BUTTERWORTH HEINEMANN

Polymer Vol. 36 No. 26 pp. 5027–5034, 1995

0032-3861/95/$10.00+0.00

Three-dimensional structure of a wholly aromatic copoly(ester carbonate)

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(Received 10 January 1995)

The three-dimensional structure of the thermotropic copoly(ester carbonate) comprised of *p*-hydroxybenzoic acid (HBA), hydroquinone (HQ) and carbonate units has been investigated by X-ray methods, focusing on the copolymer containing a 75/25 HBA/HQ mole ratio. The fibre diagrams contain non-periodic layer lines, and we have previously shown that these arise from a structure consisting of arrays of parallel chains with a completely random comonomer sequence. The chains have highly extended conformations, in which the carbonate groups are distorted from the minimum-energy planar structure, such that the 1,4-axes of the phenylene groups are all approximately parallel to the fibre axis. The X-ray data also contain a number of sharp equatorial and off-equatorial Bragg maxima due to the presence of three-dimensional order. We have first addressed the determination of the structure by calculation of the cylindrically averaged intensity transforms of single chains averaged over all possible sequences. We then considered the interference effects due to packing of the copolymer chains. The results show that the planes of successive phenylene rings, linked either by ester or carbonate groups, are mutually inclined by $\sim 60°$. This leads to a pseudo-dimer repeat unit, which explains the existence of the layer line at $Z = 1/13.1$ Å, between the equator and the first observed meridional maximum. The off-equatorial maxima are predicted when we require that short, random segments form 'crystallites' by registration of the central monomer units. This registration is relatively minimal, in that there is a distribution of the centre of the sequences about the registry plane, with a standard deviation of ~ 1 Å. It is seen that copoly(ester carbonate) chains with distorted carbonate groups can pack in a more ordered structure than is possible in the wholly aromatic copolyesters prepared from HBA and 2-hydroxy-6-naphthoic acid (HNA).

(Keywords: copoly(ester carbonate); three-dimensional structure; X-ray fibre diagrams)

INTRODUCTION

This paper continues our analysis[1] of the solid-state structure of a thermotropic liquid crystalline copoly(ester carbonate) prepared from *p*-hydroxybenzoic acid (HBA) and hydroquinone (HQ), with the addition of necessary carbonate units. The bulk properties of these copolymers are sensitive to relatively small changes in the monomer composition[2] and are similar to those of wholly aromatic copolyesters[3]. Their X-ray fibre diagrams are also similar to the data described previously for copoly(HBA/2-hydroxy-6-naphthoic acid (HNA))[4–6] and copoly(HBA/terephthalic acid/2,6-dihydroxynaphthalene)[7]. *Figure 1* shows the diffraction patterns obtained from melt-drawn fibres of the copoly(ester carbonate) prepared with an HBA/HQ mole ratio of 75/25. These data point to a high degree of molecular orientation parallel to the fibre axis, and the existence of equatorial and off-equatorial Bragg reflections requires the existence of three-dimensional order. The layer lines are non-periodic, similar to those observed for thermotropic wholly aromatic copolyesters[4–7], for which the data are reproduced by structures consisting of arrays of extended chains with a completely random sequence. The first meridional maximum occurs at $d = 6.47$ Å, which is significantly different from the value of d of 6.35 Å which is observed for the homopolymer, poly(HBA), and corresponds approximately to the average advance per phenylene unit along the chain-axis direction.

Analysis of the three-dimensional structure of the copoly(ester carbonate) presents an intriguing problem in that the minimum energy conformation for an isolated chain has *trans-,trans*-carbonate groups, leading to highly non-linear chains, which would be likely to have significant packing problems in the solid state. However, we have shown[1] that the positions and approximate intensities of the non-periodic meridional intensity maxima are predicted for an array of parallel extended chains containing conformationally distorted carbonate units, in which the 'kinks' are partially removed, thus leading to approximately linear chains. The crystallinity, as measured by traditional X-ray methods for semi-crystalline polymers, is around 50% for the as-drawn fibres. This suggests a relatively high degree of three-dimensional order, which is perhaps remarkable when one considers that the copolymer chains have random sequences.

In the work described above, the intensity along the fibre axis (meridional) direction was predicted[1] by

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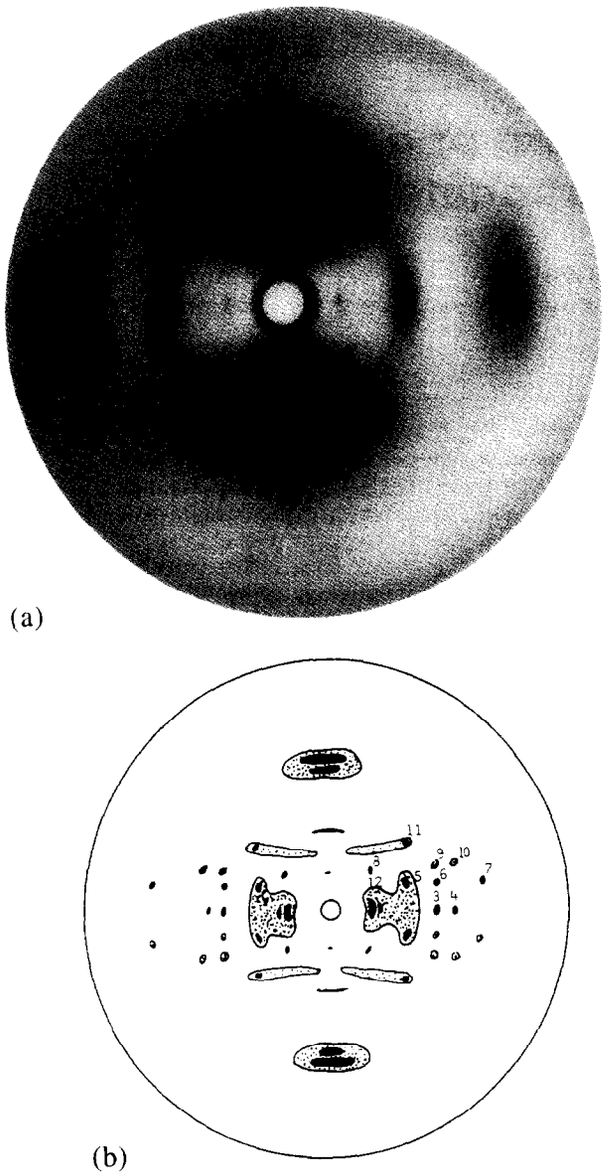

Figure 1 (a) X-ray fibre pattern for the 75/25 (HBA/HQ mole ratio) copoly(ester carbonate) with the fibre axis perpendicular to the beam direction. (b) Diagram of the same data

considering the one-dimensional structure, i.e. the projection of the structure on to the chain axis. We have now extended these simulations to consider the three-dimensional structure. First, we have calculated the cylindrically averaged intensity transform for a single chain of random sequence, and then considered the effects of chain packing on this function. Procedures to calculate the scattering by single chains and by three-dimensional arrays of packed chains were developed by Biswas and Blackwell[8-10], as steps towards determining the three-dimensional structure of the HBA/HNA copolyester. This paper describes analysis of the structure of the copoly(ester carbonate) by using a similar approach.

MODEL BUILDING AND DIFFRACTION SIMULATION

Scattering by a single infinite chain of random sequence

Chivers and Blackwell[9] derived expressions for the scattering by isolated chains of copoly(HBA/HNA) at two extremes of possible conformational variability. The first extreme is an extended conformation in which the mutual orientation of the planes of successive aromatic groups is random. Such a structure is modelled by the cylindrical averaging of each residue independently in real space. The cylindrically averaged intensity transform, $I(R, Z)$ can be written as follows:

$$I(R,Z) = \sum_{A} p_A F_{AA}(R,Z) + 2\,\mathrm{Re}\sum_{A}\sum_{B} p_A F_{AB}(R,Z) \times \frac{M_{AB}\exp(2\pi i Z z_B)}{1 - M_{AB}\exp(2\pi i Z z_B)} \quad (1)$$

where R and Z are the radial and axial coordinates, respectively, in reciprocal space, p_A is the fractional molar proportion of monomer A, M_{AB} is the probability that monomer A is followed by monomer B, and z_B is the axial advance for monomer A where Re represents the *real* component. To allow for non-linearity of the chain, $\exp(2\pi i Z z_B)$ in equation (1) is replaced by $p_{B_j}\exp(2\pi i Z z_{B_j})$, where p_{B_j} is the fraction of residue B with the axial advance z_{B_j}. For a continuous (infinite) chain, M_{A_j} (where j = A, B ...) must be unity. M_{AB} and $F_{AB}(Z)$ are expressed as follows:

$$M_{AB} = \frac{r_{AB}\,p_B}{\sum_j r_{A_j}\,p_j}$$

Here, $r_{AB} = 1$ for allowed combinations in random sequences, and deviates from unity depending on the statistics of non-random sequences; $r_{AB} = 0$ (and hence $M_{AB} = 0$) when the A–B combination is chemically excluded. When there is cylindrical averaging of each monomer in real space we obtain the following:

$$F_{AB}(R,Z) = \sum_j \sum_k f_{A_j} f_{B_k} J_0(2\pi R r_{A_j}) J_0(2\pi R r_{B_k}) \times \exp[2\pi i Z(z_{B_k} - z_{A_j})] \quad (2)$$

where J_0 is the zeroth-order Bessel function for the argument specified, r and z are real space atom coordinates, and the subscripts A_j and B_k denote the jth atom of monomer A and the kth atom of monomer B.

The second extreme is a rigid conformation in which the mutual orientations of successive aromatic units are fully defined. In this case, $I(R, Z)$ is derived by cylindrical averaging of the three-dimensional intensity transform in reciprocal space: $F_{AB}(R, Z)$ in equation (1) is now:

$$F_{AB}(R,Z) = \sum_j \sum_k f_{A_j} f_{B_k} J_0(2\pi R r_{A_j B_k}) \times \exp[2\pi i Z(z_{B_k} - z_{A_j})] \quad (3)$$

where $r_{A_jB_k}$ is the distance between the projections on the jth atom in monomer A and the kth atom in monomer B on to the xy plane. The intensity along the meridian, $I(0, Z)$, is the same for both models, since they have the same coordinates in the chain-axis direction (z).

The data for the poly(ester carbonate), as with those for poly(HBA/HNA), indicate that the chains are packed

in a two-dimensional orthorhombic unit cell. This cell contains two chains passing through the centre and corner, which are staggered by one monomer unit, such that there is a herringbone packing of the monomers on adjacent chains and an approximate body-centred structure. This is achieved by having a chain conformation in which the planes of successive aromatic units are mutually inclined by $\sim 60°$, although the simulations of the X-ray scattering for poly(HBA/HNA)[8–10] suggest that these orientational correlations are maintained over only a few monomers along the chain axis. Consequently, the actual structure is intermediate between the two conformational extremes treated above.

Three-dimensional arrays of packed chains

Biswas and Blackwell[10] showed that the intensity scattered by a bundle of parallel chains can be separated into intra- and interchain components:

$$I(R,Z) = I_1(R,Z) + I_2(R,Z) \tag{4}$$

The intrachain component is given by:

$$I_1(R,Z) = mI_a(R,Z) \tag{5}$$

where m is the number of chains and $I_a(R,Z)$ is the interference between monomers of the same chain, given by:

$$I_a(R,Z) = \sum_{\mathrm{A}} p_{\mathrm{A}} F_{\mathrm{AA}}(R,Z) + 2\,\mathrm{Re}\sum_{\mathrm{A}}\sum_{\mathrm{B}} F_{\mathrm{AB}}(R,Z)T_{\mathrm{AB}}(Z) \tag{6}$$

in which N is the number of monomers in the chain. The $F_{\mathrm{AB}}(R,Z)$ terms are as defined above, and $T_{\mathrm{AB}}(Z)$ is a component of the matrix $\mathbf{T}(Z)$:

$$\mathbf{T}(Z) = \mathbf{P}\left[\frac{\mathbf{H}(Z)}{\mathbf{I}-\mathbf{H}(Z)} - \frac{\mathbf{H}(Z)[\mathbf{I}-\mathbf{H}^N(Z)]}{N[\mathbf{I}-\mathbf{H}(Z)]^2}\right] \tag{7}$$

where $\mathbf{I}$ is the unity matrix and $\mathbf{H}(Z)$ is a matrix with components $H_{\mathrm{AB}}(Z)M_{\mathrm{AB}}\exp(2\pi i Z z_{\mathrm{B}})$.

The interchain component, $I_2(R,Z)$, for a system with no rotational correlation between monomers on adjacent chains, is given by the following[10]:

$$I_2(R,Z) = A(Z)I_b(R,Z)I_c(R) \tag{8}$$

where $A(Z)$ is the distribution function describing axial register:

$$A(Z) = \exp(-2\pi^2 Z^2 \sigma_b^2) \tag{9}$$

in which the standard deviation σ_b defines the probability that the origin atom of each chain will be on the register plane, as shown in *Figure 2*[11].

$I_c(R)$ describes the interference due to the packing on the basal plane. As will be seen below, the chains are packed on an orthorhombic lattice with dimensions $a = 8.88$ Å and $b = 4.98$ Å, which contains two chains with their axes passing through $(0,0)$ and $(0.5,0.5)$. However, it has been convenient to use a one-chain unit cell, treating the two chains as though they were identical. For this, we have defined an orthorhombic unit cell with dimensions $a = 4.44$ Å and $b = 2.49$ Å, in which the array of chains has m_1 repeats of a and m_2 repeats of b, with vacancies at $pa + qb$ when $p + q =$ odd

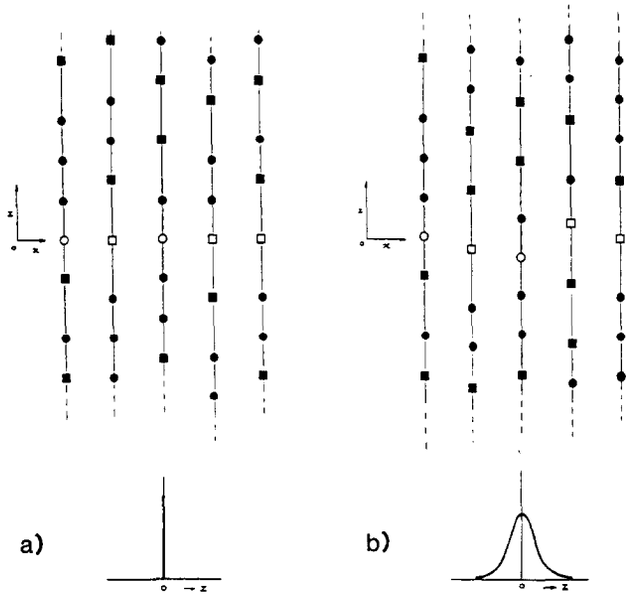

Figure 2 Schematic of registration of non-periodic chains of random sequence: (a) exact registration of a reference atom of the central monomer of finite chains; (b) preferred registration defined by the standard deviation σ_b (from ref. 10)

(where p, q are integers). $I_c(R)$ is given by:

$$I_c(R) = \sum_{p=0}^{m_1-1}\sum_{q=0}^{m_2-1}(m_1-p)(m_2-q) \times J_0(2\pi R(p^2a^2+q^2b^2)^{1/2});\ p+q = \text{even} \tag{10}$$

$I_b(R,Z)$ is the interchain interference function and is given by a series of equations analogous to those derived previously for the copoly(HBA/HNA) system, in which all monomer pairs are allowed[12]. The latter equations have been modified for copolymers in which certain monomer pairs are chemically disallowed. The expressions used in the present work are as follows:

$$I_b(R,Z) = \mathrm{Re}\left(\sum_{\mathrm{A}}\sum_{\mathrm{A}'} p_{\mathrm{A}}p_{\mathrm{A}'}\left(F_{\mathrm{AA}'} + \sum_{\mathrm{B}'}F_{\mathrm{AB}'}K^*_{\mathrm{A}'\mathrm{B}'} + \sum_{\mathrm{B}}F_{\mathrm{BA}'}K_{\mathrm{AB}} + \sum_{\mathrm{B}}\sum_{\mathrm{B}'}F_{\mathrm{BB}'}K_{\mathrm{AB}}K^*_{\mathrm{A}'\mathrm{B}'}\right)\right) \tag{11}$$

where * designates the complex conjugate; A,A′ are the zeroth monomers in the first and second chains, respectively, while B,B′ are the first monomers in these chains. K_{AB} is given by:

$$K_{\mathrm{AB}} = \frac{H_{\mathrm{AB}}^{N-1}}{1-H_{\mathrm{AB}}} \tag{12}$$

where

$$H_{\mathrm{AB}} = M_{\mathrm{AB}}\exp(2\pi i Z z_{\mathrm{A}}) \tag{13}$$

EXPERIMENTAL

X-ray fibre diagrams were recorded on Kodak Direct Exposure scientific imaging film using a Searle toroidal

Table 1 Atomic coordinates for the various components of the copoly(ester carbonate)

Component	Coordinates (Å)		
	x	*y*	*z*
HBA			
O(ester)	0.00	0.00	0.00
O(carbonyl)	0.02	2.24	0.31
C(carbonyl)	0.00	0.30	4.97
C	0.21	0.75	4.07
C	0.22	0.50	2.69
C	0.02	0.80	2.22
C	0.18	1.84	3.12
C	0.20	1.60	4.49
C	0.01	1.14	0.77
O(ester)	0.00	0.00	6.35
HQ			
O	0.00	0.00	0.00
C	0.00	0.03	1.38
C	0.00	1.23	2.11
C	0.00	1.20	3.49
C	0.00	0.01	4.16
C	0.00	1.20	3.44
C	0.00	1.18	2.05
O	0.00	0.00	5.54
Carbonate unit			
O	0.00	0.00	0.00
C	0.00	1.13	0.68
O(carbonyl)	0.85	1.99	0.63
O	1.09	1.16	1.43

focusing camera and Ni-filtered CuKα radiation, with the fibre axis direction perpendicular to the beam. The *d*-spacings were calibrated using CaF_2.

The atomic coordinates for the HBA, HQ and carbonate units are given in *Table 1*. Both terminal ester oxygens are included in each case. These were given a weight of one half in the calculation of the $F_{AB}(R, Z)$ terms. The chains constructed from these monomers are not completely straight, and the monomer advance along the chain-axis direction is defined by a relatively narrow distribution about an average of the length of the *z*-axis projection of the ester oxygen–ester oxygen vector. In our previous work[1], we obtained a good match between observed and simulated meridional intensity data using average axial advances for HBA and HQ of 6.25 and 5.44 Å, respectively, and a Gaussian distribution with a standard deviation of $\sigma = 0.1$ Å. For the carbonate unit an average advance of 1.61 Å and a σ value of 0.5 Å were used, corresponding to a distorted carbonate with deviations from the all *trans*-,*trans*-conformation of 40° for each of the two O–CO torsion angles. The F_{AB} terms vary only very slowly with changes in the monomer orientation (with respect to *z*), and the computed values using the coordinates for fully extended monomers were taken as adequate approximations for all axial advances.

In order to be able to define the orientation of successive phenylenes, the chain was redefined as a sequence of three chemical moieties, each composed of a *p*-phenylene unit but followed by either an 'up-ester' (PE), a 'down-ester' (PF), or a carbonate group (PC), as shown in *Figure 3*. In the present copoly(ester carbonate), 75% of the linkages are ester groups and 25% are carbonates. Since we can reasonably assume an equal probability for 'up' and 'down' ester groups in any chain, $p_{PE} = p_{PF} = 0.375$ and $p_{PC} = 0.25$. From these three

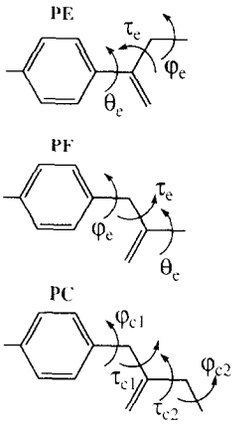

Figure 3 Phenyl ester and phenyl carbonate monomer units: (a) PE; (b) PF; (c) PC

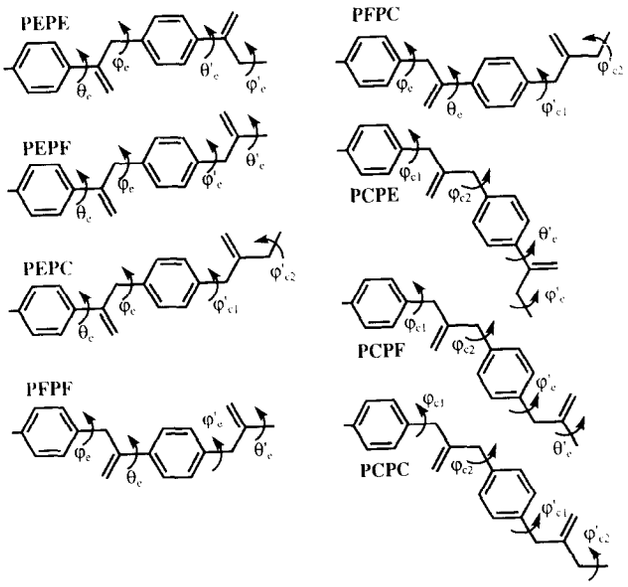

Figure 4 The eight dimers of the copoly(ester carbonate) system

moieties, eight possible 'dimers' can be defined, namely PEPE, PEPF, PEPC, PFPF, PFPC, PCPE, PCPF and PCPC (*Figure 4*) with the following compositions: $p_{PEPE} = p_{PFPF} = 22.5\%$, $p_{PCPC} = 4\%$, $p_{PEPC} = p_{PCPF} = 6\%$, $p_{PFPC} = p_{PCPE} = 15\%$, and $p_{PEPF} = 9\%$.

For the ester linkages, the phenyl–carbonyl torsion and ester–phenyl angles, θ_e and ψ_e, were set at 0° and ±60°, respectively, where zero torsion angles correspond to planarity. For the carbonate groups, the angles φ_{c1} and φ_{c2} were set to ±30°, in order to obtain approximately linear conformations, consistent with our previous work[1]. The conformation angles for the eight dimers were those given in *Table 2*. These conformations have the planes of successive phenylene rings inclined at ~60° to each other, and this alternation is maintained along the chains regardless of sequence. Other dimer conformations are compatible with this mutual inclination of the phenylenes, but the differences are small, involving, for example, a 180° rotation of the plane of the ester group. Their inclusion would probably have only a

Table 2 Torsion angles defining the dimer conformations

Dimer	Conformation angle (°)
PEPE PFPF PEPF	$(\theta_e, \varphi_e, \theta'_e, \varphi'_e) = (0, 60, 0, -60)$
PEPC	$(\theta_e, \varphi_e, \varphi'_{c1}, \varphi'_{c2}) = (0, 60, -30, -30)$
PFPC	$(\varphi_e, \theta_e, \varphi'_{c1}, \varphi'_{c2}) = (60, 0, -30, -30)$
PCPE	$(\varphi_{c1}, \varphi_{c2}, \theta'_e, \varphi'_e) = (30, 30, 0, -60)$
PCPF	$(\varphi_{c1}, \varphi_{c2}, \varphi'_e, \theta'_e) = (30, 30, -60, 0)$
PCPC	$(\varphi_{c1}, \varphi_{c2}, \varphi'_{c1}, \varphi'_{c2}) = (30, 30, -30, -30)$

minor effect, and the additional computation necessary was not merited. For these investigations, σ was set at 0.1 for ester–ester dimers and at 0.5 for dimers containing a carbonate group.

To simulate the diffraction from arrays of chains, we constructed models consisting of 168 chains of 13 dimers. Each chain is averaged over the sequence in the calculation of $I(Z)$, as described above. The average chain was constructed from the dimers listed in *Table 2*, with no rotational correlation between successive dimers, i.e. each *dimer* is cylindrically averaged. A pair of chains were packed in an orthorhombic unit cell with dimensions $a = 8.88$ Å and $b = 4.98$ Å, with the ester oxygen (or first carbonate oxygen) of the twelfth monomer in register at $z = 0$, and with their axes passing through $(0,0)$ and $(0.5, 0.5)$. A total of 84 such unit cells were arranged on a 7×12 lattice to give a crystallite with lateral dimensions ~ 60 Å $\times$ 60 Å. Sinuosity of the chains was modelled by incorporation of a distribution of axial projection lengths for the monomers, with standard deviation $\sigma = 0.1$ for PE and PF and $\sigma = 0.5$ for PC. The standard deviation describing the probability that an origin dimer will be on the reference plane, σ_b, was varied between $\sigma_b = 0$ Å and $\sigma_b = 5$ Å in steps of 0.5 Å; the nematic condition was simulated by taking $\sigma_b = 10$ Å. $I(R, Z)$ was calculated for one quadrant at 0.0025 Å^{-1} increments along the positive R- and Z-axes, respectively, within the range $(R^2 + Z^2)^{-0.5} = 0.5$ Å^{-1}. Four quadrants are displayed for comparison with the X-ray fibre diagrams. The calculated intensities between zero and a convenient cut-off value were put on a linear scale of 256 shades of grey (white = 0, black = 255); intensities higher than the cut-off were displayed as black, so as to allow us to focus on weaker intensities.

RESULTS AND DISCUSSION

The d-spacings and R, Z-coordinates of the observed Bragg reflections in the fibre diagram of the polyester carbonate are given in *Table 3*. The R-coordinates are indexed by a two-dimensional orthorhombic unit cell, with dimensions $a = 8.88 \pm 0.05$ Å and $b = 4.98 \pm 0.05$ Å, which contains the projections of two chains. The equatorial reflections are indexed by a one-chain unit cell. The two-chain unit cell is required by the layer line reflections. If we assign l as the number of the layer line, then we have an approximately body-centred structure with $h + k + l =$ odd being systematically absent. As was the case for copoly(HBA/HNA)[8,15] the

Table 3 Assigned hk indices and d-spacings for the observed Bragg reflections plus comparison of observed and calculated radial reciprocal space coordinates

hkl[a]	d_{obs} (Å)	$1/R_{obs}$[b] (Å^{-1})	$1/R_{calc}$ (Å^{-1})
200	4.44	4.44	4.44
110	4.34	4.34	4.34
020	2.48	2.48	2.49
400	2.25	2.25	2.22
210	3.21	3.28	3.31
020	2.44	2.48	2.49
320	1.91	1.93	1.91
112	3.65	4.35	4.34
312	2.45	2.59	2.56
402	2.11	2.22	2.22
213	2.63	3.31	3.31

[a] l corresponds only to the 'number' of the layer line
[b] $R_{obs} = (1/d^2_{obs}) - (1/z^2_{obs})$

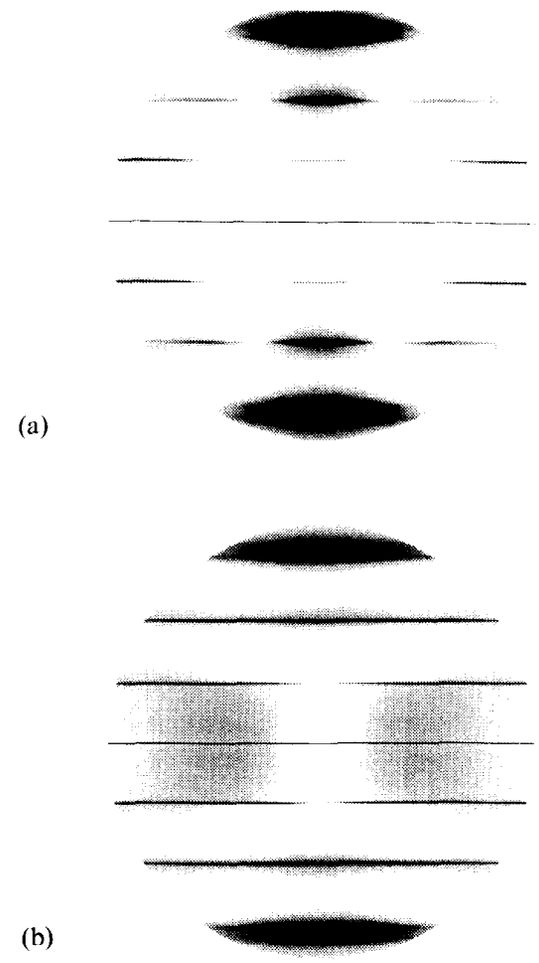

Figure 5 Predicted scattering by infinite chains constructed of monomers: (a) random model; (b) rigid model

first layer line at $d = 13.1$ Å requires a 'repeat' involving two aromatic units along the chain. It appears that the structure for the copoly(ester carbonate) is similar to that for copoly(HBA/HNA), with successive aromatic units inclined to each other and adjacent chains staggered by one monomer, such that there is a herringbone packing of the aromatic rings.

In our initial simulations (*Figure 5*), we predicted the

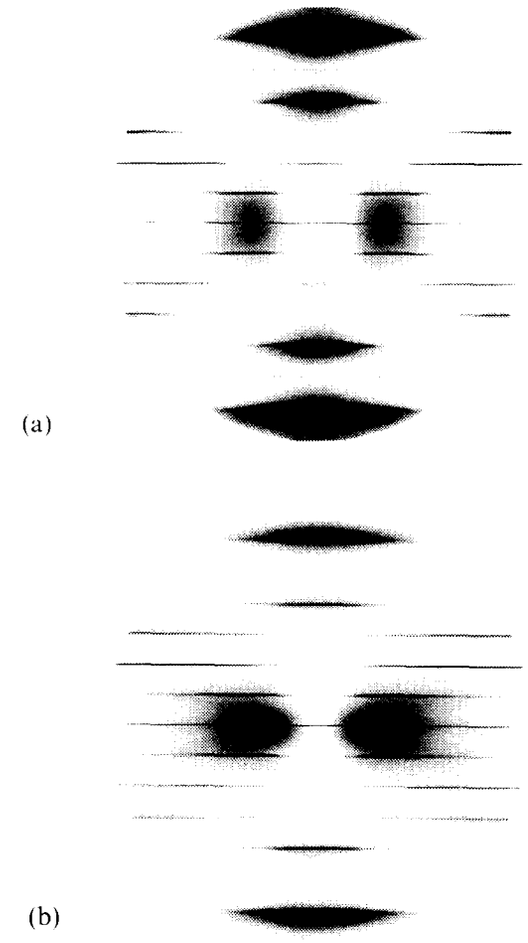

Figure 6 Predicted scattering by infinite chains constructed of rigid dimers: (a) random model; (b) rigid model

scattering by single infinite chains constructed from random sequences of HBA, HQ and carbonate monomers. The data for random and rigid models contained layer lines that are extensions of the meridional maxima at $d = 6.49$, 3.22, 2.14 and 2.04 Å^{-1}. To some extent we can say that the random model (with free torsional rotation of the individual monomers) gave better agreement, in that the calculated intensity on the second layer line is concentrated towards the meridian rather than off the meridian in the case of the rigid model.

To obtain the intermediate layer lines, it is necessary to utilize models constructed using the dimers given in *Table 2*. *Figure 6* shows the cylindrically averaged intensity transforms for the two models: in the random model the phenylene units of each dimer are mutually inclined at $\sim 60°$, but there is no correlation between the torsional orientation of successive dimers; in the rigid model, the alternating 60° mutual inclination of successive phenylenes is maintained along the entire chain. It can be seen that both models predict the observed odd layer lines and that these are weak on the meridian. In any case, meridional intensities for l = odd would be essentially eliminated as a result of the approximately body-centred structure. For both models, the first layer line is predicted to be strong in the region of the observed reflection at $d = 3.21$ Å. However, the random dimer model gives qualitatively the better agreement overall, in that the intensity on the second layer line is concentrated on the meridian, whereas the rigid model leads to a stronger intensity off the meridian. Thus, while there is a definite preference for a dimer repeat via $\sim 60°$ mutual orientation of successive phenylenes, these correlations break down relatively rapidly as one proceeds further along the chain. This is not at all surprising, given the problems that must occur in packing random sequences. In the work on arrays of chains which is described below, we have limited our simulations to models containing the random dimer conformation.

Our investigation of the three-dimensional structure of the poly(ester carbonate) has centred on the determination of σ_b, which defines the deviation from registration of the central ester oxygen of adjacent chains. For this work we have effectively used a one-chain unit cell, and have varied σ_b to determine the condition necessary for Bragg sampling on the first three layer lines. At $\sigma_b = 0$, Bragg sampling occurs on all layer lines, and is eliminated progressively as σ_b increases. This investigation of disorder along the chain-axis direction is unaffected by the choice of the two-dimensional (ab) unit cell. The copoly(ester carbonate) unit cell contains two chains arranged with a herringbone packing, analogous to the structure of poly(HBA/HNA). However, the simulation methods applied to poly(HBA/HNA), in which there are only four possible dimers, become much more time consuming for the poly(ester carbonate) with eight possible dimers, and the only gain would be cosmetic, in that the calculated data would reproduce the Bragg reflections of the approximately body-centred structure: when we use the one-chain model, the Bragg reflections fall on row lines for the primitive lattice.

Figure 7a shows the calculated diffraction pattern for a columnar array of 168 chains, each of 13 dimers; adjacent chains were identical, i.e. there was no herringbone packing, and there was no axial registration, which was simulated by $\sigma_b = 10$ Å. Bragg maxima are predicted on the equator, and the layer lines are continuous, as is to be expected. A model with all sequences registered at the central ester oxygen was simulated by setting $\sigma_b = 0$. This yielded the data shown in *Figure 7b*, where we see Bragg sampling on all layer lines. The row lines have reflections on every layer line because in this model we have a one-chain unit cell. Otherwise, the main difference between *Figure 7b* and the observed data is that, in the latter, Bragg reflections occur only on the first three layer lines: the outer layer lines are continuous streaks. This indicates less than perfect register at the centre of the ordered layer, which was explored by varying σ_b in increments of 0.5 Å from 0 to 5 Å (*Figure 8*). For $\sigma_b \geq 3$ Å sampling occurs only on the first layer; at $\sigma_b = 2$ Å we see sampling on the first and second layers. Peaks appear on the third layer line in the range $\sigma_b = 1.0$–1.5 Å. At lower values of σ_b we obtain sampling on higher layer lines which are continuous in the observed data. At $\sigma = 1.5$ Å, the reflection at $d = 2.63$ Å is predicted to be relatively weak and diffuse, in contrast to the sharp observed reflection, and on this basis a value of σ_b should be closer to 1.0 Å. At this value, σ_b is approximately the same as the difference in length between the PC and PE units (0.8 Å). Consequently, the poly(ester carbonate) structure should be viewed as an array of parallel chains

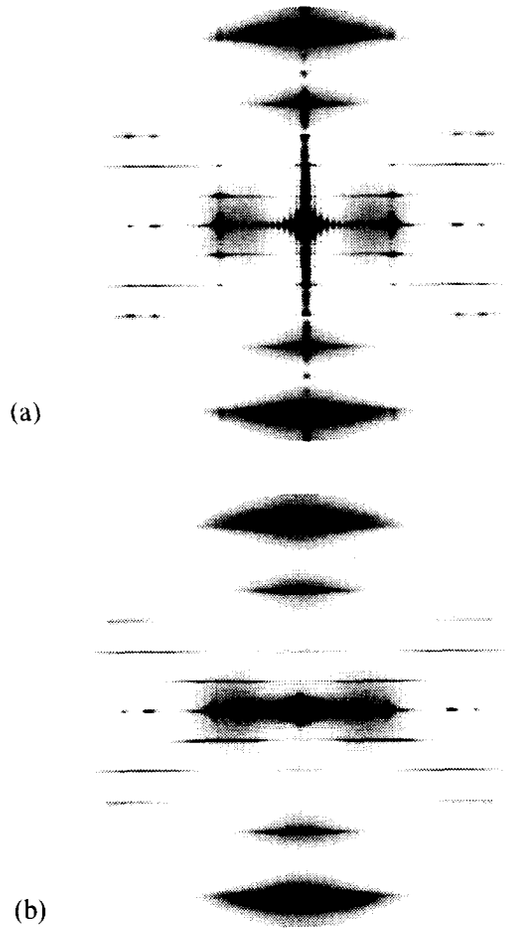

Figure 7 Predicted X-ray diffraction for an array of 168 chains of 13 dimers: (a) $\sigma_b = 0$; (b) $\sigma_b = 10$ Å

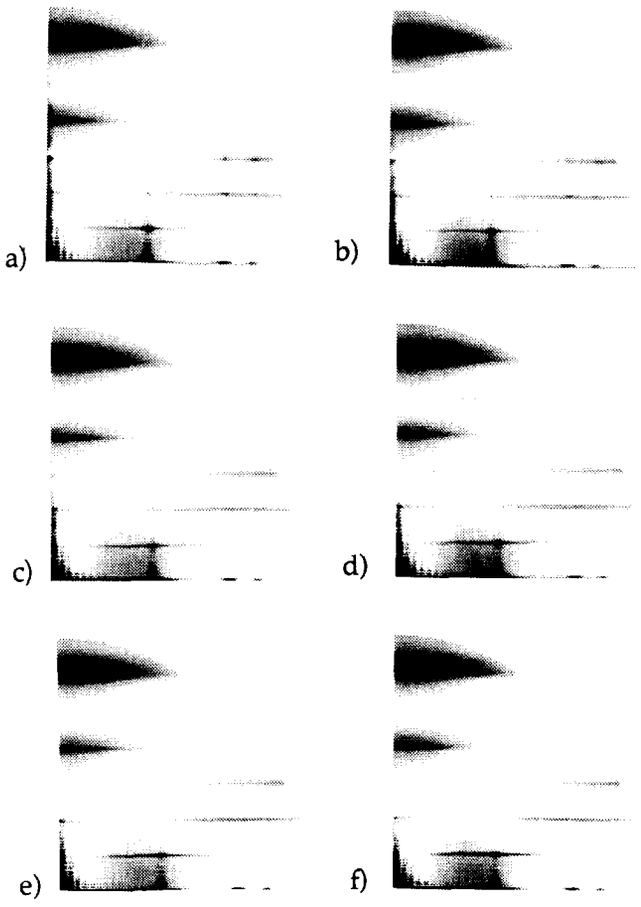

Figure 8 Predicted X-ray diffraction patterns for arrays of 168 chains of 13 dimers in a herringbone packing for varying values of σ_b: (a) 0.5; (b) 1.0; (c) 1.5; (d) 2.0; (e) 2.5; (f) 3.0 Å

that are arranged so as to maximize the overlap of the aromatic rings.

Perhaps the most striking feature of the observed diffraction pattern of the copoly(ester carbonate) is that it indicates that the structure is considerably more ordered than that found for 75/25 copoly(HBA/HNA). At this monomer ratio, copoly(HBA/HNA) contains a similar number of defects to that of the present copoly(ester carbonate), where there is a ratio of 75/25 of ester and carbonate linkages. When distorted from the *trans-,trans-* conformation, as necessitated by the extended conformation, the carbonate group results in an off-set of the backbone, analogous to that of the naphthalene unit. Nevertheless, the 'degree of crystallinity' for as-spun fibres is ~50% for the copoly(ester carbonate), compared to ~25% for copoly(HBA/HNA). After thermal annealing, these figures increase to ~60% and ~50%, respectively, which are closer, but the order in the copoly(ester carbonate) as judged by the sharpness of the Bragg reflections is still significantly better. In addition, $\sigma_b \sim 2$ Å for the as-spun copoly(HBA/HNA), giving us Bragg sampling only on the first layer line, compared to $\sigma_b \sim 1$ Å for the copoly(ester carbonates), for which we have sampling out to the third layer line.

Therefore, the higher order of the copoly(ester carbonate) arises from more perfect register of the random sequences in the ordered layers. The HNA monomers result in larger defects in the ordered packing of the chains than do the carbonate units, which is the opposite of what one probably would have expected if one assumed that the latter had the minimum-energy kinked conformation. When it is distorted, the phenyl-carbonate unit has an axial advance of 7.1 Å, which is much closer to the advance of 6.3 Å for HBA than is the 8.5 Å advance for the HNA units. *Figure 9* shows molecular models for the two copolymers: the chains have an approximate herringbone packing, and are fully registered at the centre ($\sigma_b = 0$) but the structures have not been optimized otherwise. Both models contain 19 different chains, each consisting of 8 aromatic units, with sequences chosen at random; the overall monomer compositions are 75/25 HBA/HNA and ester/carbonate, respectively. The visual impression is that the copoly(ester carbonate) is inherently more registered. We have performed molecular-mechanics energy minimization on these structures, the details of which will be described in a later paper. The preliminary conclusion is that the copoly(ester carbonate) structure looks like a distorted version of the homopolymer structure, which is definitely not the case for the arrays of chains of copoly(HBA/HNA).

ACKNOWLEDGEMENTS

This work was supported through the NSF Materials Research Group on Liquid Crystalline Polymers (DMR 91-22227).

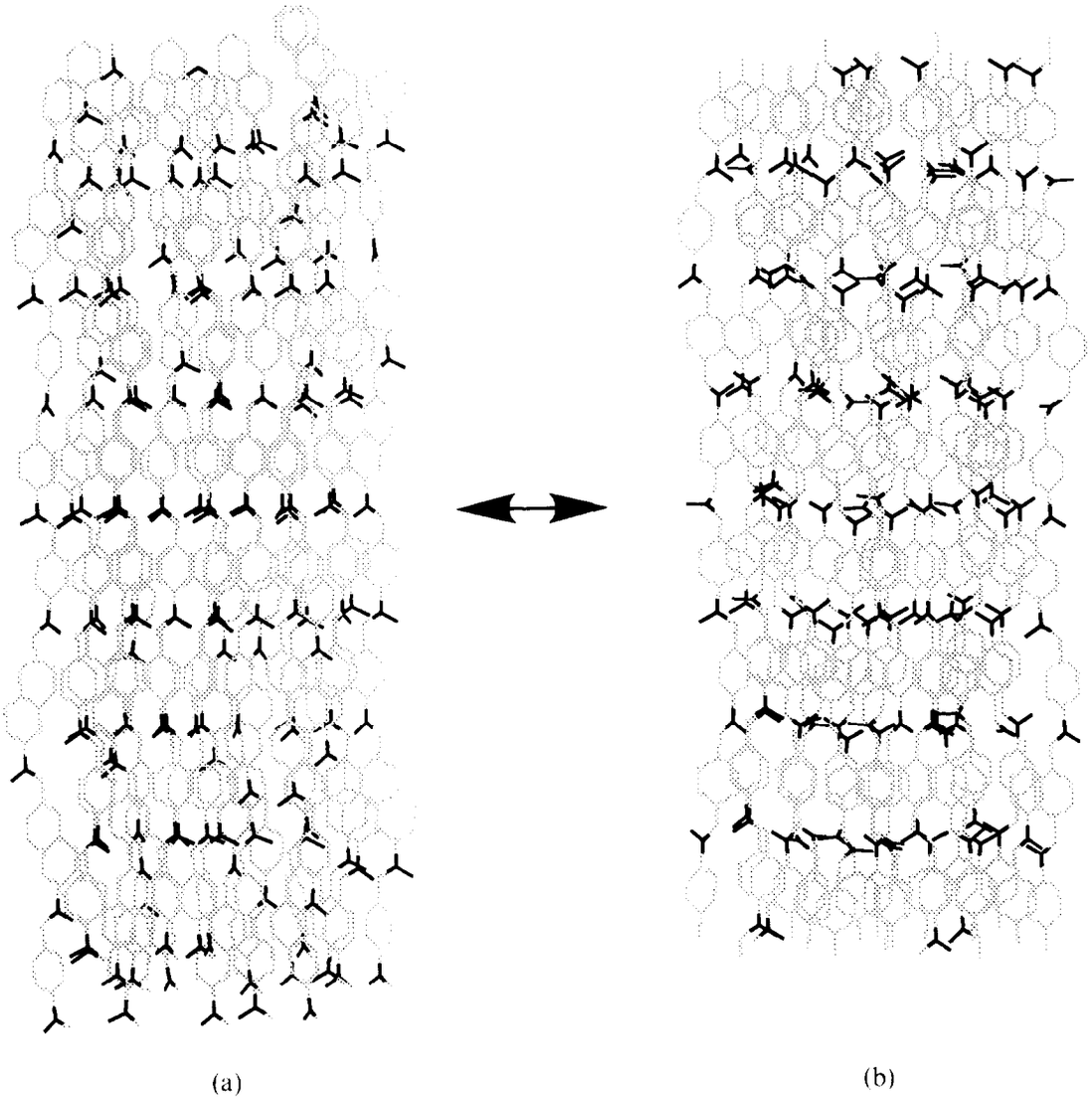

Figure 9 Molecular models of arrays of: (a) 75/25 copoly(HBA/HNA); (b) 75/25 HBA/HQ copoly(ester carbonate). The ester and carbonate oxygens are black; the register (origin) plane is marked with an arrow

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