ELSEVIER

Polymer 42 (2001) 5727–5735

polymer

www.elsevier.nl/locate/polymer

Levels of structural order in crystals of PET/PEN random copolymers

G.E. Welsh, A.H. Windle*

Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, UK

Received 13 June 2000; accepted 24 October 2000

Abstract

Models are built of crystalline random copolymers in which the degree of longitudinal register between adjacent chains is varied by moving the chains relative to each other within a prescribed axial range. The chains are placed at the relative positions which give the greatest total number of ethylene glycol matches between them. The models are built without any disposition to create matches between identical contiguous sequences of units, or any other type of imposed register. Calculation of diffraction patterns from both two- and three-dimensional models, shows that a good fit to the experimental data occurs with a level of register which is achieved after comparatively little longitudinal shuffling (searching). While this best-fit model shows some evidence of sequence matched entities, they are shorter and less regular than those envisaged in previous studies. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Random copolyester; Longitudinal register; Fibre diffraction patterns

1. Introduction

The issue of the presence of three-dimensional order in crystals based on random copolymers has received considerable attention over the past decade or more, especially in the context of crystallites seen in thermotropic random copolyesters which melt to give liquid crystalline phases. In some random copolymer systems, crystallites are observed not only in the case of copolymers towards the homopolymer limits of the composition range, but for compositions across the entire range. The three-dimensional order cannot thus be simply accounted for by the rejection of one or other species of comonomer unit from the crystal.

The understanding built so far with respect to the structure of thermotropic liquid crystalline polymers of the HBA/HNA type has tended to focus on particular models of order which have sometimes been viewed as rivals. The models have tended to come from the schools of Blackwell (e.g. Refs. [1,2]) and Windle (e.g. Refs. [3–5]). Both models involve a degree of longitudinal register between the chains forming the crystal. Blackwell demonstrated that a single plane of longitudinal register imposed normal to the chains would produce a degree of three-dimensional order over a limited volume whereas Windle considered the possibility of longer range longitudinal motions which could enable sequence matching over limited distances in the chain direction to give non-periodic layer (NPL) crystallites.

This publication develops the topic in the context of a non-liquid crystalline system of a random copolyester of ethylene terephthalate and ethylene naphthoate (PET/PEN) which has been demonstrated to show crystallinity across the full range of random copolymer compositions [6,7]. For example, Fig. 1 is an experimental fibre diffraction pattern of 50/50 PET/PEN which shows hkl reflections that are evidence of three-dimensional crystalline order.

2. The modelling strategy

Models are built from random chains which on average contain the desired ratio of monomer units. However, each of the chain stems will have a random sequence and a composition which thus may well differ from that of the neighbouring chains. The chains are positioned on a net so that they are packed laterally with crystalline-type long range order. However, the initial model is built without any longitudinal register between the chains. Models with increasing register are then developed by the process of shifting each chain longitudinally in turn within set limits, to maximise the number of like juxtapositions of ethylene glycol residues which are of course common to both comonomers. The model differs from those previously investigated in that the only criterion for fit is the optimisation of matches between ethylene glycol residues. It does not otherwise make any assumptions as to the nature of the order.

---

* Corresponding author. Tel.: +44-1223-334321; fax: +44-1223-334637.

E-mail address: ahw1@cus.cam.ac.uk (A.H. Windle).

PII: S0032-3861(00)00786-2

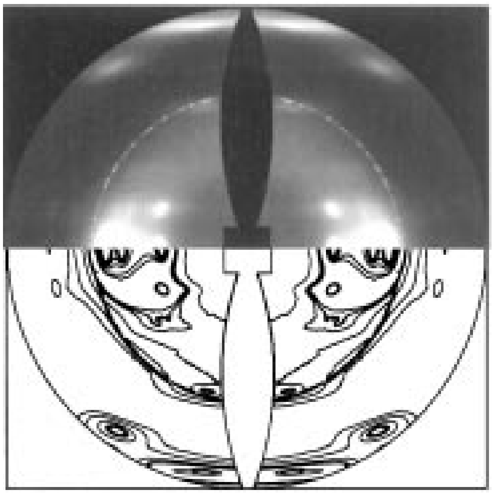

Fig. 1. Diffraction pattern from a 50/50 PET/PEN fibre. The pattern has been quadrant averaged and mapped into reciprocal space.

Both two-dimensional point models and three-dimensional atomic models have been developed. The two-dimensional point models have allowed the examination of a wide range of model crystallites and their diffraction patterns. They have also enabled the influence of different levels of register on the calculated diffraction patterns to be observed, without the complications of three-dimensional model building and scattering calculations. On the other hand, the three-dimensional models have the advantage of giving more realistic diffraction data, which can be more confidently compared with the experimental fibre diffraction patterns.

In the two-dimensional point models, crystallites were represented as planar arrays of chains with each monomer unit corresponding to a point function. In the three-dimensional models, point function chains were organised into crystals according to the regime chosen, and then the appropriate monomers were positioned on to their respective points prior to the calculation of the diffraction patterns.

3. Two-dimensional point models and their diffraction patterns

Initial model without chain register: Random chains of up to 100 monomers long were generated using a random number generator [8]. Giving the generator a single integer seed produced a very long crystallite, each chain having a different part of the long random sequence. Series of different random crystallites were produced by using different seeds. Monomers were represented by points separated from each other along the chain by 10.75 and 13.2 Å, corresponding to PET and PEN monomers, respectively. Chains of point monomers were placed parallel and equally spaced laterally to give a two-dimensional crystallite. Each crystallite consisted of an array of 100 chains spaced at a nominal 5 Å. The chains were placed initially in random register in the *z* direction, the positions being discretised at intervals of 0.05 Å for computational purposes. The chain terminations at the top and bottom limits of the crystal were initially positioned at random within a band of width 13.2 Å in the *z* direction.

Algorithm to increase longitudinal register: A point match was defined as occurring when points on neighbouring chains were lined up such that they both had the same *z* coordinate defined to within a resolution of 0.05 Å. With the chains in random register, there were in all cases a negligible number of point matches. Improvement in longitudinal register was achieved by taking each chain in turn (moving from left to right) and translating it axially a number of 0.05 Å steps, e.g. a 26.4 Å, or two PEN monomer, search would move each chain 528 0.05 Å steps. At each step, the number of point matches between the chain and its neighbour to the left was recorded. When the chain had been moved the maximum amount set, it was returned to the position of the greatest number of point matches. The maximum movement of the search set is referred to as the search length. The procedure was then repeated for each chain of the model. The direction in which a chain was moved, i.e. upwards or downwards, was chosen at random. For search lengths larger than 13.2 Å, where the longitudinal displacement of a chain exceeded this value, one or more monomers from the protruding end of the chain were transferred to the re-entrant end in order to preserve the coherence of the crystal as far as possible. A schematic diagram of a model with some degree of chain register is shown in Fig. 2, with the matches between the monomer points highlighted. The process is in some ways similar to that introduced by Hanna and Windle [9]; however, in that case the criterion was the generation of the longest contiguous sequence of matched units (sequence matching) whereas in this case there was no imposed condition that the matches had to be adjacent.

4. Measurements of degree of longitudinal register

It was useful to define a measure of crystalline perfection to give a quantitative means of comparing the level of register in crystallites built with different parameters such as search length and number of monomers per chain. A measurement of crystallite perfection, the fraction of matches, was defined as follows:

$$\text{fraction of matches} = \frac{N_{\text{match}}}{(N_{\text{chain}} - 1)(N_{\text{mon}})}, \qquad (1)$$

where N_{match} is the total number of point matches added up from all the crystallites, N_{chain} the number of chains per crystallite and N_{mon} the number of monomers per chain. The fraction of matches for crystallites of the given parameters was found by averaging over 50 different crystallites.

To examine the effect of searching on crystallite perfection, the average fraction of matches was calculated for

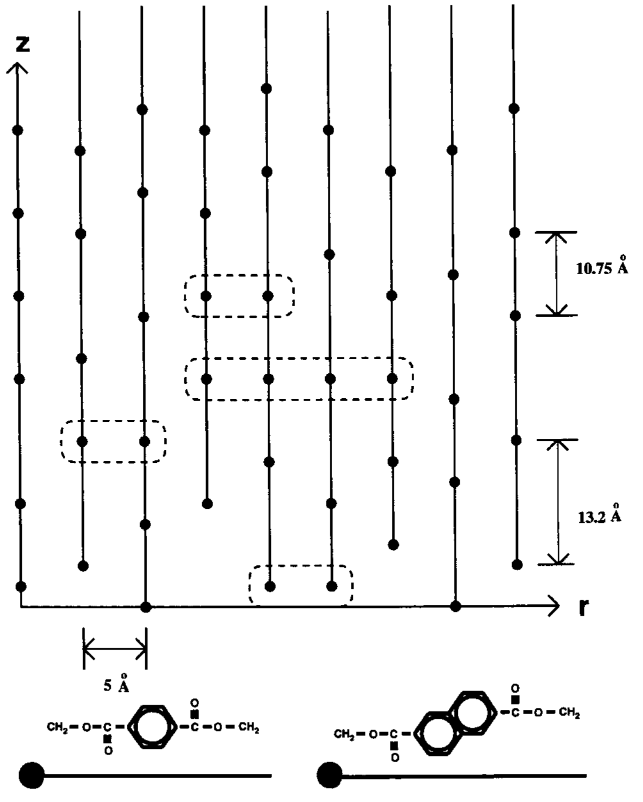

Fig. 2. A schematic representation of part of a two-dimensional crystallite. Chains are separated by 5 Å in the *r* direction and points representing the spacing of the PET and PEN monomers are separated by 10.75 and 13.2 Å, respectively, in the *z* direction. The dotted boxes highlight examples of point matching, where points on adjacent chains have the same *z* coordinate.

crystallites built with different search lengths. Crystallites with different chain lengths were also examined. Fig. 3 shows how the average fraction of matches varies with the search length for crystallites with chain lengths of 10, 20, 50 and 100 monomers with a composition of 50/50 (PET/PEN), and also for pure PEN crystallites with chains 10 monomers long. Each point on the curves is an average from over 50 crystallites built with each parameter set.

For search lengths of up to about one monomer length, the curves rise steeply. At one monomer search length (13.2 Å for PEN) the PEN homopolymer crystallites achieve perfect register as one would expect; the average fraction of matches in the random copolymer crystallites increases more slowly with the search length than in the homopolymer, the rate decreasingly markedly for search lengths greater than one monomer unit.

The shorter the chains in the crystallite model, the more perfect they become after a one monomer search, and the more rapidly they increase in perfection on further searching. It is clear from Fig. 3 that random copolymer crystallites consisting of different random sequences, but with relatively short chains, can achieve considerable perfection with quite modest axial movements of the chains relative to one another. However, crystallites with long chains achieve good register in some regions at the expense of others, resulting in a lower overall degree of perfection. In this context, it is interesting to note that crystallites in PET/PEN random copolymers are less than ten monomers long in the chain direction [7], so that a relatively high degree of axial register (defined as matching of unit ends) would not be unexpected for search lengths of the order of the crystal

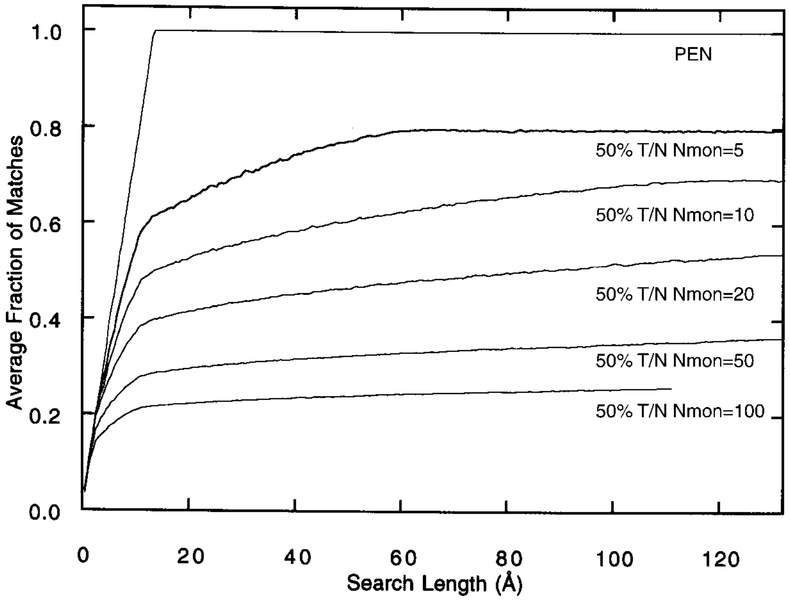

Fig. 3. The variation in the average fraction of matches with the search length for a random copolymer of 50/50 (PET/PEN). Pure PEN is also shown for comparison. N_{mon} is the number of monomers in a chain.

thickness, even for the most stringent case of 50/50 random copolymer chains.

It is apparent that a considerable degree of register can be obtained for comparatively small longitudinal adjustments (search lengths) and that the further degree of improvement at larger search lengths is comparatively limited. The next stage is to explore, for two dimensions, the relationships between the differently ordered models and their corresponding diffraction patterns.

The computationally most efficient means of calculating the diffraction patterns from an array of point functions is to use the relationship:

$$I(R,Z) = FF^{*} = \left(\sum_{j=1}^{n} \cos 2\pi(r_jR + z_jZ)\right)^2 + \left(\sum_{j=1}^{n} \sin 2\pi(r_jR + z_jZ)\right)^2, \quad (2)$$

where **R** and **Z** are the reciprocal space vectors in the equatorial and meridional directions, respectively, and r_j and z_j specify the position of the jth delta function.

For any set of parameters, the diffraction patterns were taken as the average of those from 50 models, each built using a different random number seed.

The models from which the diffraction patterns are calculated were chosen with a chain length of 10 monomers, as this is likely to be an upper limit on the axial dimension of PET/PEN random copolymer crystallites. They are all determined for the 50/50 composition case where the detrimental influence on the total order of the random sequences along the chains is likely to be most severe. The parameter, which has been varied, is the search length.

Fig. 4(a)–(d) shows in each case the model structure, with lateral chain separation of 5 Å, and one quadrant of the calculated fibre diffraction pattern. The symbols on the models represent the two types of monomer unit. There is, however, no atomic detail in this model, a delta function is located at each square or circle. The quadrant of the diffraction pattern extends to 0.4 Å^{-1} in the equatorial direction and 0.5 Å^{-1} in the meridional direction. The square root of the intensity is plotted to allow comparison of weak and strong peaks on the same plot.

Fig. 4(a) shows crystallites built with chains in random register. This could be described as a quenched structure as chains have not been given any chance to move and rearrange. The model is accompanied by the corresponding diffraction pattern, which shows continuous layer lines with only the equator sampled at the reciprocal of the chain spacing.

Fig. 4(b)–(d) shows example crystallites and diffraction patterns which have been searched over distances of 5, 13.2 and 132 Å^{-1}, respectively. Sampling of the layer lines increases with increasing search length. With the chains in random register, only the equator is sampled due to the regular lateral packing of the chains. After a 5.0 Å^{-1} search (Fig. 4(b)), sampling appears also on the fifth and sixth layer lines. A search of 13.2 Å^{-1}, or one PEN monomer length (Fig. 4(c)), brings up peaks on the first, fourth, fifth and sixth layer lines. This search length is the minimum which would be required to generate a perfect crystallite for the homopolymer case from a random starting register. In terms of layer line sampling a one monomer search diffraction pattern is in qualitative agreement with the experimental 50/50 PET/PEN diffraction pattern of Fig. 1. A search length of 132 Å^{-1} (Fig. 4(d)) leads to sampling on all the layer lines, which appears to be in excess of that observed experimentally.

From these results it can be concluded that one monomer length of relative axial movement is all that is required to produce PET/PEN random copolymer crystallites whose diffraction patterns have similar levels of layer line sampling to those observed experimentally. These results are for PET/PEN chains of the maximum possible length, shorter chains would be expected to give even more sampled patterns for a given search length. However the two-dimensional point models are perhaps too simple to permit direct comparisons to be made between simulated and experimental diffraction patterns. To examine this question more reliably, the models have been built in three dimensions, and atomic detail added.

It is interesting to compare the structures illustrated in Fig. 4 with those envisaged in the NPL model, where regions of perfect register over short copolymer sequences are dispersed throughout the structure. Such regions can be identified in the most ordered example (Fig. 4(d)); however, for the 13.2 Å^{-1} search case, the one giving the best agreement with experiment for PET/PEN, NPL crystals, where they can be identified at all, are fragmentary. It should also be noted that the diffraction patterns, previously calculated from NPL crystallites of the same system [7], also showed too much order, leading to the conclusion that the sequence matching in them was not perfect.

5. Three-dimensional atomic models

Three-dimensional atomic models have two advantages over two-dimensional point models. They allow a more direct comparison to be made between simulated and experimental diffraction patterns. They also demonstrate that the matching regime used to build the two-dimensional model crystallites can be used to build three-dimensional structures with similar levels of register for a given search length.

Three-dimensional models were constructed by building an array of two-dimensional models placed one behind another, with chains initially in random register. The chains were positioned on a two-dimensional net perpendicular to their axes. Register between a chain and its four nearest neighbours was considered. Three-dimensional searching was carried out as shown in Fig. 5. On the front row of chains, each chain was searched by cycling it past the

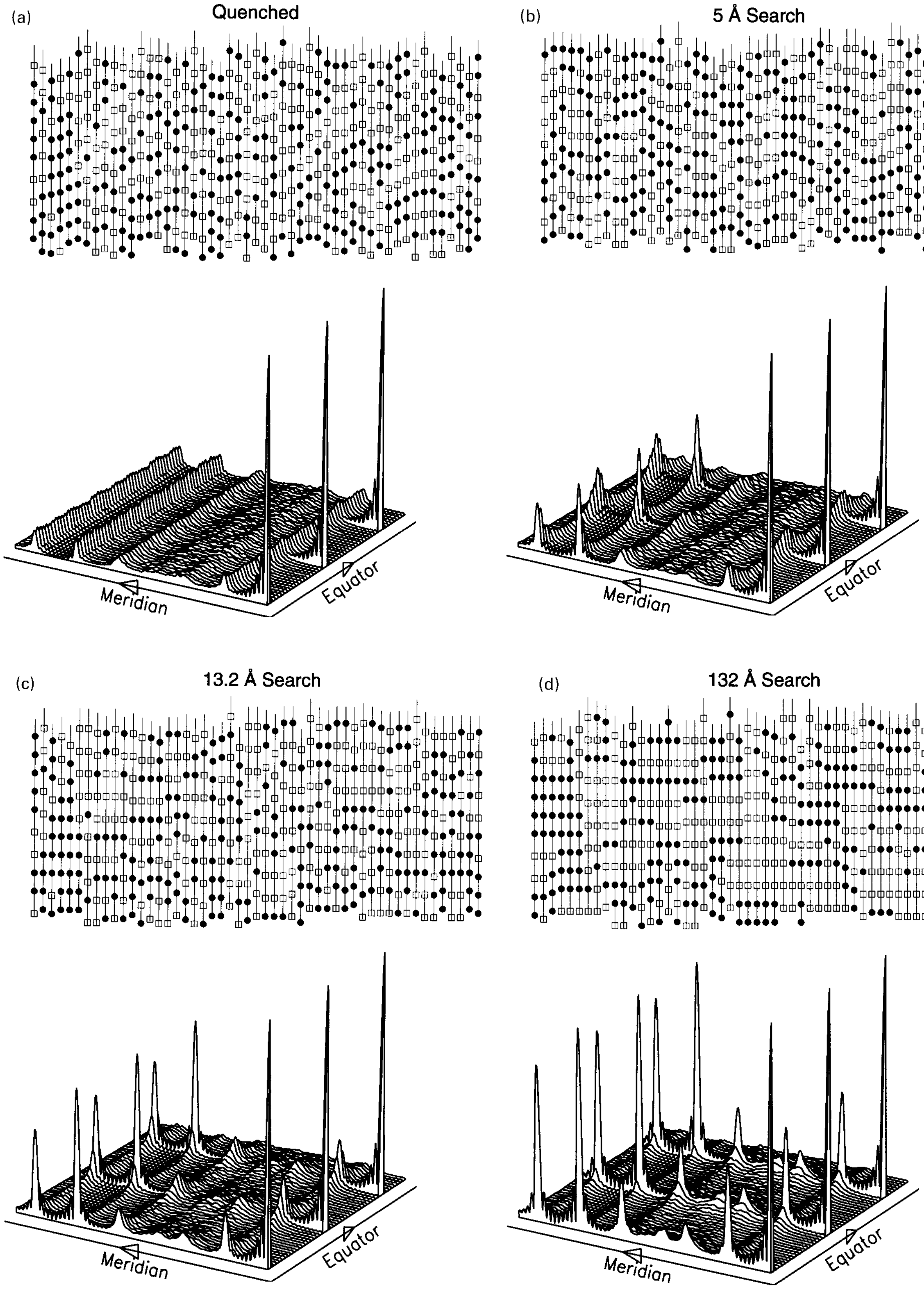

Fig. 4. Example of a two-dimensional model and the corresponding diffraction pattern calculated from 50 such models: (a) for no longitudinal order (quenched case); (b) after a chain 'search' of 5 Å; (c) after a chain 'search' of 13.2 Å; and (d) after a chain 'search' of 132 Å. The vertical axis of the diffraction patterns corresponds to the square root of intensity. Circles and squares represent units with PET and PEN monomer spacings respectively.

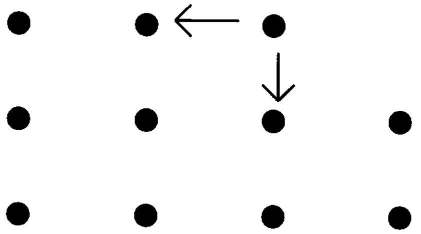

Fig. 5. A three-dimensional crystallite is built up by placing chains on to a lattice from left to right and from front to back. When searching is carried out, each chain is matched with the chain to its left and the chain on the row in front. Chains on the front row are matched only with neighbours to the left.

chain to its left, taking each chain in turn from left to right, as in the two-dimensional models. The next row of chains behind was then searched in the same way as the one in front but point matches with the chain to the left, and the chain on the row in front, were counted. This protocol was repeated on successive rows of chains until the whole crystallite had been searched.

After searching, the models were given a triclinic lattice with the same lattice parameters as PEN by changing the horizontal net from a square to a parallelogram and shifting each chain axially to make the register plane of the matches parallel to the 001 planes of a PEN lattice. In this context, it should be noted that the structure of the 50/50 copolymer is much more similar to that of the PEN than of the PET homopolymer, albeit with changed lattice parameters [6].

6. Simulating three-dimensional diffraction patterns

Simulating fibre diffraction patterns from three-dimensional random copolymer crystallites is potentially very expensive in computer time as two types of averaging need to be done: averaging over many random crystallites to obtain a pattern from a truly typical sample and averaging over all crystallite orientations about the *c* axis to obtain fibre symmetry. Since a fibre diffraction pattern from a crystalline random copolymer is the result of scattering from many different crystallites, a method was devised to achieve cylindrical averaging and averaging over different random crystallites simultaneously. A number of different crystallites were built and then placed in different orientations about the fibre axis in real space, as shown in Fig. 6. A diffraction pattern was then calculated for each crystallite in the $\psi = 0$ plane of reciprocal space, and these were averaged to give a fibre diffraction pattern. This method of averaging reduced the time of diffraction pattern computation by a factor of at least 50, compared with the time required to average cylindrically the scattering from a large number of different random crystallites in reciprocal space, and then take the average of all their diffraction patterns.

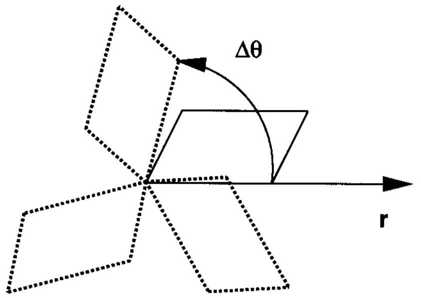

Fig. 6. An illustration of the method used to perform cylindrical averaging and averaging over crystallites built with different random seeds. The averaging is carried out by placing each crystallite in a different orientation, or value of $\Delta\theta$, about the fibre axis. The fibre axis is perpendicular to the plane of the page.

7. Including molecular structure factors

Atomic detail was incorporated into the models by placing PET and PEN monomers on to the three-dimensional lattice such that the $(CH_2)_2$ groups of the monomers were located at the positions of the point functions in the lattice. It is not known exactly what conformations the PET and PEN monomers have in random copolymer crystallites. However, the positions and intensities of the equatorial reflections in diffraction patterns from 50/50 PET/PEN fibres are more similar to those in diffraction patterns from pure PEN than from PET. The layer line spacings indicate that both the monomers are in extended conformations. As a first approximation, it was assumed that the aromatic groups in PET/PEN random copolymer crystallites were packed in a similar way to those in the homopolymer PEN. PEN monomers were given the conformation and position in the unit cell that they have in the α phase structure of pure PEN [10]. PET monomers were given a planar zigzag conformation and placed so that the benzene rings were coplanar with the naphthalene group of PEN.

Molecular structure factors were calculated using the equation:

$$F_{\mathrm{mol}T}(S) = \sum_{m=1}^{M_T} f_m(S)\cos(2\pi\mathbf{S}\cdot\mathbf{p}_m), \qquad (3)$$

where $\mathbf{p}_m$ is the position vector of the *m*th atom in the asymmetric unit, f_m is its atomic scattering factor and $\mathbf{S}$ the reciprocal space scattering vector with components R, ψ and Z in cylindrical polars [11]. Atomic scattering factors were computed using the formulae and constants in the International Tables for X-ray Crystallography [12]. Hydrogen atoms were not included. The transform of each crystallite $F(S)$ is given by

$$F(S) = F_{\mathrm{mol}T}(S)\sum_{t=1}^{T} e^{2\pi i\mathbf{S}\cdot\mathbf{p}_t} + F_{\mathrm{mol}N}(S)\sum_{n=1}^{N} e^{2\pi i\mathbf{S}\cdot\mathbf{p}_n}, \qquad (4)$$

where the sum over *t* is the sum over all PET monomers and the sum over *n* is the sum over all PEN monomers in the

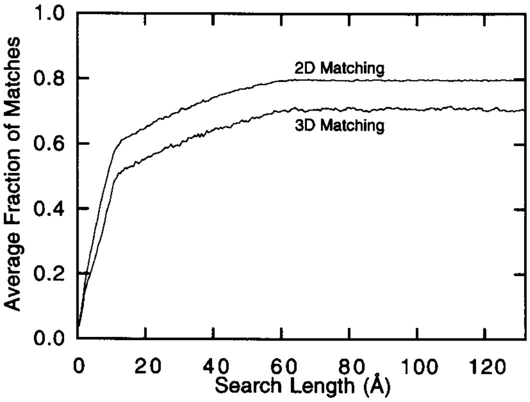

Fig. 7. The variation of the average fraction of matches with the search length for two models with composition 50/50, PET/PEN. Both models have chains five monomers long. One model was built with two-dimensional matching, the other with three-dimensional matching. In each case, the matches were counted in one direction only, as though both the models were two-dimensional. The model built with three-dimensional matching only loses about 10% of its matches in one direction by being constrained to match in two directions at once.

crystallite, and

$$\mathbf{S}\cdot\mathbf{p}_t = r_t R\cos(\theta_t + \Delta\theta) + z_t Z, \tag{5}$$

where $\mathbf{p}_t$ is the position vector of the tth PET monomer, with components r_t, θ_t and z_t in real space cylindrical polar coordinates. $\Delta\theta$ is the rotation about the fibre axis of the whole crystallite. The intensity distribution of a fibre diffraction pattern was then calculated from the equation:

$$I(R,Z) = \langle FF^{*}\rangle = \left\langle \left(F_{\mathrm{mol}T}(S)\sum_{t=1}^{T}\cos(2\pi\mathbf{S}\cdot\mathbf{p}_t) + F_{\mathrm{mol}N}(S)\sum_{n=1}^{N}\cos(2\pi\mathbf{S}\cdot\mathbf{p}_n)\right)^2 + \left(F_{\mathrm{mol}T}(S)\sum_{t=1}^{T}\sin(2\pi\mathbf{S}\cdot\mathbf{p}_t) + F_{\mathrm{mol}N}(S)\sum_{n=1}^{N}\sin(2\pi\mathbf{S}\cdot\mathbf{p}_n)\right)^2 \right\rangle, \tag{6}$$

where $I(R,Z)$ is the average intensity from 150 different random crystallites, each generated with a different random seed and placed in different equally spaced rotations (different values of $\Delta\theta$ about the fibre axis). The greater the reciprocal space radius R to which a diffraction pattern is calculated, the more the crystallites that need to be averaged. An average of over 150 crystallites was used in this work where the diffraction patterns were calculated to $R =$ 0.5 Å.

Preliminary calculations showed that chain lengths of five monomers gave layer line-widths closer to those observed experimentally than those with ten, so five monomer chains were used throughout the three-dimensional modelling.

8. Results of three-dimensional atomic model simulations

8.1. Searching

Despite searching in three dimensions, where each chain is constrained to match with two other chains, there was only a small decrease in the degree of crystallite perfection obtained for a given search length relative to that obtained for the two-dimensional models. Fig. 7 shows how the average fraction of matches varies with the search length for a two- and a three-dimensional model both with chains five monomers long. The average fraction of matches for the three-dimensional model was calculated as though it were a two-dimensional model. It is apparent that models built with three-dimensional matching only lose about 10% of their matches, measured in one direction, a result of their being constrained to match in two directions at once.

8.2. Limitations of the models

Before examining the simulations from three-dimensional random copolymer crystallites, it is worth considering the

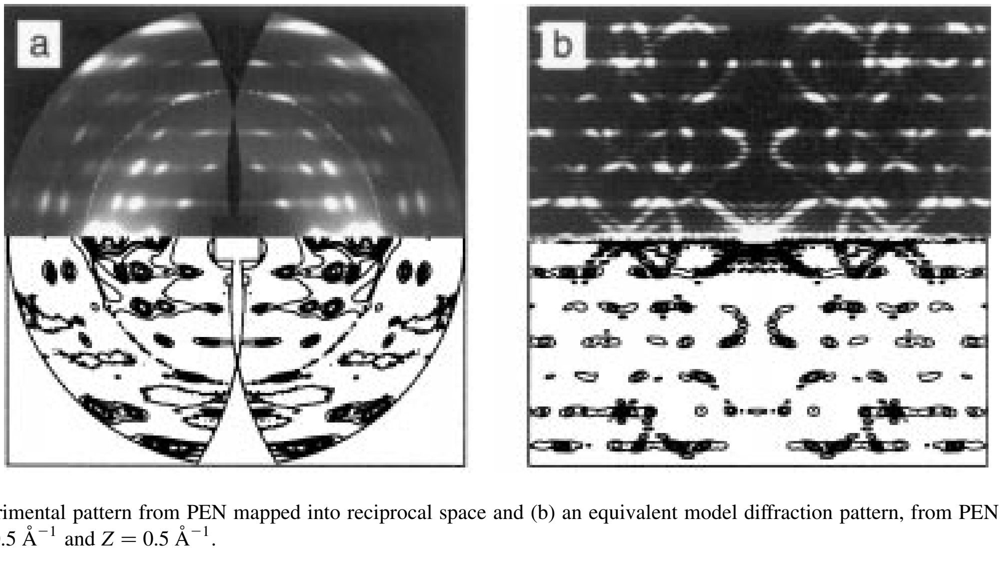

Fig. 8. (a) An experimental pattern from PEN mapped into reciprocal space and (b) an equivalent model diffraction pattern, from PEN. The patterns both extend out to $R = 0.5$ Å^{-1} and $Z = 0.5$ Å^{-1}.

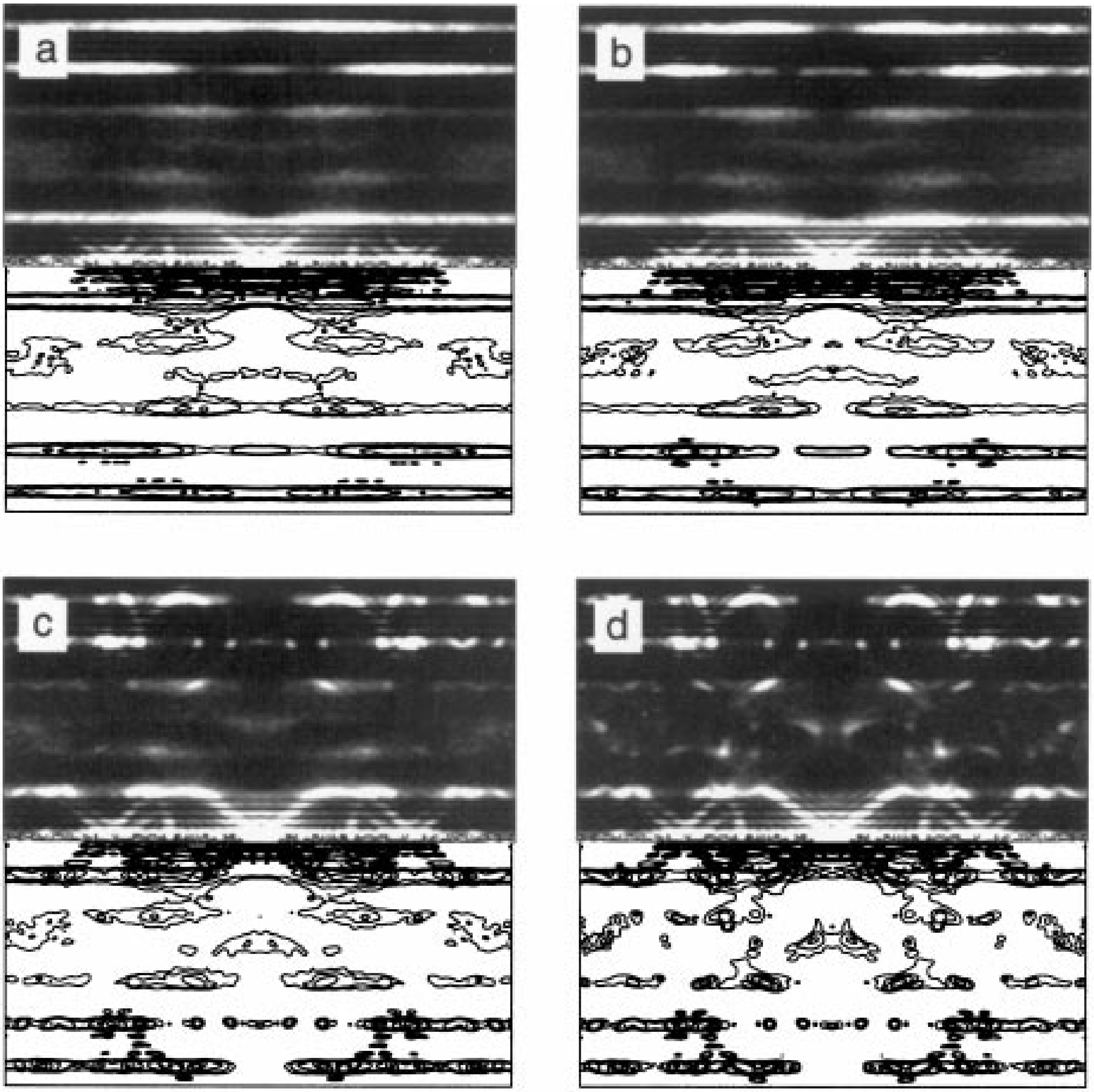

Fig. 9. Simulated diffraction patterns from three-dimensional models of the 50/50 polymer with: (a) no search; (b) a 5 Å search; (c) a 13.2 Å search; and (d) a 66 Å, or 5 monomer, search. The patterns extend to $R = 0.5$ Å^{-1} and $Z = 0.5$ Å^{-1}.

diffraction pattern from a simulated three-dimensional PEN crystallite for which the crystal structure is known [10]. Fig. 8 compares a fibre diffraction pattern from PEN (Fig. 8(a)) with a simulated pattern (Fig. 8(b)) from a PEN crystallite built with 100 chains, each five monomers long. The simulated PEN pattern has reflections in the correct positions but looks quite different from the experimental pattern. The reflections in the simulated pattern have odd shapes and there are quite a few ripples, or subsidiary maxima, between the layer lines, which are not seen experimentally. The relative intensities of the reflections are also different in the experimental and simulated patterns. These differences are due to the size and shape of the model PEN crystallites. The odd reflection shapes and ripples in the simulated diffraction pattern arise from the fixed parallelepiped shapes and sharp boundaries of the model crystallites. Although somewhat anisotropic, the crystallites in a real PEN fibre will have a variety of shapes and sizes, and there will not be a sharp boundary between the crystalline and the amorphous regions. The difference between the relative intensities of the reflections in model and simulated patterns is due to the finite size of the model crystallites. The limitations inherent in this type of modelling must be borne in mind when comparing the experimental and simulated fibre diffraction data for random copolymer crystallites.

8.3. Simulated diffraction patterns

Fig. 9(a)–(d) shows a series of simulated diffraction patterns from three-dimensional crystallites calculated using molecular structure factors. The sequence of diagrams shows the result of increasing the search length and thus the degree of longitudinal register. The model crystallites were five monomers long in the chain direction, with 10 chains in the *a* and *b* directions i.e. 100 chains in total. The average composition of the chains was 50/50. These model crystallites were built using the PEN unit cell, which lead to incorrect reflection positions on the layer lines, an effect which measurement readily reveals in the case of the first layer line in Fig. 9(c) and (d).

The extent of layer line sampling increases with the search length in a similar way to that observed with the two-dimensional point models. The quenched sample with chains in random axial stagger (Fig. 9(a)) has streaky unsampled layer lines. A 5 Å (half monomer) search (Fig. 9(b)) brings up peaks on the fifth and sixth layer lines; however, the first and fourth layer lines are still unsampled. A 13.2 Å (one PEN monomer) search (Fig. 9(c)) results in sampling on the first, fourth, fifth and sixth layer lines, and this is in reasonable agreement with the experimental patterns. A 66 Å, or five monomer, search (Fig. 9(d)) gives sampling on all layer lines but the third; however, the second layer line peak is very weak.

Comparison of these three-dimensional models with the 50/50 experimental pattern of Fig. 1 shows that a single monomer search (Fig. 9(c)) is certainly enough to produce all the layer line sampling observed experimentally. In fact, if anything, the model shows slightly too much order on the higher order layer lines. However, it should be borne in mind that there may also be conformational disorder, or possibly paracrystallinity of the type previously modelled for HBA/HNA [13], in which there is a Gaussian spread of axial chain positions about a fixed plane of register. Such disorder would tend to spread out the intensity on the fifth and sixth layer lines while the first layer line would be little affected.

The process of relative longitudinal motion of adjacent chains, referred to in this paper as 'searching' and controlled within defined limits for the purpose of generating models with different degrees of longitudinal register, begs the question as to whether it is realistic of the development of the structure in the polymer itself. In the case of the thermotropic liquid crystalline polymer HBA/HNA, it was realised towards the end of the period of intense discussion between 1985 and 1995 that the random copolymers had a chained smectic A structure in the melt, as also was the case for the poly HNA parent homopolymer. In the case of PET/PEN, which is a conventional i.e. non-liquid crystalline polymer, it might be thought that the searching mechanism would be wholly unrealistic, as once a crystal is formed it would not have the internal motion to improve longitudinal register. However, a recent study by Welsh et al. [14,15] has shown clear diffraction evidence of a transient liquid crystalline, chained smectic A phase, which appears as a precursor to crystallisation. Hence, the physical mechanism of longitudinal chain 'searching', possible in the thermotropic polymers, may be relevant to the PET/PEN system also.

9. Summary

This study has built models of random copolymers, introducing different levels of inter-chain register on a statistical basis where the only criterion is the number of comonomers in register with similar groups on neighbouring chains. These models differ from those discussed previously [1–5], in which particular types of order such as sequenced matched entities (NPL crystallites), or perfect register at one single plane normal to the chain axis, have been introduced either as a consequence of the particular type of chain sorting algorithm used or by deliberate model construction.

Comparison between experimental diffraction patterns of 50/50 PET/PEN random copolymers and models, both two and three-dimensional, built using the most general criterion for matching, show that semi-quantitative agreement can be achieved as a result of longitudinal motion over a range of the same order of the chemical repeat of the polyester.

While it is possible to recognise sequence matched entities in models built in this way to give the best fit with the experimental data, they are quite small, and in relation to NPL entities considered in earlier work, more fragmented.

The recent observation of a transient smectic phase in PET/PEN random copolymers on drawing provides the possibility of considering the mechanism of longitudinal 'searching' to occur in a way which is analogous to that already discussed for liquid crystalline polymers.

References

[1] Gutierrez GA, Chivers RA, Blackwell GA, Statamoff JB, Yoon H. Polymer 1983;24:937.

[2] Blackwell J, Biswas A, Bonart RC. Macromolecules 1985;18:2126.

[3] Windle AH, Viney C, Golombok R, Donald AM, Mitchell GR. Faraday Discuss Chem Soc 1985;79 (paper 5).

[4] Donald AM, Windle AH. J Mater Sci Lett 1985;4:58.

[5] Hanna S, Romo-Uribe A, Windle AH. Nature 1993;366:546.

[6] Lu X, Windle AH. Polymer 1995;36:451–9.

[7] Lu X, Windle AH. Polymer 1996;37:2027–38.

[8] Press WH, Teukolsky SA, Vetterling WT, Flannery BP. 18 'Numerical recipes in FORTRAN'. Cambridge: Cambridge University Press, 1992.

[9] Hanna S, Windle AH. Polymer 1988;29:207.

[10] Mencik Z. Chem Prumysl 1967;17(2):78.

[11] Cantor CR, Schimmel PR. Biophysical chemistry pt 2. New York: Freeman, 1980.

[12] Ibers JA, Hamilton WL. International tables for X-ray crystallography, vol. IV. Birmingham: Kynoch, 1974.

[13] Golombok R, Hanna S, Windle AH. Mol Cryst Liq Cryst 1988;155:281.

[14] Welsh GE, Blundell DJ, Windle AH. Macromolecules 1998;31(21): 7562–5.

[15] Welsh GE, Blundell DJ, Windle AH. J Mater Sci 2001 (in press).