# Structure Analysis of Copoly(ester carbonate)

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ABSTRACT: This paper summarizes our first analyses of the solid-state structure of a thermotropic aromatic copoly(ester carbonate) by wide-angle X-ray methods and electron microscopy (TEM). Results are presented for the copolymer prepared from *p*-hydroxybenzoic acid, hydroquinone, and biphenyl carbonate: in the resultant copoly(ester carbonate), 1,4-phenylene units are linked either by ester or carbonate groups, in the ratio 75/25, respectively. The X-ray patterns for as-spun fibers show a number of Bragg reflections on the equator and the layer lines, pointing to the existence of three-dimensional order. Similar data are obtained in electron diffraction patterns of melt-sheared films. Dark-field images of these films reveal ordered regions that are ~170 Å in length (along the chain axis) and up to 950 Å in transverse width. The layer lines in the diffraction data are nonperiodic, analogous to those reported previously for wholly aromatic copolyesters, where they are explained by a structure consisting of extended chains of a completely random comonomer sequence. Molecular models of random sequences of the copoly(ester carbonate) are inherently nonlinear and present obvious problems for packing in the solid state. The predicted X-ray data for arrays of such chains, including those with a significant nonrandom sequence, are in poor agreement with those observed and point to a more extended conformation, which requires distortion from the minimum energy conformation for an isolated chain. The most likely distortions are in the bond angles and torsion angles of the carbonate groups, and it is shown that this kind of distortion leads to good agreement with the X-ray data, as well as improved packing.

## Introduction

This paper describes the analysis of the solid-state structure of a thermotropic copoly(ester carbonate) by X-ray diffraction and electron microscopy. The copolymer studied is a member of a group of wholly aromatic main-chain thermotropic copolyesters prepared from *p*-hydroxybenzoic acid (HBA) and similar monomers. The homopolymer of HBA is a crystalline, infusible, and largely intractable material, but the presence of a comonomer such as 2-hydroxy-6-naphthoic acid (HNA) introduces defects into the structure and leads to a lowering of the melting point by as much as 300 °C. Here melting refers to a solid state to nematic transition: copoly(HBA/HNA) inevitably has an extended conformation due to the linkage geometry, and the chains are aligned parallel in the melt. The liquid crystallinity makes it possible to process high-strength fibers by melt spinning and also leads to applications as precision moldings.

The copolyester carbonate that is the subject of this paper is prepared from HBA and hydroquinone (HQ), with the introduction of the necessary carbonate groups,[1] and it is the latter groups that serve as the defect units. Analyses of the thermal and mechanical properties have been reported elsewhere for a copolymer prepared from HBA (52 mol %), HQ (21 %), terephthalic acid (TPA; 2 %), 4,4′-dihydroxybiphenyl (BP; 3 %), and diphenyl carbonate (DC; 22 %).[2-4] The reaction is a polycondensation, first in the melt and then in the solid state. This copolymer was produced by Bayer AG, and the small quantities of TPA and BP were introduced in order to modify the glass transition and melting temperatures. However, these minor components complicate the structure analysis, and for this reason we have studied the simpler copolymer, prepared from HBA, HQ, and BC at five comonomer ratios. The copolymer containing the highest mole percentage of HBA (60%, corresponding to 75/25 HBA/HQ) was the most crystalline and is the subject of the present paper.

As will be seen below, the X-ray data for the 75/25 copoly(ester carbonate) are similar to those for the wholly aromatic copolyesters such as copoly(HBA/HNA)[5-7] and copoly(HBA/TPA/2,6-dihydroxynaphthalene).[8] The fiber diagrams show that the melt-drawn specimens have a high degree of molecular orientation, and the existence of equatorial and off-equatorial Bragg reflections point to the existence of a three-dimensional order. The layer lines are found to be nonperiodic, as was the case for the wholly aromatic copolyesters, for which we showed that the data are predicted for structures consisting of arrays of extended chains of a completely random sequence. However, in the copoly(ester carbonate), the presence of the carbonate groups might be expected to have "kinked" conformations, leading to nonlinearity of the chains and thereby to serious problems in packing of the chains. The interpretation of the X-ray data in terms of the comonomer sequence and chain conformation is addressed below.

## Materials and Methods

**Synthesis.** The copoly(ester carbonate) was synthesized from hydroxybenzoic acid, hydroquinone, and diphenyl carbonate. The copolymer was prepared by melt synthesis, with removal of phenol by distillation. For example, HBA (341.6 g, 2.475 mol), HQ (90.8 g, 0.825 mol), DC (720.3 g, 3.366 mol), and magnesium oxide (0.23 g) as a catalyst were mixed in a reaction vessel with a stirrer, column, and distillation bridge. The reaction vessel was heated to 180 °C over the course of 15 min: evolution of $CO_2$ began at 160 °C. The temperature was kept constant for 60 min, after which it was raised to 200 °C and kept constant until evolution of $CO_2$ was completed.

The mixture was then heated to 250 °C, and the pressure in the reactor was lowered stepwise to 30 mbar. After 1 h, distillation had slowed down greatly, and the reaction temperature was raised

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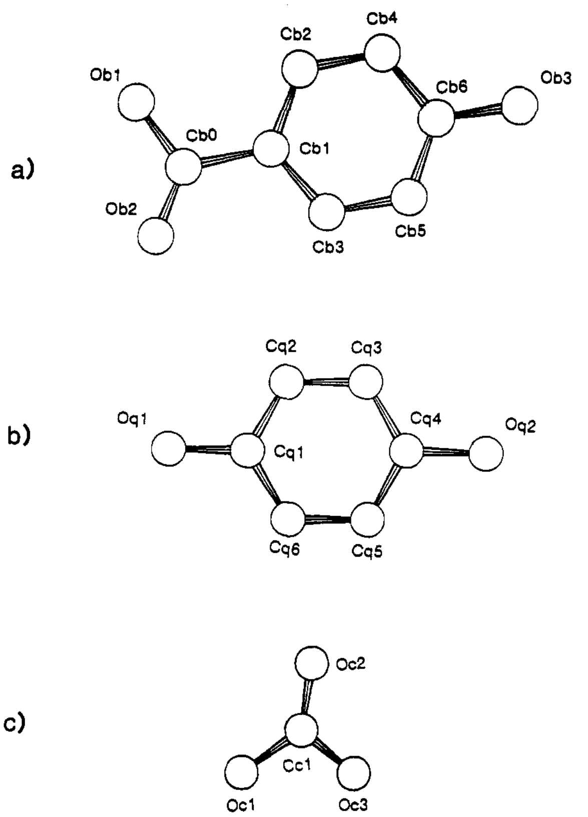

**Figure 1.** Monomer residues: (a) *p*-hydroxybenzoate (HBA), (b) hydroquinone (HQ), (c) carbonate unit (CO).

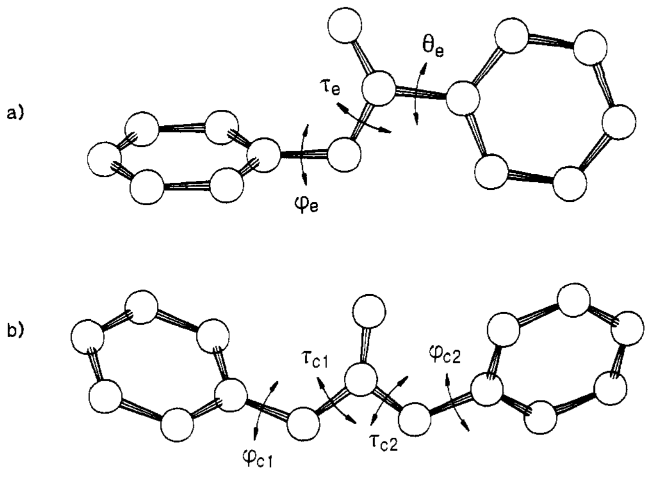

**Figure 2.** Torsion angles for (a) phenyl benzoate and (b) *trans,-trans*-diphenyl carbonate.

to 275 °C and finally to 300 °C. After the elimination of phenol had almost ceased, the pressure in the reactor was reduced to 0.2 mbar, and the reaction was terminated after a further 1 h under these conditions. The product was highly viscous in the melt: in the solid state it had a fibrous texture and was beige in color. The weight-average molecular weight was approximately 29 000, as determined by GPC using 3,5-bis(trifluoromethyl)phenol as the solvent.

**X-ray Diffraction.** Fibers were drawn by hand from the molten polymer on a hot stage and prepared as parallel bundles. X-ray fiber diagrams were recorded on Kodak No-Screen film using a Searle toroidal focusing camera and Ni-filtered Cu K$\alpha$ radiation. The *d*-spacings were calibrated by using CaF$_2$. Meridional data were also recorded as a $\theta/2\theta$ on a Philips PN 3550/10 *diffractometer in the transmission mode with a constant slit* width.

**Electron Microscopy.** Thin films for electron microscopy were sheared from the melt between glass slides at a temperature of about 410 °C on a hot stage. The films were removed from the glass by using dilute aqueous hydrofluoric acid, mounted on copper grids, and imaged by a Philips EM 400 transmission electron microscope (TEM). Electron diffraction patterns were obtained by using the SAED technique at a camera length of 720 mm. Dark-field images were created by using the innermost equatorial reflections at an acceleration voltage of 100 kV.

**Table I**
**Atomic Coordinates for the HBA, HQ, and Carbonate Units**[a]

| | x, Å | y, Å | z, Å |
|---|---|---|---|
| HBA Ob1 | 0.0000 | 0.0000 | 0.0000 |
| Ob2 | 0.0162 | -2.2369 | 0.2985 |
| Cb0 | 0.0000 | -1.1379 | 0.7648 |
| Cb1 | -0.0226 | -0.8033 | 2.2135 |
| Cb2 | -0.6271 | 0.3537 | 2.7196 |
| Cb3 | 0.5877 | -1.7072 | 3.0844 |
| Cb4 | -0.6112 | 0.6067 | 4.0964 |
| Cb5 | 0.6134 | -1.4542 | 4.4612 |
| Cb6 | 0.0090 | -0.2972 | 4.9673 |
| Ob3 | 0.0000 | 0.0000 | 6.3486 |
| HQ Oq1 | 0.0000 | 0.0000 | 0.0000 |
| Cq1 | 0.0000 | 0.0349 | 1.3806 |
| Cq2 | 0.0000 | 1.2287 | 2.1111 |
| Cq3 | 0.0000 | 1.2007 | 3.4908 |
| Cq4 | 0.0000 | -0.0105 | 4.1604 |
| Cq5 | 0.0000 | -1.1966 | 3.4432 |
| Cq6 | 0.0000 | -1.1829 | 2.0533 |
| Oq2 | 0.0000 | 0.0000 | 5.5354 |
| CO Oc3 | 0.0000 | 0.0000 | 0.0000 |
| Oc2 | 0.0000 | -1.9571 | 1.2693 |
| Cc1 | 0.0000 | -0.7623 | 1.0776 |
| Oc1 | 0.0000 | 0.0000 | 2.0216 |

[a] Each of the three units is defined with the linkage ester oxygens along the *z* axis.

**Model Building.** Molecular models for the HBA, HQ, and carbonate units were constructed by using standard bond lengths, bond angles, and torsion angles derived from appropriate model compounds.[9,10] The atomic coordinates are given in Table I: the numbering of the atoms is shown in Figure 1. As starting models the phenyl, ester, and carbonate grups were each taken to be planar, and the monomer lengths are defined as the distance between their terminal oxygens. The torsion angles in the ester linkages (Figure 2) were set at $\theta_e = 9.8°$, $\varphi_e = 65°$, and $\tau_e = 180.0°$, as observed in phenyl benzoate.[9] The starting conformation for the carbonate group was trans-trans, such that the torsion angles $\tau_{c1}$ and $\tau_{c2}$ are 180° and 180° (cis = 0°). In later work we used a distorted carbonate group with $\tau_{c1}$ and $\tau_{c2}$ torsion angles 120° and 240°, in which the linkage bonds are parallel. The $\varphi_{c1}$ and $\varphi_{c2}$ torsion angles were ±45°,[10-12] such that the planes of the adjacent phenylenes are either parallel or perpendicular to each other.

## Intensity Calculations

The intensity on the meridian, $I(Z)$, depends only on the projection of the structure onto the fiber axis. For a chain of point monomers, $I(Z)$ is derived as the Fourier transform ($\mathcal{F}$) of the autocorrelation function, $Q(z)$, which defines the probability of the pairs of monomers separated by $z$ along the chain axis.

$$I(Z) = \mathcal{F}(Q(z)) \qquad (1)$$

Here $Z$ is the reciprocal space coordinate in the axial direction, corresponding to the meridional direction in film space. For an infinite chain, $I(Z)$ can be expressed in terms of $H_1(Z)$, the Fourier transform of the $Q_1(z)$, the first nearest-neighbor probability component of $Q(z)$.

$$I(Z) = 1 + 2\,\mathrm{Re}\left(\frac{H_1(Z)}{1 + H_1(Z)}\right) \qquad (2)$$

where *Re* signifies the real component and

$$H_1(Z) = Q_1(z) \qquad (3)$$

For a copolymer of two or more monomers, it is convenient to represent $H_1(Z)$ as the product of three matrices:

$$H_1(Z) = \mathbf{P}\cdot\mathbf{M}\cdot\mathbf{X}(Z) \tag{4}$$

In the present case, we define HBA, HQ, and carbonate as separate monomers. The HBA unit has a sense, depending on whether the CO group precedes or follows the phenylene, and thus from the physical point of view there are four monomers: up-HBA, down-HBA, HQ, and carbonate, which will be further abbreviated as B, D, Q, and C, respectively, for use as subscripts.

$$\mathbf{P} = \begin{bmatrix} p_B & 0 & 0 & 0 \\ 0 & p_D & 0 & 0 \\ 0 & 0 & p_Q & 0 \\ 0 & 0 & 0 & p_C \end{bmatrix} \quad \mathbf{M} = \begin{bmatrix} M_{BB} & 0 & 0 & M_{BC} \\ 0 & M_{DD} & M_{DQ} & 0 \\ M_{QB} & 0 & 0 & M_{QC} \\ 0 & M_{CD} & M_{CQ} & 0 \end{bmatrix}$$

$$\mathbf{X}(Z) = \begin{bmatrix} X_B(Z) & 0 & 0 & 0 \\ 0 & X_D(Z) & 0 & 0 \\ 0 & 0 & X_Q(Z) & 0 \\ 0 & 0 & 0 & X_C(Z) \end{bmatrix} \tag{5}$$

$p_A$ in the **P** matrix is the fractional molar proportion of monomer A. We assume equal proportions of up- and down-HBA; i.e., $p_B = p_D = 0.3$ and $p_Q = p_C = 0.2$ in the present case. In the **M** matrix, $M_{AB}$ is the probability that monomer A is followed by monomer B. Of the 16 possible pairwise combinations, eight are forbidden by the chemistry (e.g., HQ cannot be followed by HQ), and those $M_{AB}$ terms are zero. For chain propagation the sum of the remaining terms on each row must be unity. $M_{AB}$ can be expressed as

$$M_{AB} = r_{AB}p_B / \sum_j r_{Aj}p_j \tag{6}$$

in which the $r_{AB}$ terms define the degree of randomness in a chain, and the summation is over all monomers. $r_{AB} = 0$ when the A–B combination is chemically excluded; otherwise, $r_{AB} = 1$ for allowed combinations in random sequences. The $r_{AB}$ terms can be varied from unity in order to simulate nonrandom sequences. (Note that this simple treatment is for nonrandom statistics determined by first-nearest-neighbor probabilities. More complex nonrandomness involving, e.g., restrictions on second- or third-nearest neighbors would require larger matrices, but the principles are the same.) The **X** matrix contains phase terms of the form $X_A = \exp(2\pi i Z z_A)$, where $z_A$ is the axial advance for monomer A.

The atomic coordinates of the monomers are introduced by multiplying each $H_{AB}(Z)$ component of $H_1(Z)$ by $F_{AB}(Z)$, the Fourier transform of the cross convolution of monomer A with monomer B

$$F_{AB}(Z) = \sum_i \sum_j f_{A,i} f_{B,j} \exp(2\pi i Z(z_{B,j} - z_{A,i})) \tag{7}$$

where $f$ is the atomic scattering factor of an atom with axial coordinate $z$, and the subscripts designate the $i$th atom of monomer A and $j$th atom of monomer B. $I(Z)$ is now given by

$$I(Z) = \sum_A p_A F_{AA}(Z) + 2\,\mathrm{Re} \sum_A \sum_B p_A F_{AB}(Z) \frac{M_{AB}X_A(Z)}{1 - M_{AB}X_A(Z)} \tag{8}$$

In models of actual copolymer sequences there is considerable torsional freedom about the linkage bonds, with the result that the axial advance per monomer is not constant: rather there is a distribution of axial advances even for highly extended conformations. The distributions can be defined as histograms obtained by determining the individual axial advances for each monomer type in a large number of models of chains of different sequence. Our procedure was to set up chains of 15 monomers of random sequences consistent with the overall monomer ratio, setting randomly the phenylene–COO torsion angles at ±9.8° or ±189.8° and the COO–phenylene torsion at ±65° or ±115°. The carbonate "kinks" were required to alternate as "zigs" and "zags" to maintain linear progression. We found that this condition could be achieved by restricting the chain conformations to those with a diameter of 24 Å or less, which effectively eliminated chain reversals. (N.B.: most of the chains had much smaller projected cross sections.) The chain axis was defined as the best least-squares line through the atomic coordinates. Any chain with an atom more than 12 Å from this axis was discarded, and a new chain with the same sequence but a different combination of torsional angles was generated. Histograms of axial advances for each monomer were derived from 500 such chains and were incorporated into the intensity calculations as terms of the **X** matrix

$$X_A = \sum_i p_{i,A} \exp(2\pi i Z z_{i,A}) \tag{9}$$

where $p_{i,A}$ is the fraction molar proportion of monomer A, having an axial advance of $z_{i,A}$. In work on chains containing distorted carbonate groups, possible nonlinearities were modeled by incorporating Gaussian functions to describe the distribution of axial advances for each monomer.

## Results and Discussion

The X-ray fiber patterns for as-drawn fibers of the 75/25 copolymer are shown in Figure 3a. A number of Bragg reflections are apparent, significantly more than are seen for as-spun fibers of copoly(HBA/HNA),[5-7] indicating a more ordered three-dimensional structure. Information on the structure and conformation of the chains comes from the intensity along the meridian, which derives from the projection of the structure onto the fiber axis. In Figure 3a, we see three meridional maxima, at $d$ = 6.47, 3.22, and 2.15 Å. Figure 3b shows the X-ray pattern recorded with the fiber tilted at 22° from the position perpendicular to the beam, in which a fourth meridional is seen at $d$ = 2.05 Å. Figure 4 (curve a) shows the $\theta/2\theta$ diffractometer scan in the fiber axis direction for the same specimen, and the same four maxima are seen. Figure 5a shows the electron diffraction pattern obtained for a melt-sheared film of the copolymer. The specimen had been annealed at 200 °C for 1 h. The electron diffraction are similar to the X-ray fiber diagrams in Figure 3a, and meridional maxima are seen at $d$ = 6.50, 3.21, 2.18, and 2.06 Å.

The four meridional $d$-spacings are nonperiodic, reminiscent of the effects seen previously for the analogous copolyesters.[5,8] The effects are not quite so obvious, because the first three maxima are within experimental error of being orders of 6.47 Å (X-ray data). Initially it seemed possible that the copoly(ester carbonate) could be blocky and that the crystallinity was due to organization of the poly(HBA) blocks. The homopolymer would give meridional maxima at 6.35, 3.17, and 2.12 Å, which are all less than observed: the differences are not large, but it will be seen below that the introduction of random carbonates produces just this effect, since it increases the average separation between phenylene groups. An important additional point is that the homopolymer does not predict the meridional at $d$ = 2.05 Å. Hence, we have

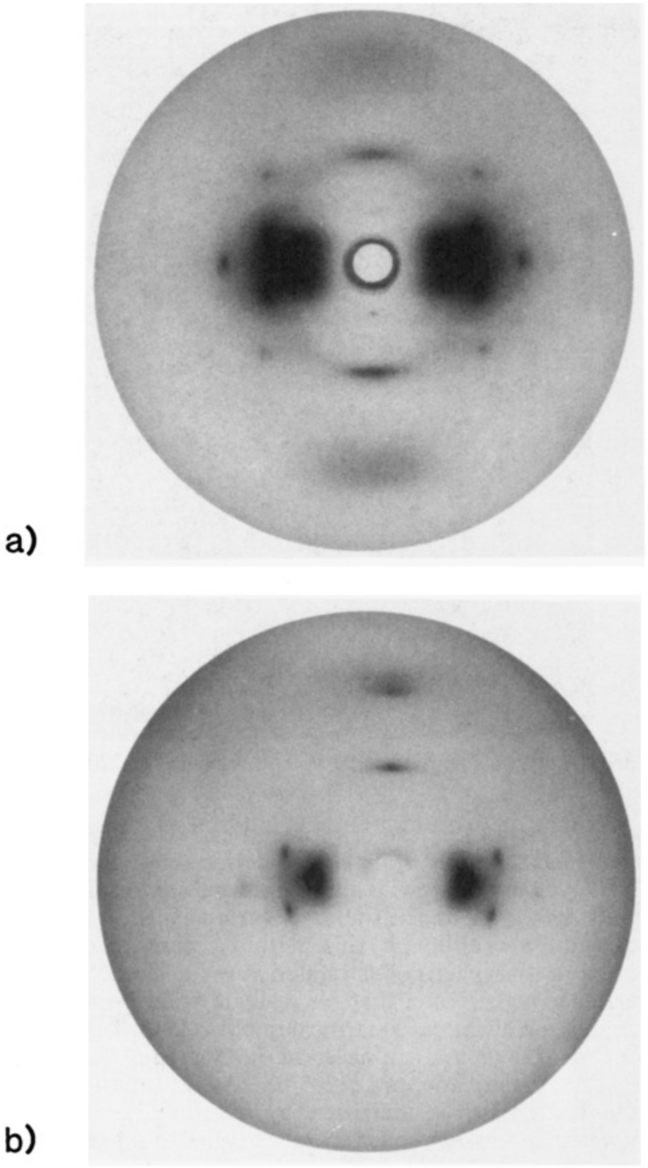

**Figure 3.** X-ray fiber diagram of 75/25 copoly(ester carbonate): (a) fiber perpendicular to the beam direction; (b) fiber tilted 21° toward the beam direction.

investigated the possibility that the nonperiodic data can be accounted for by a random copolymer sequence.

The copoly(ester carbonate) forms a homogeneous nematic melt, in which the chains presumably have relatively extended conformations. When one constructs models of the random copolymer sequences, the kinks of ~60° due to the carbonates lead to difficulties in generating extended conformations. A possible solution is to require the kinks to alternate in "zigzag" conformations, examples of which are shown in Figure 6. Even so, there would be problems in packing such chains if the sequences are random, because the zigzags would not be in phase. If we ignore the latter problem for the moment, we can proceed to predict the meridional scattering for an array of random copolymer chains, using the equations above. For this the axial advances for the HBA, HQ, and carbonate units are 5.50, 4.80, and 2.02 Å, respectively, assuming a constant tilt of 30° of HBA and HQ to the fiber axis, with the carbonates symmetrically disposed at the kinks.

The predicted meridional scattering is shown in Figure 4 (curve b). The agreement with the observed data (curve a) can only be described as poor when compared to that obtained for analogous copolyesters.[5-8] We predict a doublet at 5.86/5.29 Å, a very broad peak at 2.71 Å, and a peak at 1.80 Å: the peaks are broader than observed, and the *d*-spacing match is outside experimental error. When we allow reasonable torsional variability, the axial advances for each monomer can be defined as histograms, as described above. These data are introduced into the calculations as components of the **X** matrix in eq 4. The calculated meridional intensity for this model is shown in Figure 4 (curve c): doublets are predicted at 6.11/5.55, 3.15/2.87, and 2.07/1.96 Å. Although the *d*-spacings have increased compared to those in curve b, the agreement with the observed data is still poor.

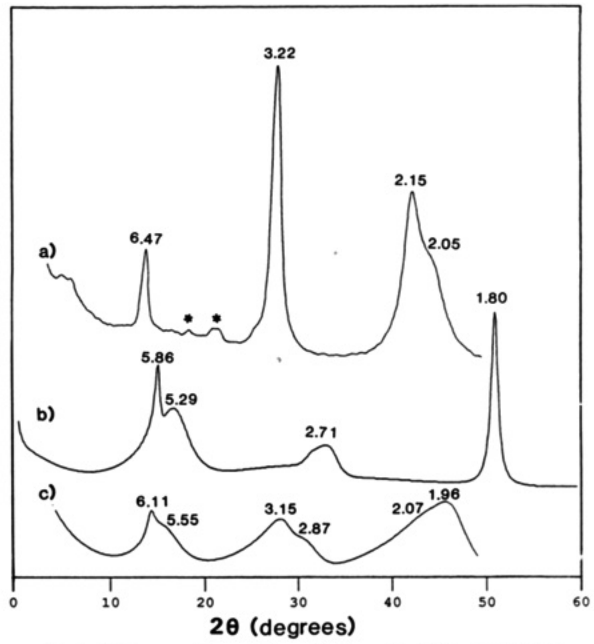

**Figure 4.** (a) Observed meridional intensity data ($\theta 2/\theta$ diffractometer scan). (b) Calculated meridional scattering for an array of random copolymer chains with undistorted carbonate groups, assuming constant axial advance. (c) Calculated meridional scattering for a similar model, incorporating distributions of axial advances.

An alternative possibility is that the chains are not random but blocky, which can be simulated by modification of the $r_{AB}$ terms in the **M** matrix in eq 4. The most reasonable structure to consider is one where HBA–HBA nearest neighbors are more likely than they would be in the random copolymer. This requires an increased probability of HQ–carbonate linkages (leading to poly(phenyl carbonate) sequences) and a decreased probability for the cross reactions. The $r_{AB}$ terms for the cross reactions were set equal, and we defined blockiness by a ratio $R = r_{\text{HBA-HBA}}/r_{\text{HBA-HQ}}$, which is the relative increase in the probability of the homopolymer reaction compared to that for the cross reaction between the monomers. For a random copolymer, $R = 1.0$; for a blocky polymer involving poly(HBA) or poly(phenyl carbonate) sequences, $R > 1.0$. When such effects are introduced into the calculations, we see a steady change in the predicted meridional intensity. As $R$ increases to 2.0 (Figure 7a), there is a transition to a series of peaks that are orders of 5.50 Å, the monomer advance for the poly(HBA) sequences, and at still higher $R$ (Figure 7b), weaker peaks for the (tilted) poly(phenyl carbonate) sequences are resolved. Of course, as the homopolymer sequences get longer, the zigzag conformation gets even more unreasonable and should be more realistically replaced by one in which the poly(HBA) sequences are parallel to the chain axis, and the kinks are in the poly(phenyl carbonate) regions. In this case we obtain a series of meridional maxima that are orders of

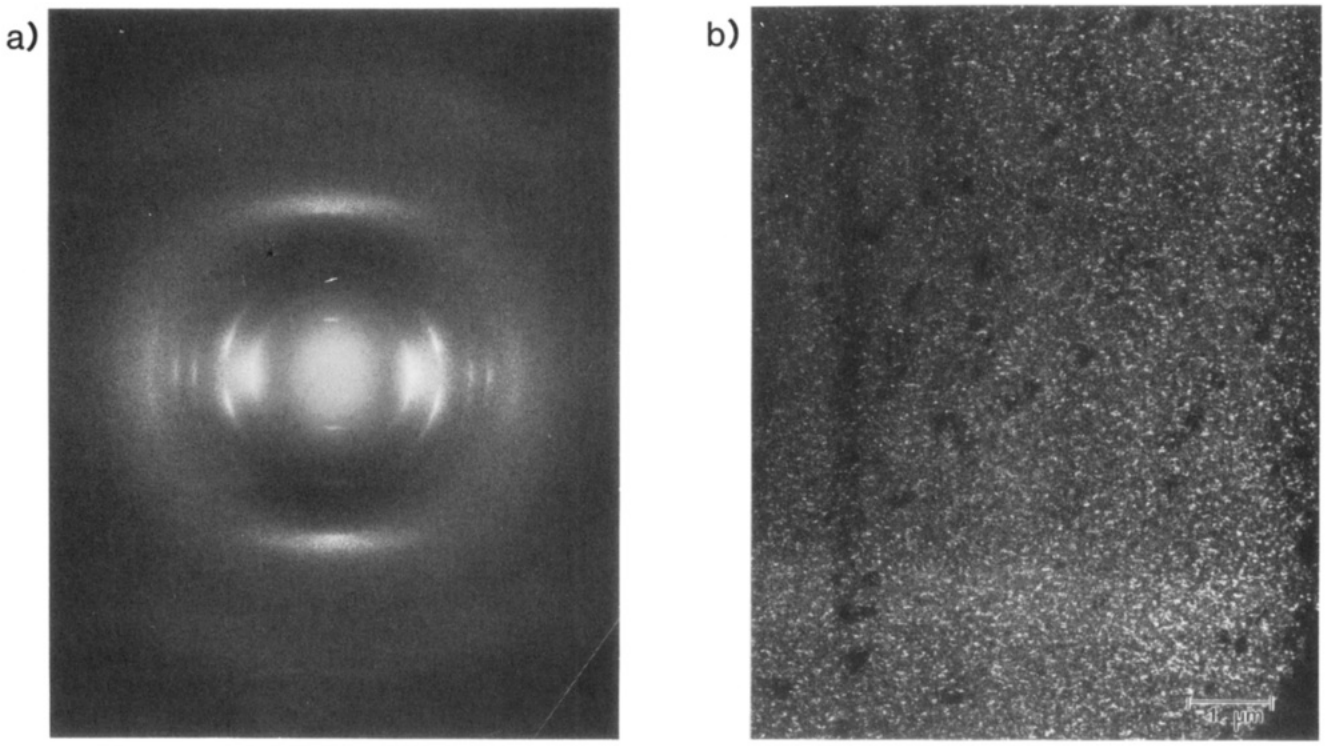

**Figure 5.** (a) Electron diffraction pattern (SAED) of a copoly(ester carbonate) film sheared at 410 °C and annealed at 220 °C for 1 h. (b) Dark-field image obtained by using the inner equatorial reflection.

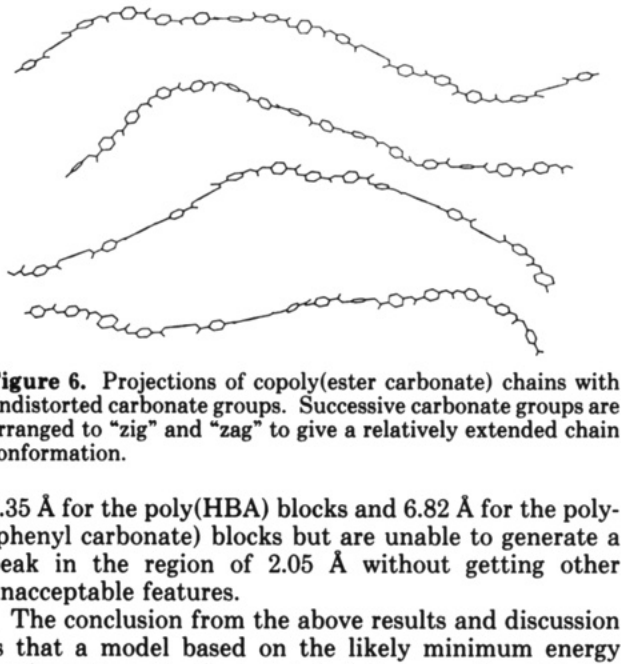

**Figure 6.** Projections of copoly(ester carbonate) chains with undistorted carbonate groups. Successive carbonate groups are arranged to "zig" and "zag" to give a relatively extended chain conformation.

6.35 Å for the poly(HBA) blocks and 6.82 Å for the poly(phenyl carbonate) blocks but are unable to generate a peak in the region of 2.05 Å without getting other unacceptable features.

The conclusion from the above results and discussion is that a model based on the likely minimum energy conformations for the isolated chains cannot explain the observed data. The most telling piece of observed data is the $d$-spacing of 6.47 Å for the first maximum. This maximum corresponds approximately to the average advance per phenylene unit [$((6.35 \times 3) + 6.82)/4 = 6.47$ Å]. The copolymer can be thought of as 1,4-phenylene units linked by either ester or carbonate units, and it is the phenylenes that dominate the scattering. In the kinked chains in Figure 5a, the average advance per phenylene unit is 6.06 Å, and the only way we can increase this advance to 6.47 Å is to use a more extended chain.

The most reasonable method to produce a more extended conformation is to introduce torsional distortions into the carbonate group. Not only are the carbonate groups the sources of the nonlinearity but also distortions in these groups result in the lowest potential energy gain. In the crystal structure of biphenyl carbonate, the carbonate has the trans–trans conformation shown in Figure 2. Conversion to the trans–cis conformation results in a small energy gain, estimated variously at 1.1–2.75 kcal/mol,[13–15] although this requires passage over a potential energy barrier estimated at ~5 kcal/mol. This barrier is higher than that for a single bond because of conjugation of the carbonate group but is lower than that for the ester group, estimated at 7.9 kcal/mol.[16] If the carbonate group adopts a (120°, 120°) conformation, the potential energy is increased by a total of ~7 kcal. However, the linkage bonds are now parallel to one another, rather than inclined at 60°, and as a result we obtain straighter chains, where the carbonate groups are "crankshaft" rather than kink distortions. The higher energy of this conformation will be more than offset by the improved packing of the chains: it would seem more likely that an amorphous structure would result if the carbonates are kinked, as is the case for many polycarbonates.

If we repeat the calculations now for the distorted structure, the idealized monomer advances are 6.35, 5.60, and 1.33 Å, for HBA, HQ, and carbonate, respectively. For this structure, the calculated meridional intensity is shown in Figure 8 (curve b). One sees immediately that the peaks are sharper, with profiles similar to those observed (curve a), and have moved to higher $d$-spacings: 6.54, 3.25, 2.16, and 2.10 Å. All of these $d$-spacings are a little higher than observed, and the relative intensities do not match well.

The above model is idealized in that it assumes each carbonate group is distorted in the same way. The actual distortions would depend on the sequences of its immediate neighbors. If two or more adjacent chains have carbonates in the same positions, they do not have to distort the same amount with chains that have the carbonate surrounded by straight sections of other chains. Consequently, it is not useful to derive histograms for isolated chains, and we used Gaussian functions to describe the distributions in axial lengths. The best fit between the observed and

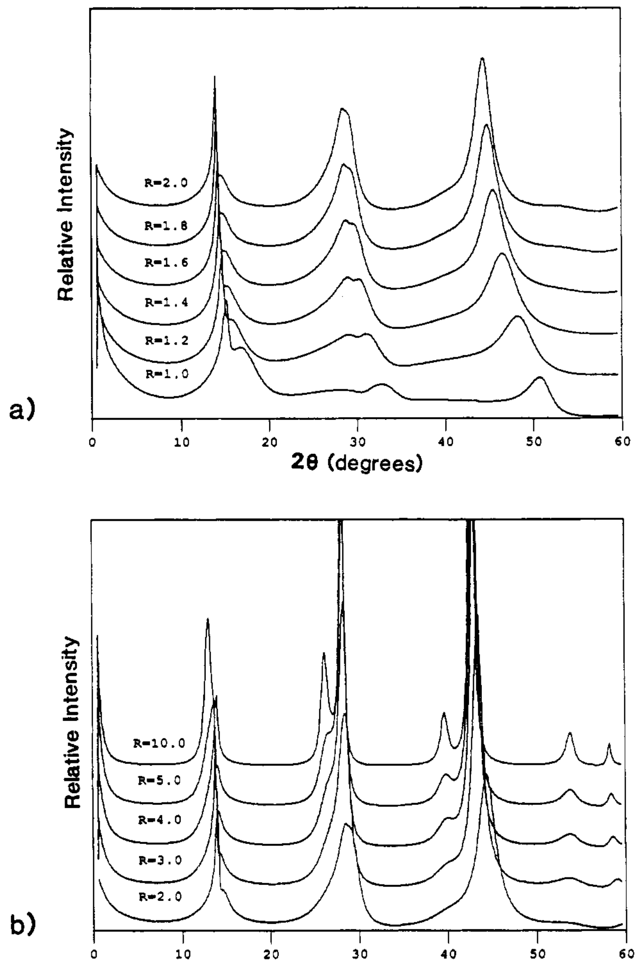

**Figure 7.** Calculated meridional scattering for nonrandom sequence distribution with (a) $R = 1.0$ (random) increasing to $R = 2.0$ and (b) $R = 2.0$ increasing to $R = 10$.

calculated intensity was obtained for carbonates with an average advance of 1.64 Å and a Gaussian distribution with a standard deviation of $\sigma = 0.5$ Å. The average axial lengths for HBA and HQ were 6.25 and 5.44 Å, respectively, each with $\sigma = 0.1$ Å. The calculated intensity is shown in Figure 8 (curve c) and compares very well with the observed data (curve a). The calculated peaks are at 6.49, 3.22, 2.14, and 2.04 Å, well within experimental error, and the relative intensities are in qualitatively good agreement. When we modify the coordination statistics to simulate blocky structures, the good agreement given by random sequences is soon lost.

Thus we conclude that the copoly(ester carbonate) is a random copolymer, with an elongated conformation in which the distortions are primarily in the carbonate groups. Preliminary infrared spectroscopic analysis of the copolymer shows that the bands due to the carbonate group are shifted in frequency and have different intensities from those for poly(phenyl carbonate). More work is necessary to understand the origin of these effects, but at this point the differences are superficially consistent with our proposals for distortion of the carbonate groups. Naturally the distortions necessary to produce a linear chain conformation will be shared with other sections of the chain, i.e., the phenyl and ester units, but are likely to be concentrated in the carbonate groups. The copolymer forms a nematic melt, where presumably the chains are relatively linear and parallel to one another. In the nematic state, the thermal energy supplied can be expected to provide the necessary energy to distort the molecules.

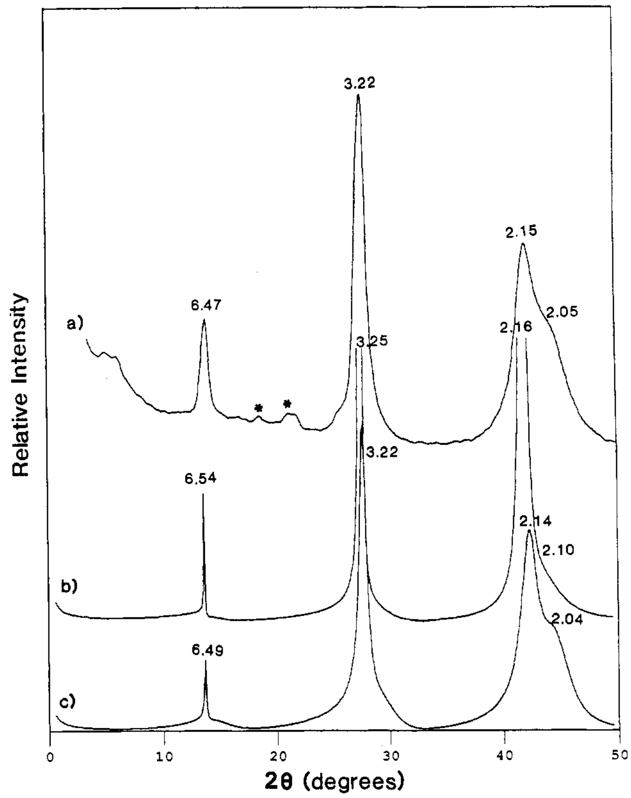

**Figure 8.** (a) Observed meridional intensity data ($\theta/2\theta$ diffractometer scan). (b) Calculated meridional scattering for an array of random copolymer chains with distorted carbonate units, assuming constant axial advance. (c) Calculated meridional scattering for a similar model incorporating a distribution of axial advances.

In the melt-spun fibers, the elongated structures will be "quenched", and the distortions will be retained so that the chains can pack in the most efficient manner possible.

Finally, it is interesting that the as-spun copoly(ester carbonate) exhibits a relatively high degree of crystallinity: we estimate ~50% based on the usual separation of the powder X-ray diffraction scan into crystalline and amorphous components, in the usual way for semicrystalline polymers, and this figure increases to ~60% on annealing. These figures are perhaps surprising when one considers that the copolymer has a random sequence and shows that extensive ordering is possible despite the need for conformational and packing distortions. Figure 5b shows the dark-field electron microscope image obtained by using the inner equatorial reflection of the diffraction pattern in Figure 5a. We see a series of bright lines running perpendicular to the long axis of the molecules. These crystallites measure ~170 Å along the chain axis direction and are separated by an intercrystalline region of 200–300 Å. In the lateral direction, the crystals average ~960 Å in width. It appears, therefore, that the sheared specimen consists of crystalline layers separated by unordered regions, which perhaps have some sort of quenched nematic structure. Based simply on the layer dimensions, the crystalline regions comprise ~40% of the total structure. The molecules have a weight-average molecular weight of ~29 000, corresponding to a contour length of ~1250 Å for an extended molecule. If the molecules are extended as a result of shear, then each one will pass through two or three crystalline layers. This presents problems for the nonperiodic lattice model (NPL) proposed by Spontak and Windle.[17] One could perhaps envisage axial shifts of the chains to match short sequences in one layer, but it is unlikely that this would also produce matching of the same chains in the adjacent layers.

We are currently involved in a study of the chain packing in the copoly(ester carbonates), and also copoly(HBA/HNA) and related systems, using molecular mechanics routines. Details of this work and also our analysis of other composition ratios for the copoly(ester carbonates) will be published shortly.

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