive of a fully periodic 3-D lattice with an 0 0 2 spacing of 0.67 nm, which would be inconsistent with both the aperiodic structure of HNA–HBA, and the axial spacings observed in the respective homopolymers[13-15].

Conclusions

We have successfully obtained lattice images of a HBA–HNA thermotropic liquid crystalline random copolymer,

showing regularly spaced 0.67 nm lattice fringes from the first aperiodic meridional diffraction peak, extending over the whole crystalline core width of individual NPL crystals. At present, we do not believe these images to contain sufficient contributions from higher order aperiodic maxima for immediate conclusions to be drawn regarding the validity of the various existing models for NPL ordering. However, we are hopeful that HREM observations using equipment with a somewhat higher point to point resolution than the Philips EM 430 ST, combined with detailed image calculations will eventually provide information to complement results from X-ray and electron diffraction studies.

References

1. Hudson, S. D. and Lovinger, A. J., *Polymer*, 1993, **34**, 1123.
2. Hofmann, D., Schneider, A. I. and Blackwell. J., *Polymer*, 1994, **35**, 5603.
3. Wilson, D. J., Vonk, C. G. and Windle, A. H., *Polymer*, 1993, **34**, 227.
4. Donald, A. M. and Windle, A. H., *J. Mat. Sci. Lett.*, 1985, **4**, 58.
5. Spontak, R. J. and Windle, A. H., *J. Mat. Sci.*, 1990, **25**, 2727.
6. Windle, A. H., Viney, C., Gulombok, R., Donald, A. M. and Mitchell, G. R., *Faraday Disc. Chem. Soc.*, 1985, **79**, 55.
7. Biswas, A. and Blackwell, J. *Macromolecules*, 1988, **21**, 3152.
8. Hanna, S., Lemmon, T. J., Spontak, R. J., Windle. A. H., *Polymer*, 1992, **33**, 3.
9. EMS electron microscopy image stimulation package: http://cimewww.epfl.ch:80/EMS/EMS.html.
10. Blackwell, J., Gutierrez, G. A. and Chivers, R. A., *Macromolecules*, 1984, **17**, 1219.
11. Plummer, C. J. G., in *Advanced Thermoplastics and their Composites*. ed. H. H. Kausch, Hanser, Munich, 1993.
12. Kaito, A., Kyotani, M. and Nakayama, K., *Macromolecules*, 1990, **23**, 1035.
13. Yoon, D. Y., Masciocchi, N., Depero, L. E., Viney, C. and Parrish, W., *Macromolecules*, 1989, **23**, 1793.
14. Iannelli, P. and Yoon, D. Y., *J. Polym. Sci. - Polym. Phys Ed.*, 1995, **33**, 977.
15. Iannelli, P., Yoon, D. Y. and Parrish, W., *Macromolecules*, 1994, **27**, 3295.