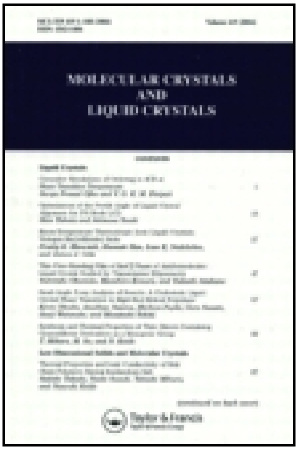

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Order in Main Chain Thermotropic Random Copolymers

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ORDER IN MAIN CHAIN THERMOTROPIC RANDOM COPOLYMERS

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Abstract Model calculations are presented which account for some of the main features of fibre diffraction patterns of main chain thermotropic random copolymers. It is shown that non-periodic layer (NPL) crystallites are consistent with these features, in particular the relative concentrations of the 1st, 2nd and 3rd layer lines onto the meridian, provided that a small degree of randomness is allowed in the longitudinal register between the chains. A partially ordered fringe area, which surrounds each NPL crystallite, is shown to retain some degree of register.

Introduction

The fibre diffraction patterns of certain main-chain thermotropic copolyesters have been shown[1,2] to contain features indicative of a much higher degree of order than might be expected from packing of molecules with a random disposition of monomer units. Figure 1 shows the fibre diffraction pattern of a copolymer of hydroxybenzoic (HBA) and hydroxynaphthoic (HNA) acids containing 75% of HBA units which had been annealed for 29 hours at 260°C. The random disposition of the HBA units in such copolymers has been verified by nmr techniques[3], and detailed analyses of the positions of the meridional difraction maxima[4,5].

The important features of figure 1 can be summarised as:

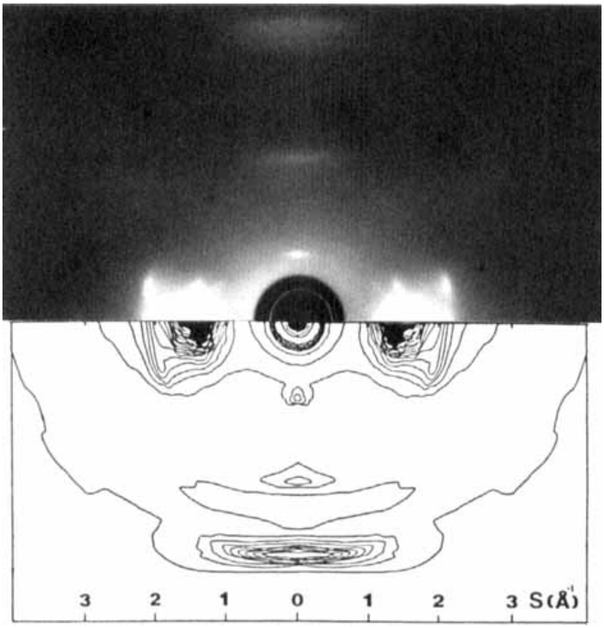


Figure 1. A wide angle x-ray diffraction pattern of an annealed fibre of a random copolyester of hydroxybenzoic and hydroxynaphthoic acids in the ratio of 75:25. The top half is a flat plate photograph and the bottom half a diffractometer scan of a planar section through reciprocal space. The concentration of the first layer line on the meridian is clearly apparent. ($s=(4\pi/\lambda)\sin\theta$).

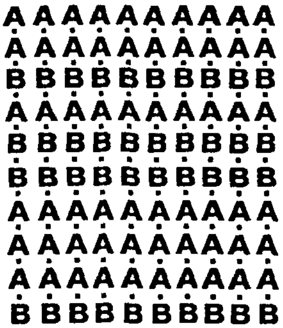


Figure 2. An NPL crystallite. The monomer units are represented by letters A and B, and the chains are vertical.

a) The first meridional maximum is concentrated on that axis with minimal lateral spread, confirming the high degree of preferred orientation indicated by the equatorial maxima.

b) The lateral spread of the third meridional maximum is relatively much more marked.

c) The main interchain peak (on the equator) has both a sharp component and a diffuse component.

A model for crystallisation of rigid rod random copolymers has been proposed[6] and described in some detail[7]. This model invokes the concept of non-periodic layer (NPL) crystallites. An NPL crystallite is formed when sections of adjacent chains containing the same, but random, sequence are arranged in a structure without long range periodicity in the chain direction, but with crystalline order between the chains. (See figure 2).

The purpose of this paper is to demonstrate the relationship between various degrees of interchain longitudinal register and the resultant fibre diffraction patterns. The models investigated range from a random longitudinal disposition of differently sequenced chains to NPL type order.

The Model

Simple models have been chosen for this work; monomer units are represented by point functions, chains are uniformly spaced and parallel. Ignoring atomic detail in this way means that the intensities of the calculated peaks will not be those observed in the experimental diffraction patterns, however, the relative peak widths will be meaningful. Models of this type are preferable at this stage, where the principles relating packed random chains to their diffraction patterns are the prime focus of interest. Atomic refinements to the models may be the subject of future work. Furthermore, fibre symmetry is assumed and only 2-dimensional models are considered which means that the calculations are limited to a planar section through reciprocal space.

To speed computation, diffraction calculations are made for a number of comparatively small models using the same statistical parameters. In the results discussed below the intensity distribution was the average over 50 models each of 10 chains of 10 monomer units. The small size of the models puts a lower limit on the width of any peak in the calculated diffraction pattern. However this effect is well understood and does not detract from the assessment of the relative lateral widths discussed below. Most of the calculations have been made on models of units of length 6Å and 8Å, present in equal proportions. The effects of units whose lengths are not in simple ratio and compositions other than 50/50 are also briefly considered.

Transformation

Transformation from real to reciprocal space was carried out as follows. A chain's position is defined by the position of one monomer unit (usually the end unit):

$$\underline{P}_n = \underline{X}_n + \underline{Y}_n \qquad (1)$$

where $\underline{X}_n$ gives the position of the nth chain along the x axis and $\underline{Y}_n$ gives the distance of the chain from the x axis. In all our models $\underline{X}_n = n\underline{d}$ where $\underline{d}$ represents the distance between chains, set in this case at 4Å.

The position of the ith unit on the nth chain is given by:

$$\underline{P}_{i,n} = \underline{X}_n + [j\underline{L}_A + k\underline{L}_B] \qquad (2)$$

where j and k are the numbers of A and B units respectively between the chain origin and the ith unit, and:

$$j + k = i - 1$$

$\underline{L}_A$, $\underline{L}_B$ give the lengths of units A and B parallel to the y-axis.

A point function at position $\underline{P}_{i,n}$ is represented by a Dirac delta function:

$$\delta(\underline{r}(x,y)-\underline{P}_{i,n})$$

where $\underline{r}$ is a general vector. The whole structure is given by:

$$a(x,y) = \sum_{i,n} \delta(\underline{r}(x,y)-\underline{P}_{i,n}) \tag{3}$$

and its transform by:

$$A(u,v) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} a(x,y)\exp[-2\pi i(ux+vy)]dxdy \tag{4}$$

i.e.

$$A(u,v)= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \sum_{i,n} \delta(\underline{r}(x,y)-\underline{P}_{i,n}).\exp[-2\pi i(ux+vy)]dxdy \tag{5}$$

and since

$$\int_{-\infty}^{\infty} f(x)\delta(x-y)dx = f(y),$$

$$A(u,v) = \sum_{i,n} \exp[-2\pi i(\underline{k}.\underline{P}_{i,n})] \tag{6}$$

where $\underline{k}$ is the reciprocal space vector. The intensity of the diffraction pattern is given by:

$$I(\underline{k}) = A(\underline{k}).A^{*}(\underline{k}). \tag{7}$$

Results and Discussion

The first model examined is the case of random chains placed side by side with no longitudinal register between monomer units on adjacent chains. Varying degrees of additional order are then introduced culminating in an NPL crystallite, and the main features of the predicted diffraction patterns compared with those observed experimentally.

a) *The random case - Random chains of 6Å and 8Å units in equal proportions*

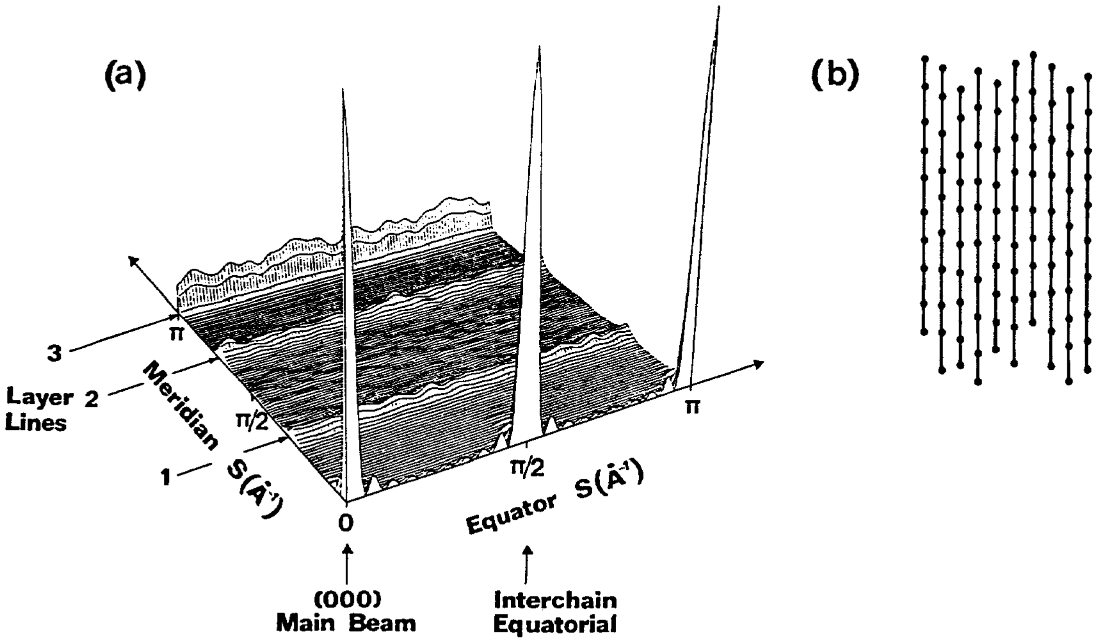


Figure 3. Surface plot (a) showing calculated intensity for a quadrant of a diffraction pattern for chains in random register as indicated in (b).

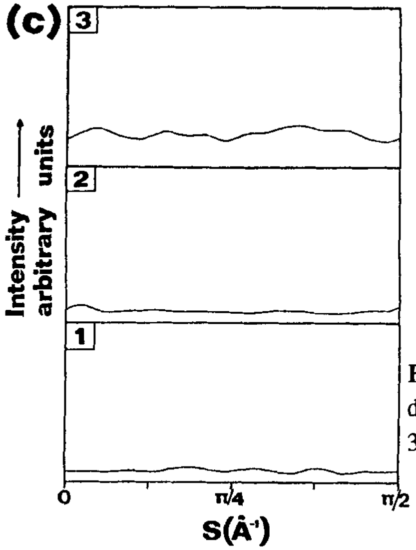
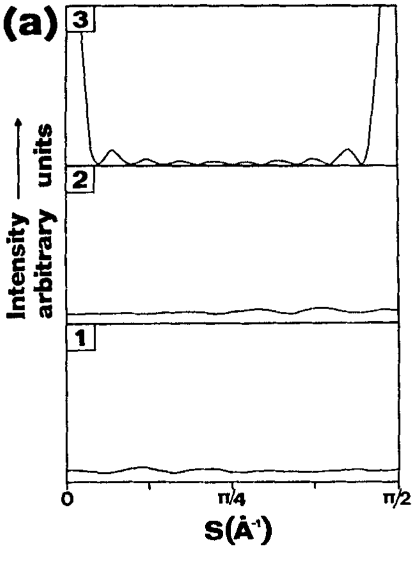


Figure 3 (c) shows the intensity distribution along layer lines 1,2 and 3.



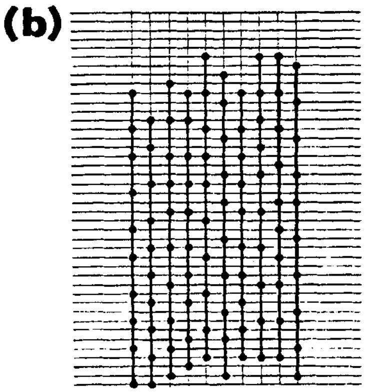


Figure 4. (a) Intensity distribution along layer lines 1,2 and 3 when the points representing the 6Å and 8Å units are positioned on a 2Å lattice but without additional correlations as shown in (b).

with no longitudinal register between them. $\underline{Y}_n$ *is thus a random length evenly distributed between 0 and 8Å.*

As would be expected from elementary diffraction theory the calculated diffraction pattern is essentially the same as the transform of a single random chain which has already been calculated for these systems[4,5], see figure 3. There are three layer lines, the first two being relatively weaker than the third. The positions of the layer lines correspond to those calculated for very long single chain models[4,5] and there is no apparent concentration of them onto the meridian. Sections through figure 3(a) are shown in figure 3(c) along the first three layer lines. The strong equatorial peaks reflect the fact that the chains are parallel and uniformly spaced.

b) *The 2Å lattice - random chains as in (a) above, but positioned such that each monomer point coincides with a point on a lattice of 2Å spacing along the chains. This is possible since 2Å is a factor of both unit lengths (6Å and 8Å).* $\underline{Y}_n=2m$ *Å where m = 0, 1, 2 or 3.*

The difference between this case (fig.4) and case (a) (fig.3) is that the 3rd layer line, which corresponds to a 2Å repeat, has concentrated completely onto the meridian to give a peak which is as sharp laterally as the main equatorial maximum, and has a half-width determined only by the finite lateral size of the model. This behaviour is exactly as would be expected from elementary diffraction theory. It is significant, however, that this type of register does not lead to any intensification of the 1st and 2nd layer lines onto the meridian.

c) *The line start - Single specified units on each chain are placed exactly opposite each other on the x-axis.* $\underline{Y}_n=0$.

This is a special case of the 2Å lattice. By placing the end unit of each chain on a line we are ordering the system in two ways. For by placing the end units in line we forbid there to be any monomer points at distances of 2,4 or 10Å from that line, while the populations at distances 6,8 and 14Å etc. will be correspondingly enhanced. At a large distance from the line start we may expect this effect to be lost and the calculated diffraction pattern to appear like the general 2Å lattice of (b).

Figure 5 shows the resultant diffraction pattern. Some of the intensity on the first two layer lines is now concentrated on the meridian. Diffraction from a region some distance from the line start, eg 100Å away

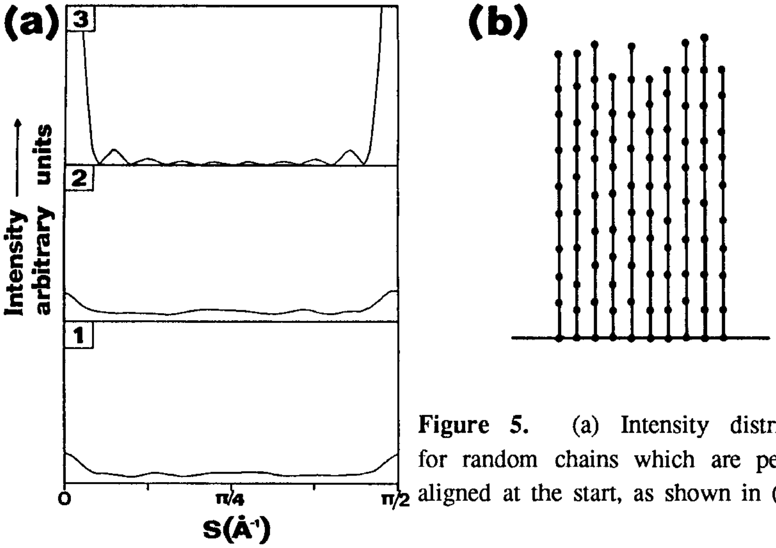


Figure 5. (a) Intensity distribution for random chains which are perfectly aligned at the start, as shown in (b).

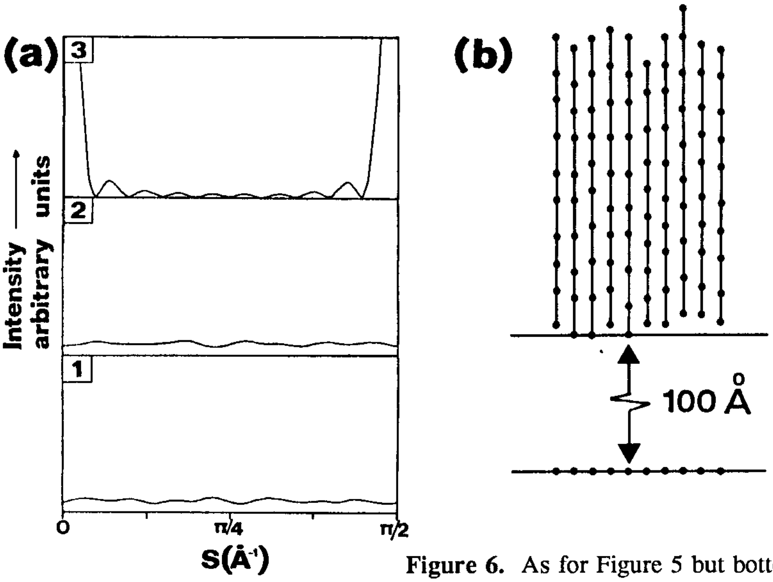


Figure 6. As for Figure 5 but bottom of modelled region 100Å above the line start.

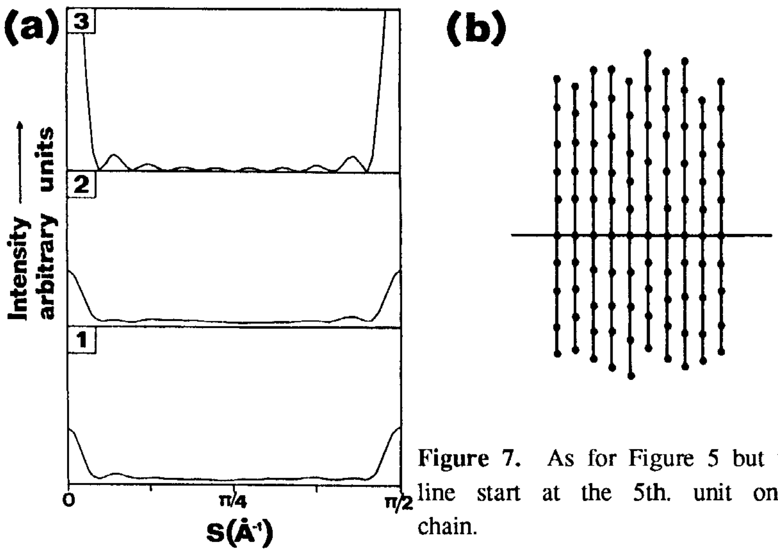


Figure 7. As for Figure 5 but with a line start at the 5th. unit on each chain.

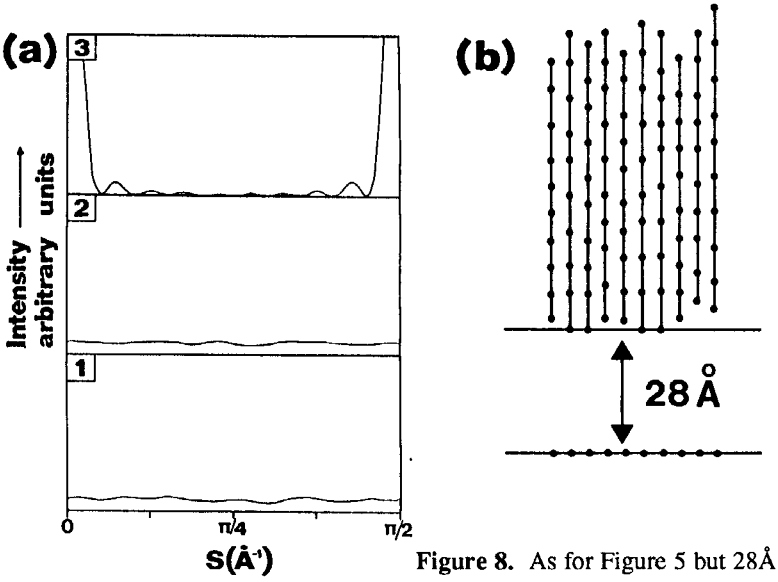


Figure 8. As for Figure 5 but 28Å above the line start.

(fig. 6) shows no such concentration. Indeed it is indistinguishable from case (b). Correspondingly, if diffraction is calculated for regions only 5 units from the line start, the meridional concentration of the first two layer lines is enhanced, as shown in figure 7 where the line start was positioned at the 5th monomer point. Thus, the additional order associated with a line start only extends a few monomer units along the chain. This limit is emphasised in figure 8 which shows diffraction from a 10 unit region beginning 28Å away from a line start. It is difficult to see any meridional concentration at all on the 1st and 2nd layer lines.

It is apparent, that as far a longitudinal register between chains is concerned, there is a partially ordered **fringe** adjacent to any ordered region, of which a line start is the simplest, although not necessarily the most relistic, example. Within the fringe area the occupation of 2Å lattice sites will deviate significantly from the mean occupancy, which can be defined as the fraction of chains with a monomer unit at a lattice site at a given distance from a line start, hence:

$$\text{Occupancy} = (P_A/N_A) + (P_B/N_B) \tag{8}$$

where P_A, P_B are the mole fractions of A and B units and N_A, N_B are the number of lattice sites per monomer point corresponding to an A or B unit. Therefore $N_A=3$ and $N_B=4$ for units of 6 and 8Å. This gives a mean occupancy of about 29%. The actual occupancy as a function of position can be calculated and is shown in figure 9 for a variety of chain compositions. We see that for $P_A=0.5$ a reasonable size for the fringe is indeed about 30Å (or 4 to 5 monomer units). Also, as the composition changes away from $P_A=0.5$, we see the size of the fringe increasing.

Thus when considering NPL crystallites it is important to remember that they will be bounded by fringe regions which will make a further contribution to the sharp meridional component of the low order layer lines. Furthermore, parameters which encourage larger NPL crystallites (eg composition greater or less than 50%, blocky chains rather than random ones) will also enhance the size of the fringe region.

d) *The NPL crystallite - The model consists 10 identical* **random** *chains.* $\underline{Y}_n=0$

Figure 10 shows that for the NPL model all the layer lines concentrate completely on the meridian, and also on the vertical row lines associated with the 4Å interchain repeat distance.

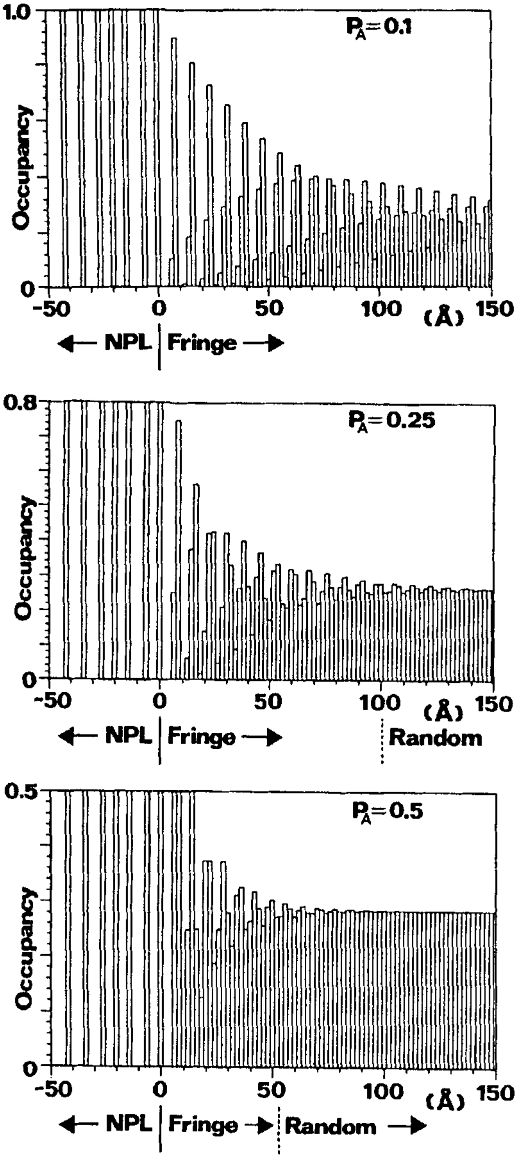


Figure 9. Plots showing the probability of occupancy of 2Å lattice sites as a function of distance from the surface of an NPL crystallite. The correlations responsible for the concentration of the 1st. and 2nd. layer line intensity on the meridian decay over a finite distance from the surfaces of the NPL crystallites producing a fringe effect. The fringes are broadened as the composition of the random chains departs from 50/50.

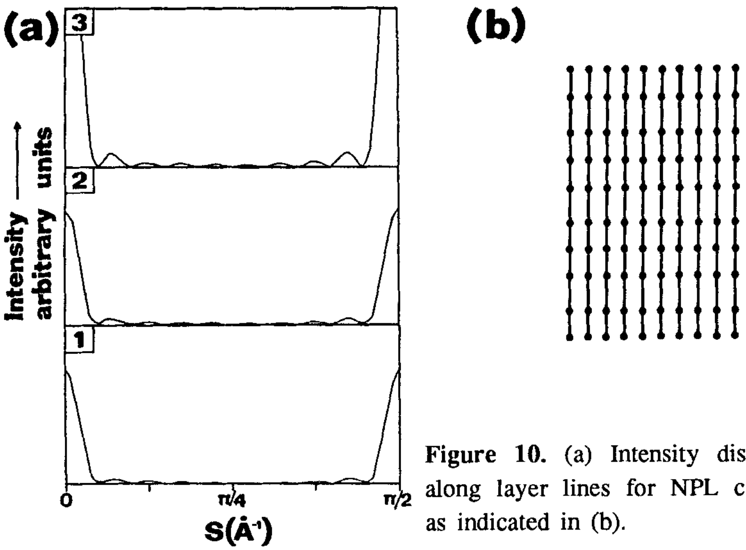


Figure 10. (a) Intensity distributions along layer lines for NPL crystallites as indicated in (b).

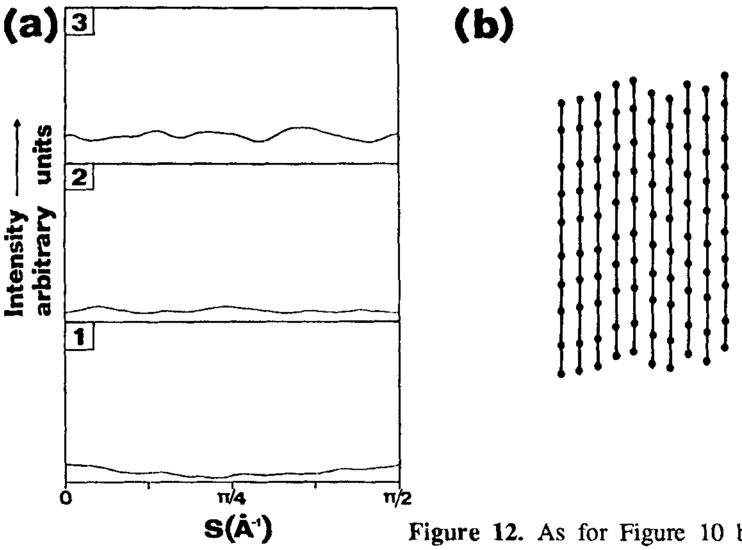
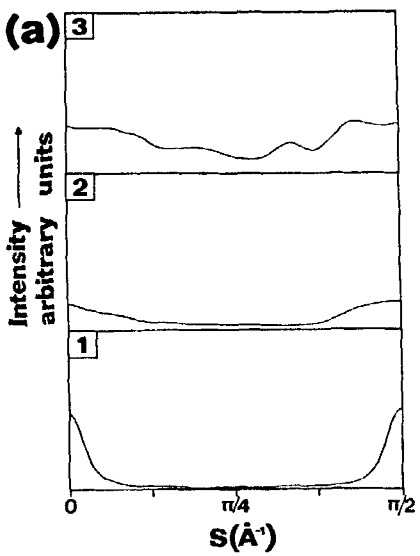


Figure 12. As for Figure 10 but with standard deviation of 2Å.



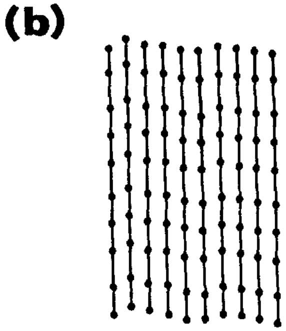
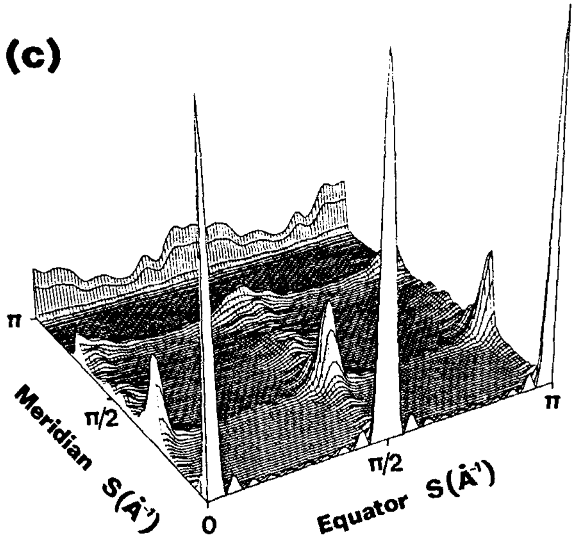


Figure 11. (a),(b) As for Figure 10 but with a randomisation of the longitudinal register by a Gaussian distribution of standard deviation 0.5Å. As the features in this case show some relation to those observed experimentally, a surface plot is also shown (c).



e) *The NPL crystallite with some randomisation in the longitudinal register - 10 identical random chains with* $\underline{Y}_n=y$ *where y is a distance taken at random from a Gaussian distribution of standard deviation δ referred to the start position of the adjacent chain.*

The diffraction pattern corresponding to δ=0.5Å is shown in figure 11. The first layer line is again fairly well concentrated on the meridian and is not dissimilar to the perfect NPL case considered above. However, the second layer line is now more laterally diffuse, while the third shows hardly any meridional concentration at all. The differential influence of the imposed Gaussian distribution occurs because a randomisation with a δ of 0.5Å will largely destroy a register based on a 2Å repeat, while having a comparatively small influence on the register corresponding to an 8Å repeat represented by the first layer line. When δ=2Å (fig. 12) all meridional peaks have spread to form layer lines and the calculated pattern tends towards that for the random case (a). A similar exercise was carried out for the line start case (c), and the effects were comparable.

f) *Monomer lengths with a much smaller highest common factor*

There should be no effect on the diffraction from NPL crystallites other than that involving the position and overall intensity of the layer lines which can be understood in terms of 1-D modelling[4,5]. The fringe contribution to meridional intensification of the layer lines, as shown by the line start calculations of figure 13, would appear to be similar for unit lengths in a less simple ratio such as 6 and 8.3Å, as it is for 6 and 8Å.

g) *Concentration of layer line intensity on row lines*

Where particular levels of longitudinal register between chains leads to a concentration of layer line intensity onto the meridian, there is, in all the models generated, an equivalent concentration onto the first and subsequent row lines above the first equatorial maximum and its higher orders. These 'hkl' maxima are not seen in the experimental patterns. Instead, there is generally a satellite close to the equatorial maximum but displaced meridionally only half the distance to the first layer line. An implication of this observation is that the units of the chain are twisted as some form of 2/1 helix to give a structural repeat twice that of the chemical repeat considered in this modelling. The transform of an individual chain would thus be of minimum intensity on the first layer line at the position of the first hkl maxima predicted by the simple point model.

Summary

In conclusion, it is apparent that the concentration of the intensity in the first layer line onto the meridian, as observed experimentally, indicates some lateral alignment of like sequences in neighbouring chains. In its fully developed form this order corresponds to NPL crystallites. These may be of differing thicknesses (in the chain direction) ranging from the extreme lower limit of a 'line start' up to crystallites which occupy the whole of the area modelled and could only result from substantial segregation involving a much greater volume of polymer. The fact that the meridional concentration in experimental diffraction patterns is progressively less marked for the second and third layer lines suggests some imperfection in the register within the NPL crystallites. It is interesting to note that disorder represented by a standard deviation of 0.5Å leads to a predicted pattern with salient features in some accord with those seen experimentally for annealed fibres.

Acknowledgement

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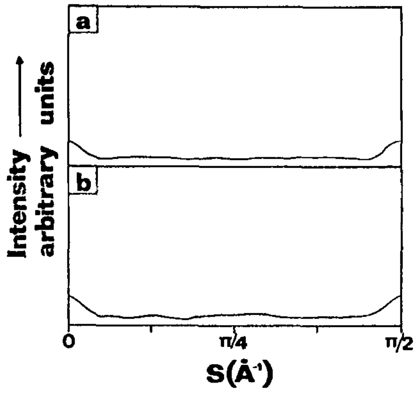

Figure 13. (a) The intensity distribution along the first layer line for a line start model based on units of 6.0Å and 8.3Å (as opposed to 8Å), compared with (b) the distribution for the line start model with unit lengths 6Å and 8Å already considered, (Figure 5). The concentration of some intensity onto the meridian due to correlations in the fringe region is not diminished by the fact that the ratio between the unit lengths is not one of small integers.

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