

# Molecular modelling of the structure of the copolyester prepared from *p*-hydroxybenzoic acid, biphenol and terephthalic acid

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The X-ray data for melt-spun fibres of the 33/33/33 copolyester prepared from *p*-hydroxybenzoic acid, biphenyl and terephthalic acid are characteristic of a completely random microstructure. Nevertheless, these copolymers adopt three-dimensionally ordered structures in the solid state, in which the chains are packed on hexagonal or orthorhombic polymorphic lattices. We have used molecular mechanics modelling to optimize the packing of random sequences in the higher-density orthorhombic form. The models consisted of 48 non-identical chains of nine monomers each. The random sequences were restricted to three monomers of each type, so that they had approximately the same length, making it possible to apply a periodic boundary condition. The initial model had the extended chains in register, i.e. their central ester oxygens were in a plane perpendicular to the chain axis direction. This structure had high potential energy due to overlap between the non-identical sequences. Energy minimization eliminated these bad contacts, at a cost of only  $\sim 1.8$  kcal mol<sup>-1</sup> per monomer, by relatively small changes in the torsion angles at the phenylene-ester linkage bonds. These small arrays also predict Bragg maxima on the equator and layer lines that match those observed. We conclude that non-identical chains can be packed in a stereochemically acceptable manner according to the geometry defined by the X-ray data. Copyright © 1996 Elsevier Science Ltd.

(Keywords: molecular modelling; X-ray diffraction; thermotropic copolyester)

## INTRODUCTION

This paper describes efforts to model the ordered solid-state structure of the copolyester prepared from *p*-hydroxybenzoic acid (HBA), biphenyl (BP) and terephthalic acid (TPA). Solution of the solid-state structures of wholly aromatic copolyesters presents some very interesting physical problems in that they possess three-dimensional order even though the chains have random microstructure. Examples of this large group of copolymers are those prepared from *p*-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA)<sup>1</sup> and copoly(HBA/BP/TPA)<sup>2</sup>, the subject of this paper, which are respectively the bases of the Vectra<sup>®</sup> (Hoechst Celanese) and Xydar<sup>®</sup> (Amoco) series of commercial resins. The homopolymers, such as poly(HBA), are infusible, relatively intractable, crystalline solids, but introduction of comonomers leads to a lowering of the melting point ( $T_m$ ), such that the copolyester can be processed by injection moulding, or melt spun to form high-strength, high-modulus fibres<sup>3–5</sup>.  $T_m$  is actually a solid state–nematic transition: the melts are thermotropic owing to the relatively stiff, rod-like conformation,

which in turn is a consequence of the monomer structures and linkage geometry.

The X-ray fibre diagrams of copoly(HBA/BP/TPA) and copoly(HBA/HNA) contain a series of Bragg reflections on the equator and several layer lines<sup>6</sup>, which point to the existence of three-dimensional order. Indeed, the data are similar to those for an oriented semicrystalline homopolymer. The possibility that the copolymers have a blocky structure, and that the crystallinity arises from segregation of homopolymer blocks, was ruled out by the fact that the layer lines are non-periodic, and shift with monomer composition. These data were shown to be characteristic of random comonomer sequences<sup>6–9</sup>. Advance along the extended copolymer chain is in a series of steps that are approximately equal to the lengths of one or other of the monomers, and non-periodic layer lines arise when these lengths are different from one another. Hence the microstructure of these copolymers was first established by X-ray methods, which could rule out all but minimal non-randomness, as has since been confirmed by deuterium and <sup>13</sup>C n.m.r. studies<sup>10,11</sup>.

It was also proposed<sup>12</sup> that the three-dimensional ordering arises from lateral matching of identical short non-repeating sequences to form non-periodic lattices. However, this is problematical if one is to account for the large crystallite size ( $\sim 60$  Å wide, corresponding to a bundle of at least 100 chains) and the degree of

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crystallinity (~25%) seen for the as-spun fibres. Morphological studies<sup>13</sup> show that there is a lamellar structure along the chain axis direction consisting of ordered and disordered regions, with dimensions such that a single extended chain passes through a number of ordered regions. Even if a section of the sequence matches that of its neighbour in one ordered region, this is unlikely to occur also in the adjacent regions. There is the possibility that annealing leads to some changes in sequence via transesterification, although one might reasonably expect this process, if it occurs, to generate blocky structures, as suggested by Lenz and coworkers<sup>14</sup>. Transesterification sufficient to change the sequences in blends occurs relatively slowly even in the melt<sup>15,16</sup>, and such rearrangement could not be expected to occur on the timescale of seconds during melt spinning.

In this laboratory<sup>17</sup> we have shown that the Bragg maxima can be accounted for by the formation of arrays of non-identical chains packed on a two-dimensional lattice with minimal lateral register: specifically, the ordered regions consist of layers of parallel, short sequences of ~10 monomers with their centres on or close to a 'register' plane perpendicular to the fibre axis. This central register plane could arise due to dipole-dipole interaction between the ester groups. When registered in this manner, a similar interaction can also occur between some of the other ester groups in the random sequences above and below the register plane. It is easy to show that the chance of such overlap is maximized if registration of the short sequences occurs at their centres rather than at some other point within an ordered lamella.

Molecular mechanics modelling of the structure of 75/25 copoly(HBA/HNA) by Hofmann *et al.*<sup>18</sup> showed that centrally registered, non-identical chains of 12 monomers could be packed on the hexagonal array defined by the X-ray data for as-spun fibres. Bad contacts between non-identical monomers were eliminated by changing the phenyl-ester torsion angles, and the resultant structures have potential energies that are comparable to those for models of the two homopolymers on the same lattices. In addition, simulated X-ray fibre diagrams for these arrays show intensity maxima on the equator, and importantly on the first layer line, indicating that the limited registration at the centres of the 12-monomer sequence generates the reflections characteristic of three-dimensional order. (Random axial stagger leads to continuous layer lines, as for a nematic structure.) This being the case, it was argued that there is no necessity to invoke sequence matching, which requires considerable rearrangement of the random structure, in order to explain the X-ray data. Indeed, the centrally registered structure predicts Bragg reflections on higher layer lines that are not present in the observed data. All that is necessary to predict those observed is a *tendency* towards registration, which can be modelled by a distribution of the centres about the register plane<sup>17</sup>.

The modelling of copoly(HBA/HNA) considered only the hexagonal structure formed in the as-spun fibres. Annealing that polymer leads to the generation of a second polymorphic structure with an orthorhombic unit cell that has a significantly higher density, and it is reasonable to ask whether such a structure can also be compatible with packing of non-identical chains. In

addition, the modelling of Hofmann *et al.*<sup>18</sup> did not apply a periodic boundary condition, but optimized the packing by a three-step process, immobilizing successively the outer, inner and again the outer sections of the model while minimizing the energy of the rest of the structure, so as to avoid contraction. This procedure was necessary because the non-identical chain segments had different lengths. Although the overall monomer ratio in the array was 75/25 HBA/HNA, the composition of the individual 12-monomer segments could be different, as the sequences were set by random selection.

In the present work, we have considered the higher-density orthorhombic structure adopted by 33/33/33 copoly(HBA/BP/TPA), which is formed in the as-spun fibres of this polymer. We have also compared different energy minimization routes and have been able to apply the periodic boundary condition when we considered models containing only chains composed of equal numbers of HBA, BP and TPA monomers.

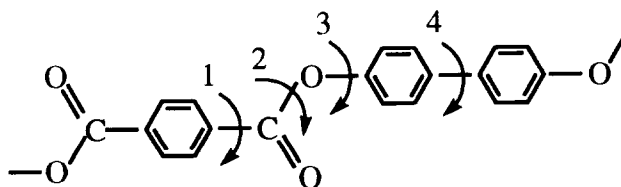
## EXPERIMENTAL

### X-ray diffraction

The X-ray data for a 33/33/33 copoly(HBA/BP/TPA) were those presented elsewhere<sup>19</sup>. The specimens were generously provided by Dr N. D. Field (Dartco). Fibres were drawn by hand from the melt using tweezers, and formed into parallel bundles. X-ray fibre diagrams were recorded on Kodak Direct Exposure X-ray film using a Searle toroidal focusing camera and Ni-filtered Cu K $\alpha$  radiation. The *d*-spacings were calibrated using CaF<sub>2</sub> powder.

### Molecular models

Models for the monomer residues were constructed using averaged bond lengths and bond angles from single-crystal structure determinations of low-molar-mass aromatic ester model compounds<sup>20-22</sup>. The bond lengths used were: C<sub>ph</sub>-C<sub>ph</sub> = 1.35 Å, C<sub>ph</sub>-C<sub>carb</sub> = 1.39 Å, C<sub>carb</sub>-O<sub>carb</sub> = 1.22 Å, C<sub>carb</sub>-O<sub>est</sub> = 1.33 Å and C<sub>ph</sub>-O<sub>est</sub> = 1.47 Å. The bond angles were: C<sub>ph</sub>-C<sub>ph</sub>-C<sub>ph</sub> = 120°, C<sub>ph</sub>-C<sub>carb</sub>-O<sub>carb</sub> = 122°, C<sub>ph</sub>-C<sub>carb</sub>-O<sub>est</sub> = 118°, O<sub>carb</sub>-C<sub>carb</sub>-O<sub>est</sub> = 120°, C<sub>carb</sub>-O<sub>est</sub>-C<sub>ph</sub> = 115°, C<sub>ph</sub>-C<sub>ph</sub>-C<sub>carb</sub> = 120° and C<sub>ph</sub>-C<sub>ph</sub>-O<sub>est</sub> = 120°. (The subscripts ph and carb designate atoms of the phenylene and carbonyl groups respectively; O<sub>est</sub> is the ester oxygen.) The conformation of the copolymer chain is defined by the torsion angles at (1) the Ph-COO, (2) the Ph-CO-OPh, (3) the COO-Ph, and (4) the Ph-Ph bonds (where Ph represents phenylene):



For bond 1, a plot of potential energy against torsion angle contains two minima at 0° and 180°, separated by a barrier of 5.6 kcal mol<sup>-1</sup> (0° defines the *cis* conformations for all torsion angles, and positive angles correspond to anticlockwise rotations). For bond 2, there is only one minimum at 180°, corresponding to the *trans* configuration for the ester group, which is coplanar with the

phenylene in the Ph-COO unit. For bond 3, four energy minima are obtained at  $\pm 60^\circ$  and  $\pm 120^\circ$  torsion angles, such that the phenylene planes of the Ph-COO-Ph units are mutually inclined by  $60^\circ$ . The minima at  $+60^\circ$  and  $+120^\circ$  (and those at  $-60^\circ$  and  $-120^\circ$ ) are separated by an energy barrier of only  $0.4 \text{ kcal mol}^{-1}$ , with a very much higher barrier ( $> 20 \text{ kcal mol}^{-1}$ ) between the two pairs. For bond 4, there are four minima at  $\pm 53^\circ$  and  $\pm 127^\circ$ . As is the case for bond 3, there is a low barrier between the minima at  $+53^\circ$  and  $+127^\circ$  (and at  $-53^\circ$  and  $-127^\circ$ ) of  $0.7 \text{ kcal mol}^{-1}$ , and a much higher barrier between the two pairs. These torsion angles are similar to those observed in single-crystal structure determinations for analogous low-molar-mass compounds<sup>20-22</sup>.

#### Arrays of chains

Arrays of 48 chains of nine monomers each were constructed in order to compare the effects of minimization with and without the application of a periodic boundary condition. The chains had non-identical sequences selected using a random number generator, subject to the allowed chemical combinations, and with the further restriction that each chain contained three monomers of each type. Terminal hydrogen atoms were added to the ester groups at the chain ends. Torsion angles 1, 3 and 4 were selected at random from local minima listed above, with the restriction that the mutual inclination of successive phenyl groups along each chain was alternately  $+60^\circ$  or  $-60^\circ$  ( $\pm 53^\circ$  in the case of the phenylenes of the BP unit), consistent with the X-ray data favouring an approximate herring-bone packing of the chain in the ordered regions. The chain axes were defined as the best least-squares line drawn through all the atoms, and were inclined parallel to the  $z$  axis. The 48 chains were packed on a  $4 \times 6$  array of unit cells, each with dimensions  $a = 7.84 \text{ \AA}$ ,  $b = 5.53 \text{ \AA}$ . Each unit cell contained two chains with their axes passing through  $x, y = 0, 0$  and  $\frac{1}{2}, \frac{1}{2}$ . The ester oxygen between the fourth and fifth monomer of each chain was set at  $z = 0$ . The plane of the phenylene group of the fifth monomer (the phenylene closest to the registered ester oxygen in the case of a BP unit) for the chain passing through  $0, 0$  was inclined at  $60^\circ$  to the  $x, z$  plane; that for the chain passing through  $\frac{1}{2}, \frac{1}{2}$  was similarly inclined at  $-60^\circ$ , leading to approximate herring-bone packing.

The monomer composition was limited to three of each type within the sequence of nine monomers in order to obtain 48 chains of the same length, so that a periodic boundary condition could be applied. Even so, the lengths were only approximately constant, all being within the range  $71.8 \pm 0.3 \text{ \AA}$  measured between the terminal hydrogens. This difference arose because of the slight non-linearity of the individual chains. (This is a consequence of the random selection of the torsion angles, and also the fact that the ester bond angles are not exactly  $120^\circ$ , which means that the phenyl-ester bonds are not quite parallel to the chain axis.) For application of the periodic boundary condition, we set  $c = 73.0 \text{ \AA}$ , to be sure that overlap of the terminal groups could not occur. The arrays of 48 chains of nine monomers contained 720 atoms (3888 carbons, 912 oxygens and 2400 hydrogens) corresponding to a 'molecular weight' of 63 680 for the 432 monomers.

In addition to the above arrays of 48 chains of nine monomers, we constructed smaller arrays in a similar

manner but without the requirement of equal numbers of each type of monomer. These structures were studied in order to explore the effects of different sequences and starting conformations.

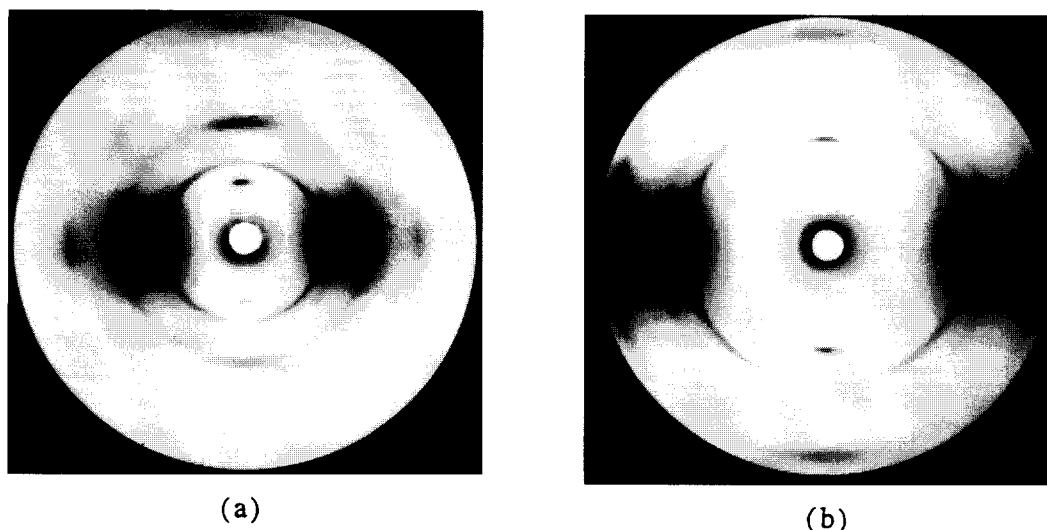
#### Energy minimization

Molecular mechanics potential-energy minimizations of the 48-chain arrays were performed using the SYBYL<sup>®</sup> software package<sup>23</sup> on a Silicon Graphics 4D 220 computer. The potential energies were computed as the sum of the contributions due to van der Waals and electrostatic forces, and also to distortions of the bond lengths, bond angles and torsion angles, and the effect of out-of-plane bending. The Tripos force field was used, as contained within the SYBYL package, except that small adjustments were made to the preferred bond lengths and angles to match the average values observed in model compounds<sup>20-22</sup>, which had been used in the construction of the models. The electrostatic terms were estimated based on point atomic charges estimated by the Gasteiger-Hückel method. The cut-off interatomic distance was reduced from the default value of  $8.0 \text{ \AA}$  to  $7.8 \text{ \AA}$  so that the periodic boundary condition as defined in the SYBYL package could be applied to the 48-chain arrays. (This requires a minimum cell dimension of four times the cut-off distance; the  $x$ -axis dimension of the 48-chain array is  $4 \times 7.83 \text{ \AA}$ .)

The energies of the starting arrays were minimized using the SYBYL MINIMIN2 routine following three strategies. First, the array was treated as a single isolated molecule, and the energy was minimized without regard to boundary conditions. The second route was to hold the outer 18 chains in their starting positions and conformations while minimizing the potential energy of the inner 30 chains. (This procedure follows the work of Hofmann *et al.*<sup>18</sup>, who optimized a hexagonal array of 19 non-identical chains of 12 monomers of copoly(HBA/HNA) in three stages: (i) the outer 12 chains were fixed while the energy of the inner seven chains was minimized; (ii) the inner chains were then fixed while the energy of the outer chains was minimized; and (iii) the inner chains were reoptimized with the outer chains fixed in their positions. For the 48-chain arrays, we found that steps (ii) and (iii) had relatively little effect on the final structure of the inner 30 chains, and they were not applied in the results presented here.) The third route was to apply the periodic boundary condition, based on an orthorhombic cell with dimensions  $a = 31.36 \text{ \AA}$ ,  $b = 33.18 \text{ \AA}$  and  $c = 73.00 \text{ \AA}$ . These three strategies will be referred to as the simple, aggregate and p.b.c. methods respectively. The smaller arrays were minimized exclusively by the simple method, i.e. without consideration of boundary effects. All energy minimizations were terminated when the energy difference between successive cycles was less than  $0.01 \text{ kcal mol}^{-1}$  per monomer unit. Simulated X-ray scattering patterns for the cylindrically averaged arrays were computed using the CERIUSt<sup>®</sup> software package<sup>24</sup>.

## RESULTS AND DISCUSSION

The X-ray fibre diagram for as-spun 33/33/33 copoly-(HBA/BP/TPA) is shown in *Figure 1*. The  $d$ -spacings for the observed Bragg reflection and the meridional maxima are given in *Table 1*. These data are similar to



**Figure 1** X-ray fibre diagram for as-spun fibres of 33/33/33 copoly(HBA/BP/TPA): (a) was recorded using a shorter specimen–film distance and a longer exposure time than (b). The fibre axis was approximately perpendicular to the beam in each case

**Table 1** Comparison of the *d*-spacings (Å) for the observed meridional maxima and the equatorial and off-equatorial Bragg reflections with those predicted for the initial and minimized arrays of 48 chains of nine monomers

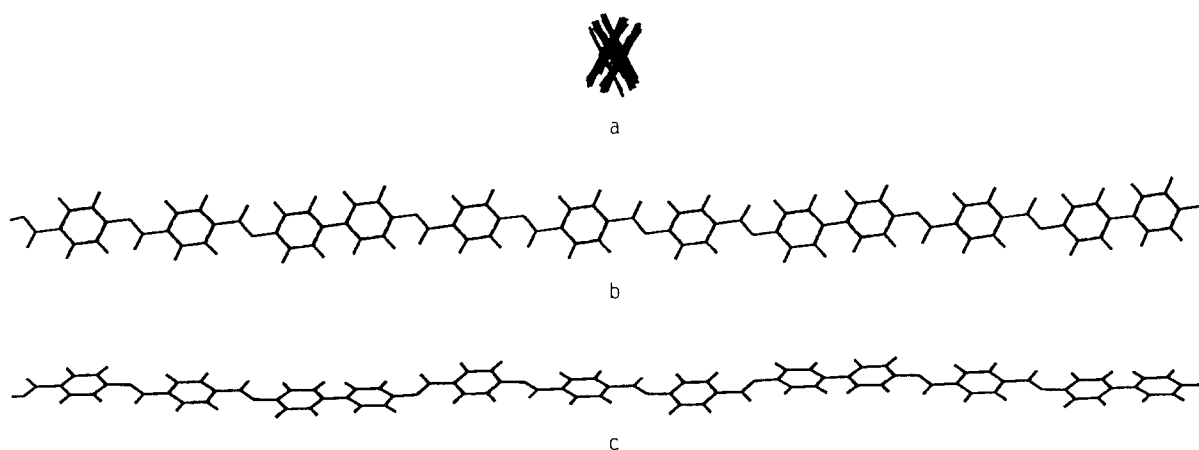
	Observed <sup>a</sup>		Minimization method			
			Initial	Simple	Aggr.	P.b.c.
Meridian	7.7	(0.1)	7.90	7.90	7.90	7.90
	5.77	(0.03)	5.85	5.85	5.85	5.85
	3.28	(0.03)	3.31	3.30	3.30	3.30
	2.90	(0.03)	2.92	2.93	2.92	2.92
	2.09	(0.02)	2.12	2.12	2.12	2.12
Equator	4.52	(0.03)	4.52	4.43	4.52	4.42
	3.92	(0.02)	3.92	3.70	3.92	3.92
	2.38	(0.02)	2.38	2.25	2.38	2.38
	2.27	(0.02)	2.27	–	–	–
Layer 1	3.08	(0.03)	3.10	2.95	3.10	3.10
	2.54	(0.02)	2.56	2.50	2.57	2.57
Layer 2	2.46	(0.02)	2.48	2.40	2.48	2.48
	2.10	(0.02)	2.10	2.02	2.12	2.12
Layer 3	3.08	(0.03)	3.10	3.05	3.11	3.11
	2.46	(0.03)	2.48	2.40	2.47	2.47

<sup>a</sup> Experimental error shown in parentheses

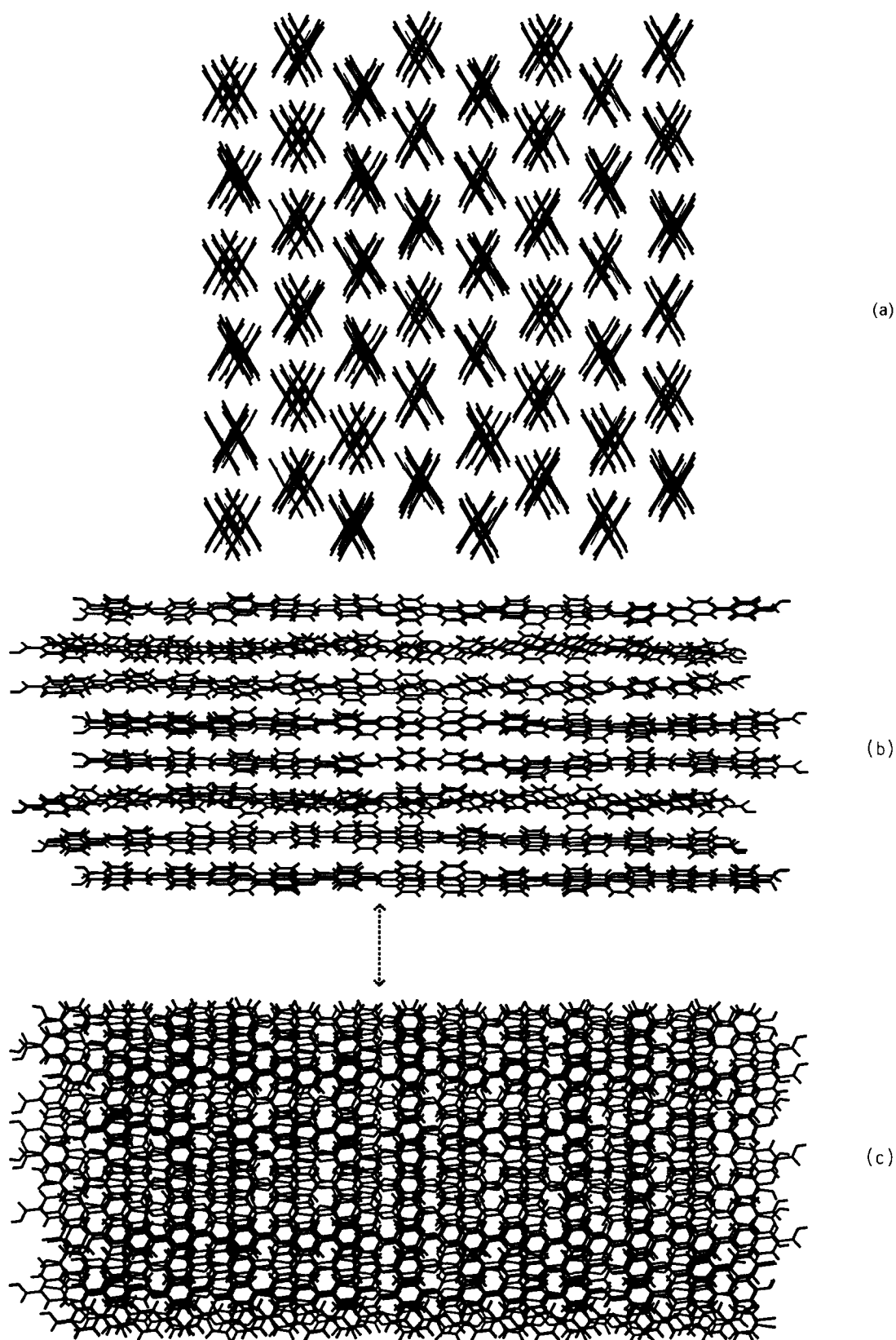
those reported by Blackwell *et al.*<sup>6</sup> and by Field *et al.*<sup>25</sup> The four equatorial reflections can be indexed (110, 200, 210 and 220, respectively) by an orthorhombic two-dimensional unit cell with dimensions  $a = 7.84 \text{ \AA}$ ,  $b = 5.53 \text{ \AA}$ , and containing two chains. The meridional maxima are non-periodic due to the random microstructure, and hence there is no repeat in the fibre axis direction. The distances between the terminal oxygens in the atomic models of the three monomer residues are 6.35, 7.22 and 9.88 Å, leading to an average advance of 23.5 Å for three monomer units. These dimensions yield a calculated density of  $1.42 \text{ g ml}^{-1}$ , which is in good accord with the observed density of  $1.37 \text{ g ml}^{-1}$ .

*Arrays of 48 chains*

Figure 2 shows projections of a copoly(HBA/BP/TPA) chain of three monomers of each type. The subsequent Figures 2–4 show the projections of an array of 48 chains of nine monomers: the starting model (Figure 3); and after energy minimization by (a) the simple, (b) the aggregate and (c) the p.b.c. methods (Figure 4). The planes of most of the aromatic units are approximately perpendicular to the chain axis, and appear as straight lines. For the simple minimization, there has been



**Figure 2** The (a) *x, y*, (b) *y, z* and (c) *x, z* projections of a copoly(HB/BP/TPA) chain composed of three monomers of each type in random sequence

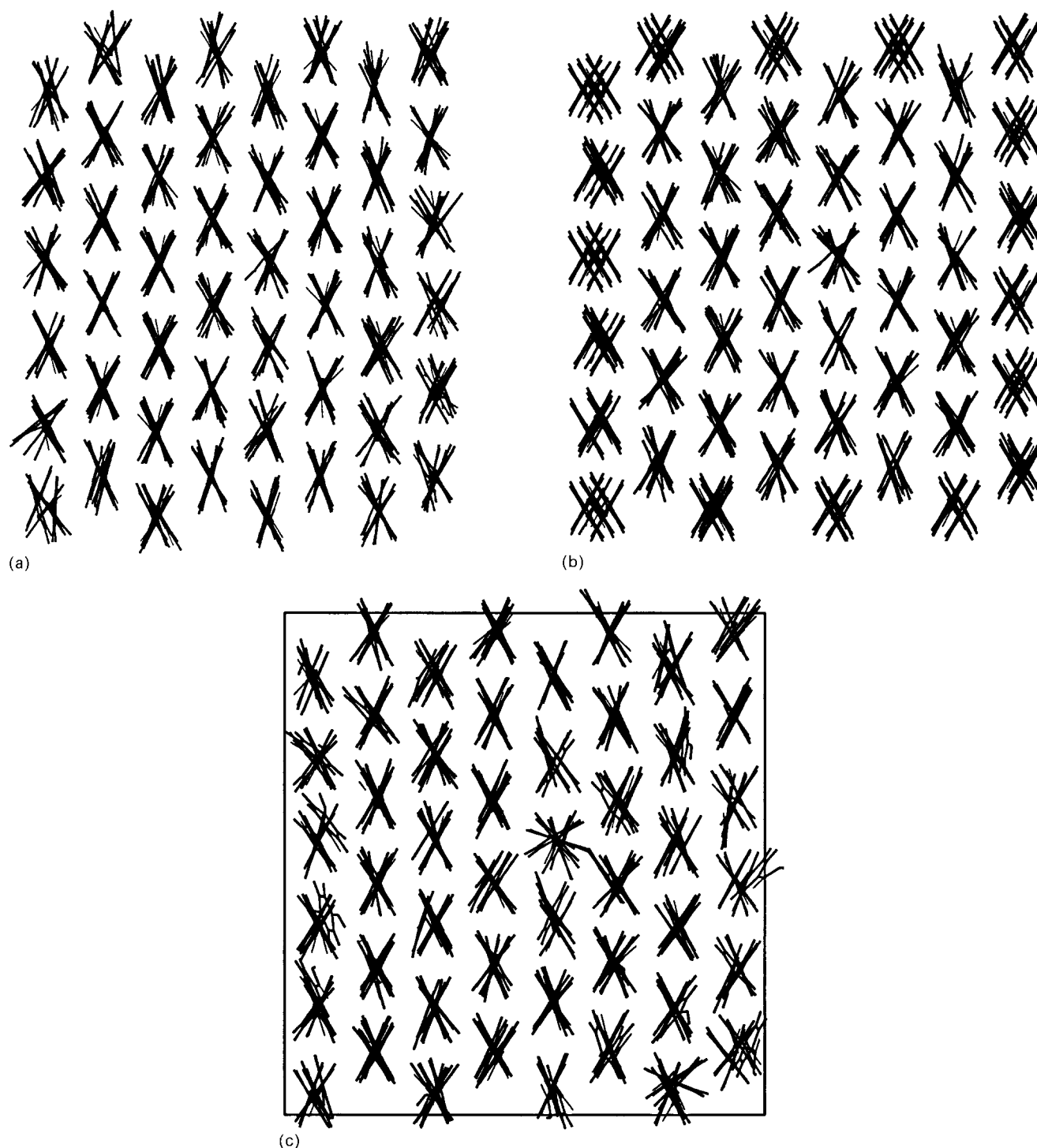


**Figure 3** The (a)  $x, y$ , (b)  $x, z$  and (c)  $y, z$  projections of a starting array of 48 non-identical chains of nine monomers: in (a) the  $x$  axis is horizontal; in (b) and (c) the  $z$  axis is horizontal. The registration point along the  $z$  axis is indicated by the double-headed arrow

significant contraction along the  $x$  axis: the  $a$  dimension has been reduced from  $7.84 \text{ \AA}$  to an average of  $7.38 \pm 0.05 \text{ \AA}$ . However, there has been little change along the  $y$  and  $z$  axis directions. The contraction translates to an increase of the density to  $1.53 \text{ g ml}^{-1}$

(6.3%), and has been effected by small changes in the mutual inclination of adjacent phenylenes, as will be discussed further below. Contraction of the aggregate and p.b.c. models is precluded by definition.

The potential energies for the arrays shown in *Figures*

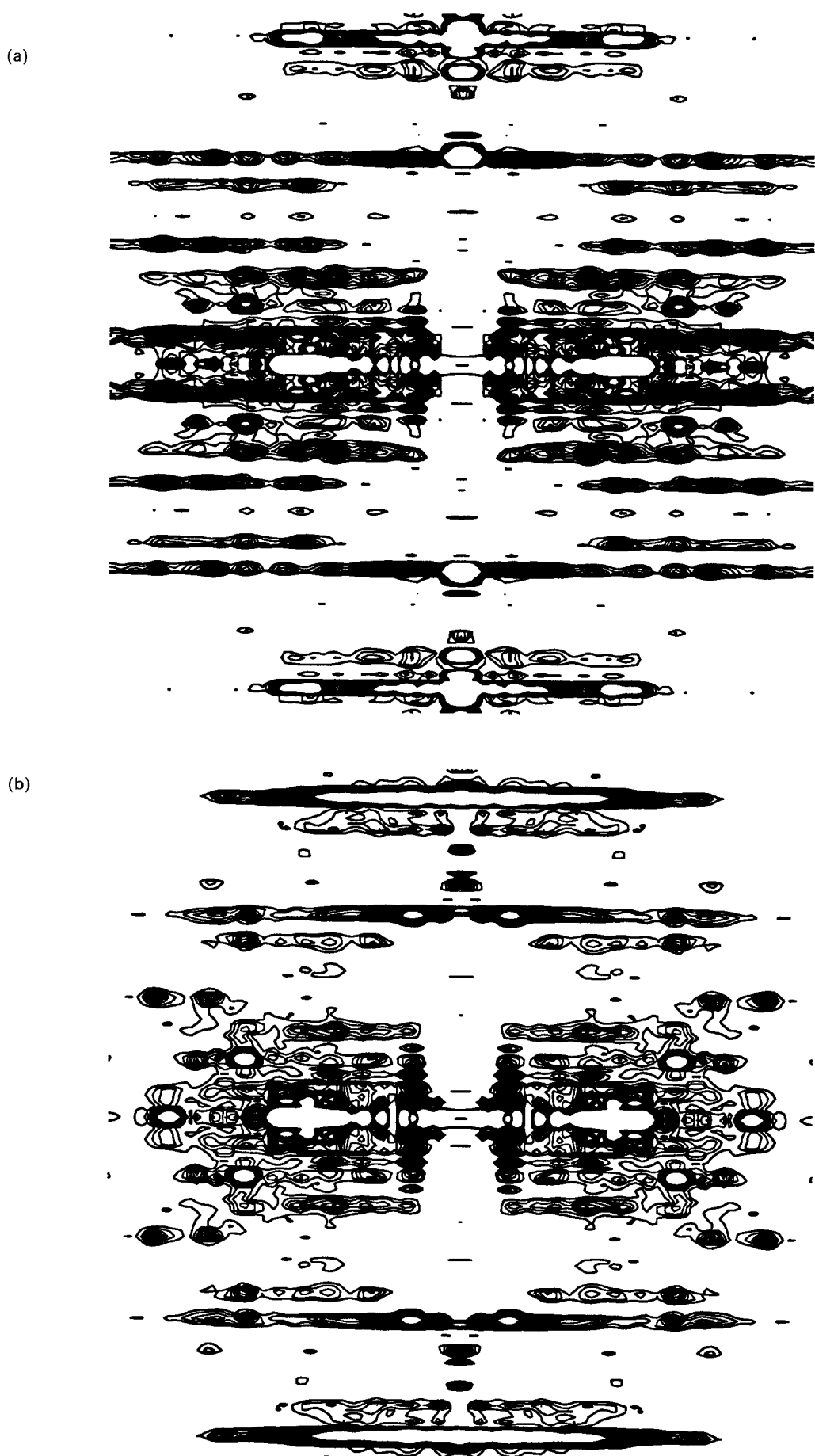


**Figure 4** The  $x, y$  projections for the array shown in *Figure 3* after energy minimization using the (a) simple, (b) aggregate and (c) p.b.c. methods. The  $x$  axis is horizontal in each case

3 and 4 are given in *Table 2*, which lists the contributions by the different components to the total. These data are for the inner 30 chains only, so as to eliminate differences due to edge effects for the purposes of comparison. The initial array has a high positive potential energy exceeding  $12\,600\text{ kcal mol}^{-1}$ , due to the existence of many van der Waals short contacts, demonstrating the intuitively obvious problem of packing random copolymer chains with the imposition of such regular conformations. All three minimization routes have reduced the total potential energy: to  $-1944\text{ kcal mol}^{-1}$  for the simple method; and to  $-1802$  and  $-1793\text{ kcal mol}^{-1}$  for

the aggregate and p.b.c. methods, respectively. The latter two figures are indistinguishable; the lower energy for the simple method reflects the contraction discussed above, which results in an unacceptably high density. For all three models, the important conclusion is that the van der Waals overlap has been eliminated, reducing that component of the total energy by  $\sim 15\,000\text{ kcal mol}^{-1}$ . This improvement has been achieved at the sacrifice of  $\sim 500\text{ kcal mol}^{-1}$  in torsional energy and  $\sim 80\text{ kcal mol}^{-1}$  in bond angle distortions; the changes in the other components are negligible.

Elimination of the van der Waals overlap has been



**Figure 5** Simulated X-ray patterns for cylindrically averaged arrays of 48 chains of nine monomers: (a) the starting array (*Figure 3*); (b) the same array after minimization using the p.b.c. method (*Figure 4c*)

**Table 2** Potential energy components (kcal mol<sup>-1</sup>) for the inner 30 chains of the arrays of 48 chains of nine monomers, before and after minimization

Energy terms	Initial array	Minimized arrays		
		Simple	Aggr.	P.b.c.
Bond stretching	13	31	28	29
Angle bending	25	112	102	96
Torsional	495	998	990	990
Out of plane	0	9	8	8
van der Waals	12 614	-2 550	-2 415	-2 405
Electrostatic	-534	-544	-515	-511
Total energy	12 613	-1 944	-1 802	-1 793

achieved mainly by changing the phenylene-ester torsion angles at the monomer linkages, meaning that the planes of the aromatic units have been rotated about the  $z$  axis in order to avoid contacts with neighbouring chains. To give some idea of the magnitude of these changes, it is useful to survey the torsion angles in the minimized models. For the Ph-COO torsions, the average angles remain at 0° or 180°, with average deviations of  $\pm 10^\circ$  for the 432 monomers in the simple model and  $\pm 5^\circ$  for both the aggregate and p.b.c. models. The torsion within the ester group (PhCO-OPh) remains at an average of 180° for all three models, with average deviations at  $\pm 2^\circ$ . The main changes in the models are in the COO-Ph torsions, which were originally set at  $\pm 60^\circ$  ( $\pm 120^\circ$ ). Here the averages are shifted to  $\pm 53^\circ$  ( $\pm 127^\circ$ ) for the simple method, with an average distribution of  $\pm 15^\circ$  about each position. For the aggregate and p.b.c. methods, these torsion angles shift to averages of  $\pm 56^\circ$  ( $\pm 124^\circ$ ), with average distributions of  $\pm 8^\circ$ . In all three cases, the changes in the average torsion angle result in a net 'flattening' of the chain conformations, which is most extreme for the simple model, where it in part facilitates the contraction along the  $x$  axis direction. The phenyl-phenyl torsion angles retain their original average value of  $\pm 53^\circ$ , with a distribution of  $\pm 8^\circ$  for all three models.

The above data indicate that the changes in torsion angles have been relatively minimal. The projections of the chains in the minimized arrays have a more cylindrical appearance, but this reflects cumulative changes along the chain: the local changes at each phenylene-ester linkage have been small. It is interesting to note that the torsion angles have not flipped from the starting positions to any of the other local minima. A change in the COO-Ph torsion from  $+60^\circ$  to  $120^\circ$  would require passage through a barrier of only 0.4 kcal mol<sup>-1</sup>, but would not be compatible with the approximate herring-bone packing. A change of 180° in the Ph-COO would maintain the herring-bone packing scheme, but requires passage through a higher barrier of 5.8 kcal mol<sup>-1</sup>. Similarly the  $z$  coordinates for the chains scarcely change during the minimization. This probably accounts for the fact that the electrostatic component of the total energy is essentially unchanged during the minimization, since the separations between the ester groups on adjacent chains depend mainly on the  $z$  coordinates. All such changes are unlikely in a molecular mechanics minimization, since they require cooperative motions of relatively large parts of the structure.

The changes in torsion angles occur very early during

the energy minimization, driven by the pressing need to eliminate the bad contacts. At later stages, there is some relaxation towards the original values. While the  $\sim 500$  kcal mol<sup>-1</sup> increase in torsional energy for the array ( $\sim 1.8$  kcal mol<sup>-1</sup> per monomer) is very small compared to the  $\sim 14\,500$  kcal mol<sup>-1</sup> decrease in the van der Waals component, this is not trivial in the absolute sense. Molecular dynamics modelling might be expected to optimize the packing by facilitating the kinds of shifts and ring flips discussed above, probably leading to some reduction in the electrostatic and torsional energy components.

#### Simulated X-ray data

Figure 5 shows the simulated X-ray patterns for (a) the initial array and (b) the structure minimized using the p.b.c. method, respectively. These data are the predicted scattering for the 48 chains of nine monomers after cylindrically averaging about the chain axis direction,  $z$ . The equivalent data for the arrays minimized using the simple and aggregate methods are qualitatively very similar to those in Figure 5b and are not shown to save space. The  $d$ -spacings of the main maxima predicted for all four models on the equator and layer lines 1–3 are compared with those observed in Table 1. Both sets of data contain intense scattering close to the origin, as well as significant subsidiary maxima between the primary (non-periodic) layer lines, all of which would be eliminated or smoothed away if we were to consider much larger models with a distribution of sizes. When we focus on the equator and primary layer lines, it can be seen that both models predict Bragg maxima at positions comparable to those observed.

Table 1 lists only the  $d$ -spacings of reflections in the region of those observed. The data for the aggregate and p.b.c. models are indistinguishable from those for the starting model; the  $d$ -spacings for the sample model have declined from the starting values due to contraction. All the simulated patterns exhibit more Bragg maxima (i.e. on higher layer lines) than are observed, probably because the registration of the centres of the random sequences is more perfect than occurs in the actual structures. Biswas and Blackwell<sup>17</sup> showed for copoly-(HBA/HNA) that perfect registration of the centres of the sequences led to Bragg sampling on all layer lines, but that when this registration condition is relaxed by allowing a distribution of the centres about the register plane, the sampling occurred only on the inner layer lines. This distribution was modelled as a Gaussian function with standard deviation  $\sigma$ ; for copoly(HBA/HNA), a value of  $\sigma \approx 2.0$  Å led to sampling only on the first layer line, as is observed in the X-ray data for that system. When one realizes that a value of 2.0 Å for  $\sigma$  corresponds approximately to the difference in the lengths of the two monomers (6.35 Å versus 8.52 Å), one can see that the extent of registration in copoly(HBA/HNA) is quite minimal. To obtain Bragg sampling out to the third line, as occurs for copoly(HBA/BP/TPA), a narrower distribution is necessary, with  $\sigma \approx 0.5$  Å. After energy minimization, the axial shifts in the 48-chain arrays are all less than 0.1 Å. Consequently, the optimized structures retain more perfect registration than appears to occur in the actual structures, and sampling of the higher layer lines is predicted. However, our only concern here is to demonstrate that the



minimized structures do generate all the maxima that are observed. One does not need any form of sequence matching in order to obtain the Bragg maxima. Rather, the models formed by registration of parallel random sequences give more Bragg maxima than are observed, and need to be distorted by the introduction of axial shifts in order to be consistent with the observed diffraction pattern.

Looking at the data in *Table 1* in more detail we see that the initial and all three refined models predict the non-periodic maxima on the meridian. However, the  $d$ -spacings are all slightly higher than those observed, indicating that the chain models are a little too extended. Blackwell *et al.*<sup>6</sup> found that the observed meridional  $d$ -spacings were reproduced by a model in which the axial advances for each monomer unit were approximately 3% less than the distances between their terminal ester oxygens. The contraction was thought to result from chain sinuosity, as was invoked by Troughton *et al.*<sup>26</sup> to explain the mechanical properties. The method used to construct the chains, with random selection of the different inter-residue minimum-energy conformations, leads to a somewhat sinuous chain, but the structures are still more extended than those which are observed. It seems likely that the constraints that prevent axial shifts also prevent significant contraction during the molecular mechanics minimizations. Overall, there has been an improvement in the match of meridional intensities compared to that predicted for the isolated chain, in that the maximum at  $d = 2.92 \text{ \AA}$  is now more intense, and a weak maximum at  $d = 2.32 \text{ \AA}$ , which is not seen for the observed data, also disappears in the simulations for the minimized arrays.

There is excellent agreement between the observed equatorial and layer line  $d$ -spacings and those predicted for the p.b.c. and aggregate models. We were not able to identify the 200 reflection in the region of  $d = 2.27 \text{ \AA}$ , which may be overlapped with its neighbours or lost among the subsidiary maxima that arise as a result of the small crystallite size. This maximum is relatively weak in the observed data. Similarly, the observed weak reflection on the third layer line at  $d = 3.11 \text{ \AA}$  cannot be resolved. Overall, it is striking that the maxima listed in *Table 1*, which match those observed, actually become more prominent after the refinement, probably because the fine detail predicted for the starting array is smoothed away. When we considered smaller models, we found that even an array of nine non-identical chains of six monomers minimized by the three-step aggregate method of Hofmann *et al.*<sup>18</sup> predicted the observed Bragg maxima. That on the first layer line at  $d = 3.11 \text{ \AA}$  was particularly prominent, and the strong maxima on the second and third layer lines could also be resolved. It appears that the features responsible for the Bragg reflections on the layer lines are fundamental to the arrangement of immediate neighbours.

We conclude that refinement by the aggregate method leads to much the same results as does the p.b.c. method: the final energies and the X-ray agreement are indistinguishable. Consequently, we need not be so concerned about the effect of the boundary in considering arrays of non-identical chains. Application of the p.b.c. condition requires a sacrifice when modelling the randomness, in that we must restrict ourselves to chains containing the same number of residues of each type. Even this is less

than perfect because there remain slight differences in the lengths unless we constrain the ester groups to be more symmetrical and restrict the selection of torsion angles. Consequently the value of the p.b.c. refinement is felt more in the lateral directions. Even the simple minimization model is useful for comparison of models, if one accepts that a certain amount of contraction will occur. We minimized the energy of a number of smaller models by the simple method in order to compare structures with different sequences, different starting conformations and different  $x, y$  positions for the same set of chains. Arrays of 24 non-identical chains of nine monomers (without restriction to equal numbers of monomers of each type) minimized to energies in the range of 1550–1608 kcal mol<sup>-1</sup>, suggesting that these are just a few of the very large number of subsidiary minima that can occur for such arrays. These results parallel the earlier work on copoly(HBA/HNA), where energy minimization for a number of arrays of 19 chains of 12 monomers with different sequences and starting conformations all led to structures that had energies in a relatively narrow range, and that were also compatible with the X-ray data. Given that the copoly(HBA/BP/TPA) structure is  $\sim 400^\circ\text{C}$  below  $T_m$  and  $\sim 250^\circ\text{C}$  below the  $\alpha$  transition ( $T_g$ ),<sup>25</sup> it is possible that the as-spun fibres contain a large number of these different local minima with almost the same energies. It seems unlikely that there will be a large energy difference between these and the actual global minimum, but the latter may somehow have optimal packing that minimizes the torsional distortions and maximizes the dipole–dipole interactions. Such optimization would be expected to be the result of prolonged thermal annealing, which is known to increase the degree of crystallinity and lateral crystallite size.

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