Structure of Annealed Copoly(*p*-hydroxybenzoic acid–2-hydroxy-6-naphthoic acid). 1. Chain Conformation and Packing

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ABSTRACT: The structure of thermally annealed melt-spun fibers of the thermotropic copolyester prepared from *p*-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) has been investigated by X-ray diffraction. Annealing the as-spun fibers of 75/25 copoly(HBA/HNA) gives rise to additional Bragg maxima on the equator and on the nonperiodic layer lines. In addition, there is an appreciable increase in the crystallinity. The new reflections point to the generation of a second orthorhombic polymorphic structure (unit cell dimensions a = 7.6 Å, b = 5.7 Å), which coexists with the less dense orthorhombic (pseudohexagonal) structure (a = 9.2 Å, b = 5.2 Å) present in the as-spun fibers. The dimensions of these unit cells are very similar to those reported by Lieser[1] for forms I and III of homopoly(HBA), respectively, suggesting similar chain conformations and packing in the copolymer. We have developed a model for the annealed copolymer structure via a refinement of form I of poly(HBA) based on the equatorial and first layer line intensities for annealed 75/25 copoly(HBA/HNA). First we considered a model with space group $P2_12_12_1$, as proposed previously, in which the unit cell dimensions were a = 7.6 Å, b = 5.7 Å, and c = 12.6 Å, and the poly(HBA) chains have a 2_1 helical conformation. This model was inferior to one with the monoclinic space group $P2_1$, in which the 2_1 axis is parallel to, but halfway between, the two chains in the unit cell. The latter structure is in turn close to one with space group $Pbc2_1$, for which the X-ray agreement is not significantly different. The refined chain conformation has successive residues related by the c glide. The phenyl–OCO and OCO–phenyl torsion angles are 55.2° and −5.2°, which are similar to those determined for the model compound phenyl benzoate, and for polymers such as poly(phenyl phenylene terephthalate), and lead to a mutual inclination of successive phenylene units of approximately 60°. The model contains no unacceptable stereochemical contacts and is in good agreement with the X-ray intensity data (R = 0.18).

Introduction

The structures of wholly aromatic thermotropic copolyesters have been studied extensively in recent years. One of the simplest of these copolymers is that prepared from *p*-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA), marketed as Vectra by Hoechst-Celanese Corp. Figure 1 shows the X-ray diffraction pattern of melt-drawn fibers of copoly(HBA/HNA) with a 75/25 comonomer mole ratio. We observe a series of nonperiodic layer lines, and these vary steadily in position with the HBA/HNA mole ratio across the entire composition range. Bragg maxima are seen on the equator at $d \cong 4.6$, 2.6, and 2.3 Å, which are indexed as the 110, 200, and 220 reflections for an orthorhombic (pseudohexagonal) unit cell with dimensions a = 9.2 Å, and b = 5.2 Å. In addition, an off-equatorial maximum is observed at d = 3.1 Å, which points to the presence of some three-dimensional order. Several papers[2-4] from our laboratory have shown that the nonperiodic layer lines seen for these and related copolymers are due to a structure comprised of parallel, highly extended chains with completely random monomer sequences.

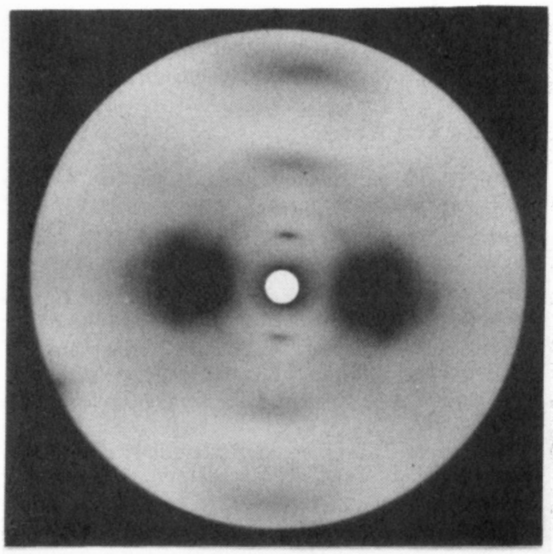

Figure 1. X-ray diffraction pattern from as-spun fibers of HBA/HNA (75/25).

Biswas and Blackwell[5] showed that the layer line spacing for the off-equatorial maximum is approximately equal to the "average dimer" length for that composition. Since the chemical structure is random, the existence of this layer line means that the chain conformation has some sort of physical repeat. In order to explain the sharp equatorial and off-equatorial Bragg maxima, they introduced the concept of a "register plane" that requires approximate chain register at one point only in a sequence[6] and showed that the observed diffraction characteristics are predicted when such limited register occurs between the adjacent chains. This allowed them to consider different models for the chain conformation,[7] and they found best agreement with the intensity data for the as-spun fibers when successive aromatic units are mutually inclined by approximately 60°, a structure analogous to that for poly(*p*-phenyleneterephthalamide).[8]

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Since the first patents were issued for this class of material,[9] it has been known that thermal annealing leads to an improvement in the mechanical properties, notably an increase in the tensile strength and modulus. These polymers also behave in a similar manner to semicrystalline repeating polymers, for which thermal annealing generally results in an increase in the crystallite size and crystallinity. The structural changes on annealing have been discussed qualitatively by Field et al.[10] for Xydar (produced by Amoco), which is the copolyester prepared from HBA, biphenol (BP), and terephthalic acid (TPA). They reported an increase not only in crystallinity but also in the development of one or more new polymorphic structures. Golombok et al.[11] have reported that annealing of copoly(HBA/HNA) results in a concentration of the X-ray intensity on the layer lines onto the meridian and interpret this as indicating improved lateral alignment of neighboring chains. Also, Cheng et al.[12] have reported thermal and X-ray diffraction studies of the structural transitions of several thermotropic copolyesters, including copoly(HBA/HNA) and copoly(HBA/BP/TPA). Two endotherm DSC peaks were observed for the annealed samples, indicating that two polymorphs coexisted, one with hexagonal packing corresponding to the quenched state and an orthorhombic form that developed after annealing. The content of the quenched form decreased during the heat treatment but apparently was not eliminated completely.

In this paper we address some of the changes in the structure of copoly(HBA/HNA) that occur on annealing. It will be seen that a new polymorphic structure is found in the annealed fibers of the 75/25 copolymer, which coexists with the structure first reported for the as-spun state. These two structures show striking similarities to those for homopoly(HBA), and we have refined a model for the 75/25 copolymer based on analogy to the homopolymer structure, using the linked atom least-squares (LALS) method to obtain the best agreement between the observed and calculated X-ray intensities.

Experimental Section

Specimen Preparation. Specimens of copoly(HBA/HNA) with a comonomer mole ratio of 75/25 were obtained from the Hoechst-Celanese Corp. and had been prepared as described by Calundann.[13] Fibers were drawn by hand from a pellet of the copolymer melted on a hot stage. The fibers were sealed under vacuum in a glass tube and annealed for up to 30 days in sand at 275 °C.

X-ray Diffraction. X-ray diffraction patterns of the as-spun and annealed samples were recorded on Kodak no-screen X-ray film by Searle toroidal X-ray camera, with Cu Kα X-ray radiation. The d spacing of the Bragg reflections were calibrated by dusting the sample with CaF_2 powder.

The intensities of the Bragg reflections were determined from the films using an Optronics P-1000 densitometer. The digitized data were manipulated by programs obtained from Dr. K. H. Gardner of E. I. du Pont de Nemours & Co., Inc., Wilmington, DE, which were based on the work of Fraser et al.[14] The data were corrected point by point for Lorentz and polarization effects. The average background around the perimeter of each Bragg reflection was subtracted from each of the points within, and these were summed to give the integrated intensity.

Intensities were determined for 10 observed reflections: seven on the equator and three on the first layer line. In addition, nine unobserved reflections with predicted $d > 2$ Å on the equator (two) and on the first layer line (seven) were included in data to be used in the structure refinement. The latter reflections were assigned intensities of half the estimated threshold intensity in the region where each was predicted to occur.

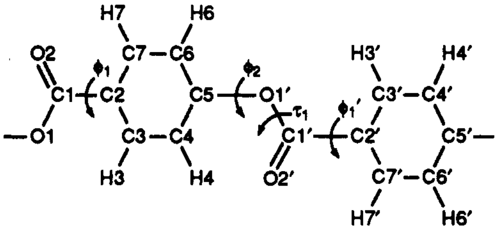
Table I
Bond Lengths and Bond Angles

bond lengths, Å		bond angles, deg	
phenyl C—C	1.400	phenyl C—C—C	120.0
phenyl C—H	1.080	phenyl C—C—H	120.0
CA1—CA2	1.487	OA2—CA1—OA1	122.1
CA1—OA1	1.371	CA2—CA1—OA1	114.5
CA1═OA2	1.194	CA3—CA2—CA1	120.0
OB1—CA5	1.413	CA4—CA5—OB1	119.0
		CA5—OB1—CB1	118.3

Table II
Torsion Angles in Aromatic Esters

	ϕ_1, deg	ϕ_2, deg	χ, deg	
phenyl benzoate	−9	−55	178	X-ray (single crystal)[17]
phenyl benzoate	−6	−52	177	ab initio[18]
poly(phenylene terephthalate)	0	−60	180	empirical[19]
poly(phenyl phenylene terephthalate)	−3	−59	180	X-ray (fiber)[20]
copoly(50/50 phenyl phenylene terephthalate/phenyl ethyl phenylene terephthalate)	−7	−56	180	X-ray (fiber)[21]

Model Building. The repeating dimer for poly(HBA) is shown below, indicating the numbering of the atoms for discussion in the text. The standard bond lengths and angles used are given in Table I. The phenyl groups were assumed to be planar. The conformation is defined by the phenyl–ester torsion angles, ϕ_1 (O1–C1–C2–C3) and ϕ_2 (C4–C5–O1′–C1′), and the ester group torsion angle, χ (C5′–O1′–C1′–C2′).



ϕ_1, ϕ_2, and $\chi = 0°$ for the cis conformations and are positive for anticlockwise rotations. χ was assumed to be 180°, corresponding to the trans-planar conformation for the ester group.

Thermal Analysis. The thermal analyses were performed on a Perkin-Elmer DSC7 scanning calorimeter. The heating rate was 20 °C/min, with the specimens under dry nitrogen. The specimens were the as-received copolymer and pellets that had been annealed at 270 °C for 2, 5, 8, 15, and 30 days.

Results and Discussion

Figure 2 shows the X-ray diffraction pattern for fibers of 75/25 copoly(HBA) that had been annealed for 30 days. Compared to the data for the as-spun fibers (Figure 1), it can be seen that a number of new equatorial and off-equatorial reflections have been generated, indicating that the three-dimensional order has been greatly improved. Development of the new reflections and the overall sharpening increased steadily with annealing over the 30-day period. However, despite these changes, the data remain nonperiodic in the fiber axis direction. Analysis of this nonperiodicity will be the subject of a later paper. For the present we will confine our discussion to packing of the chains, as can be derived from the Bragg reflections.

The d spacings of the seven equatorial and three first layer line reflections are listed in Table III. Reciprocal space R coordinates [$R = ((1/d)^2 - Z^2)^{1/2}$] for the first layer line reflections are within experimental error of those for the 010, 110, and 210 reflections. The values of $1/R$ for these reflections were added to the equatorial d-spacing data for refinement of the lateral unit cell dimensions. The reflections are indexed by a two-dimensional orthorhombic unit cell with dimensions $a = 7.6$ Å and $b =$

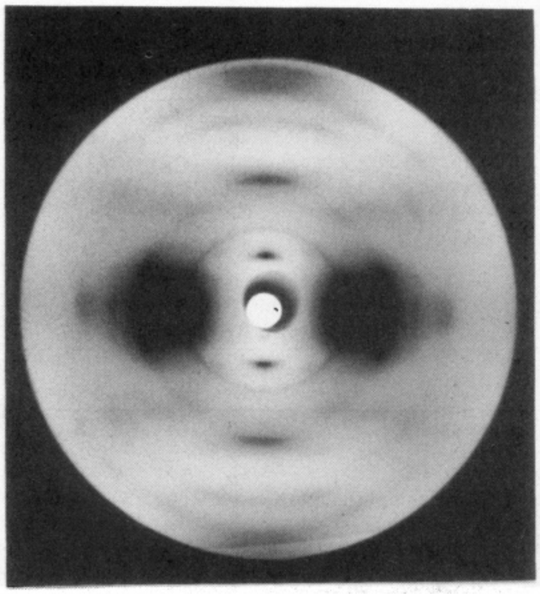


Figure 2. X-ray diffraction pattern of fibers of HBA/HNA (75/25) after annealing at 275 °C for 30 days.

5.7 Å. (There is no *c* dimension, since the chains are nonperiodic.) The *hkl* indices and calculated *d* spacings are listed in Table III. The first layer line reflections are assigned $l = 1$ for convenience.

The *a* and *b* dimensions are similar to those for one of the crystalline forms of homopoly(HBA) identified by Lieser[1] using electron diffraction techniques. He found that, at room temperature, the homopolymer has an orthorhombic unit cell with dimensions $a = 7.5$, $b = 5.7$, and $c = 12.5$ Å, which was designated form I. A second polymorph, form II, was also seen at room temperature for a low molecular weight specimen. Form II is also orthorhombic, with unit cell dimensions $a = 3.8$, $b = 11.1$, and $c = 12.9$ Å. At elevated temperatures (above 290 °C), both specimens were converted to form III, which has an orthorhombic unit cell with dimensions $a = 9.2$, $b = 5.3$, and $c = 12.4$ Å, and this change is reversed on cooling. Form III is pseudohexagonal ($a = \sqrt{3}b$) and has a lower calculated density (1.32 g cm^{-3}) than either form I (1.48 g cm^{-3}) or form II (1.49 g cm^{-3}). It has been proposed that there is some conformational disorder in form III, leading to the more open structure.

Thus the structure in as-spun copoly(HBA/HNA) is analogous to form III of the homopolymer: thermal annealing leads to generation of a structure analogous to form I. The chain conformation is extended due to the linkage geometry, and this extension is relatively independent of changes in the aromatic–ester torsion angles. It is likely that the nematic state consists of parallel arrays of chains with extensive torsional variation and approximately cylindrical cross sections. In the quenched fiber these chains pack in the pseudohexagonal structure, analogous to form III, and the presence of the comonomers probably prevent rearrangement to the structure analogous to form I on cooling to room temperature. However, this rearrangement is achieved slowly by thermal annealing.

The similarity of the X-ray data for the 75/25 copolymer to those for the homopolymer is perhaps not surprising in view of the high content of HBA. It should be noted that the observed reflections for the annealed specimen on the equator at $d = 4.57$, 2.69, and 2.33 Å and on the first layer line at $d = 3.04$ Å are indexed by both copolymer structures. Thus the data are consistent with the presence of both forms. DSC scans were obtained for as-spun fibers and those subjected to annealing for different times. The as-spun specimen showed a single melting transition for the pseudohexagonal form. After annealing two peaks were obtained, suggesting that both forms were present. These results are consistent with those reported earlier by Cheng et al.[12]

Given the complexity of the annealed copolymer structure, we approached the analysis by analogy with form I of poly(HBA). The Fourier transforms of single chains of the homopolymer and the 75/25 copolymer are likely to be very similar on the equator and first layer lines. Thus it should be only a minor approximation to treat the equatorial and first layer line reflections of the copolymer as *hk*0 and *hk*1 reflections for poly(HBA). In view of the increasing nonperiodicity of the higher layer lines, we did not include the other reflections in the data for the refinement. Lieser[1] proposed a $P2_12_12_1$ space group for form I of the homopolymer, based on the absence of odd order *h*00, 0*k*0, and 00*l* reflections from the electron diffraction data. The unit cell contains dimer sections of two antiparallel chains that have a 2_1 helical conformation. The fiber diagram of annealed 75/25 copoly(HBA/HNA) contains weak 100 and 010 reflections, plus meridional intensity on the first layer line, but it is possible that the presence of the HNA component causes distortions that prevent complete absence of these reflections. However, Yoon and co-workers[15] report that weak 100 and 010 reflections occur in the powder X-ray pattern for poly(HNA) and propose a structure in which the two chains in the unit cell are related by a 2_1 screw axis halfway between them and parallel to *c*. Contiguous residues along the chain are related by a glide operation, and the chains have parallel sense.

If the chain has a 2_1 helical conformation, the planes of successive phenyl rings are approximately parallel to each other, and $\phi_1 \cong \phi_2$. This structure is analogous to that proposed for poly(benzamide),[16] where $\phi_1 \cong -30$ °C and $\phi_2 \cong 30°$. It is important to note, however, that known structures for model compounds and for aromatic copolyesters, as well as theoretical analyses, favor torsion angles of $\phi_1 \cong -55°$ and $\phi_2 \cong 5°$. Some reported torsion angles[17-21] are given in Table II. Hummel and Flory[19] considered that ϕ_1 should be close to 60°, thereby avoiding the potential bad contact between the carboxyl oxygen and the ortho hydrogen, while ϕ_2 should be close to zero because of π-orbital overlap. The torsion angles in Table II lead to a mutual inclination of approximately 60° between adjacent phenyl units.

We first considered the $P2_12_12_1$ space group and then structures in which the 2_1 helical constraint had been released. The unit cell dimensions were $a = 7.6$, $b = 5.7$, and $c = 12.6$ Å. The refinements were performed by using linked-atom least-squares (LALS) procedures,[22] in which stereochemical constraints[23] are used to supplement the limited X-ray intensity data. For a 2_1 helix with *c* fixed, there is only one torsional variable, ϕ_1; the other refineable parametes are θ, the rotation of the chain about the *c* axis, and *s*, the staggering of the chains along the axis, plus an isotropic temperature factor, *B*, and a scale factor, *K*. $\theta = 0°$ when the projection of the C1–O2 bond on the *ab* plane is parallel to the *a* axis; $s = 0$ when the ester oxygen (O1) is in the *ab* plane.

For space group $P2_12_12_1$, the asymmetric unit is one residue and the unit cell contains dimer units of two chains. The structure was first refined in projection against only the *hk*0 intensities. These are the most intense reflections and define the major features of the structure. Further-

Table III
Observed and Calculated *d* Spacings for Bragg Reflections on the Equator and First Layer Line for Annealed 75/25 Copoly(HBA/HNA): Comparison of Observed and Calculated Structure Amplitudes for the $P2_12_12_1$, $P2_1$, and $Pbc2_1$ Structures

						F(calcd)		
h	*k*	*l*[a]	*d*(obsd), Å	*d*(calcd), Å	*F*(obsd)	$P2_12_12_1$	$P2_1$	$Pbc2_1$
				Observed				
1	0	0	7.60	7.60	0.8	0.0	5.0	0.8
0	1	0	5.70	5.70	5.7	0.0	10.4	0.0
1	1	0	4.57	4.56	81.2	77.9	76.5	76.5
2	0	0	3.83	3.80	48.3	52.9	54.3	55.6
2	1	0	3.13	3.16	17.4	23.3	21.2	20.6
1	2	0	2.69	2.67	9.4	1.5	12.9	6.7
3	1	0	2.33	2.32	17.8	5.7	9.8	5.3
2	2	0		2.28				
0	1	1	5.21 (5.6)[b]		1.9	4.1	2.8	0.0
1	1	1	4.29 (4.5)			overlapped with 110 reflection		
2	1	1	3.04 (3.1)		20.3	14.1	18.4	18.5
				Unobserved				
3	0	0			1.5	0.0	0.2	0.8
0	2	0			7.6	2.6	4.3	3.5
1	0	1			1.5	1.8	5.4	0.0
2	0	1			1.5	0.8	3.5	0.0
3	0	1			1.5	0.1	6.3	0.0
3	1	1			1.5	1.9	4.5	3.1
1	2	1			1.5	8.7	4.9	2.0
2	2	1			1.5	3.0	3.8	1.2

[a] *l* is used for convenience to identify equatorial and first layer line reflections. [b] 1/*R* (Å) in parentheses for the first layer line reflections.

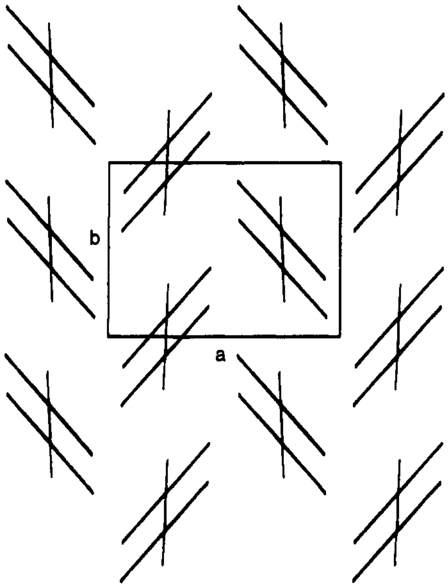


Figure 3. *ab* projection of poly(HBA) refined with $P2_12_12_1$ symmetry.

more, the axial projections of HNA and HBA are very similar, and thus application of these copolymer data to refine the homopolymer structure is most easily justified. Seven observed and two unobserved reflections were used in this refinement, and the final crystallographic *R* value was 0.22. This model was taken as the starting point for refinement in three dimensions against the full intensity data. The resultant structure is shown in Figure 3 and had an *R* value of 0.21. The fractional atomic coordinates are given in Table IV; the values of the refined torsional angles are given in Table V. Addition of the relatively weak first layer line reflections had scarcely any effect on the *ab* projection of the structure: the torsion angles changed by ~2° and θ by ~5°. The chain stagger, s = 0.44 Å, appears to depend almost entirely on the contact criteria, in that *R* is almost insensitive to *s* unless contact constraints are included. The latter constraints result in large changes in ϕ_1 and ϕ_2 such that $R > 0.30$, except in the range $s = \pm 1.3$ Å. The refined values of $\phi_1 = 36.0°$ and $\phi_2 = 36.9°$ for the $P2_12_12_1$ model (Table II) are close to the torsion angles of ~ 30° proposed for the $P2_12_12_1$ structure of polybenzamide.[16] The refined structure has no intermolecular bad contacts, but the chain itself has a bad contact distance of 2.10 Å between the carbonyl oxygen and the ortho hydrogen of the next residue.

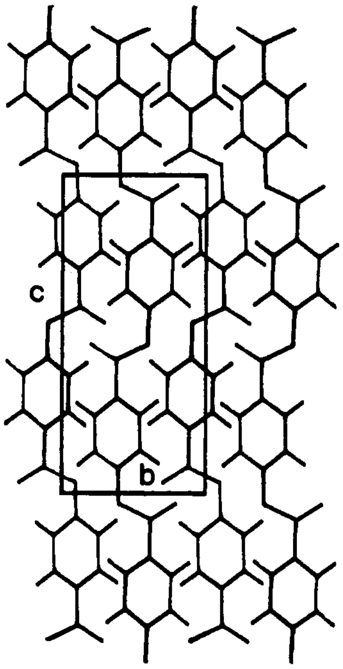


Figure 4. *bc* projection of structure of poly(HBA) refined with $P2_12_12_1$ symmetry.

We have noted above that the equatorial reflections at d = 4.57, 2.69, and 2.33 Å are also indexed by the quenched copolymer structure, analogous to form III of poly(HBA), and that the DSC traces indicate that both forms are present in the annealed specimen. It is not possible to estimate the contribution of form III to the three equatorials, but it is not reasonable to assume that the entire intensity is due to form I. As a test we reduced the intensities of these three reflections to half their observed

Table IV
Fractional Atomic Coordinates of Poly(HBA) Refined with $P2_12_12_1$ Symmetry

atom	X	Y	Z
O1	0.2532	0.0943	0.0351
C1	0.2456	−0.1220	0.0828
C2	0.2461	−0.1160	0.2015
C3	0.3514	0.0447	0.2552
C4	0.3519	0.0503	0.3661
C5	0.2469	−0.1048	0.4235
C6	0.1415	−0.2655	0.3698
C7	0.1411	−0.2711	0.2588
O2	0.2393	−0.2992	0.0321
H3	0.4330	0.1652	0.2107
H4	0.4337	0.1751	0.4080
H6	0.0600	−0.3860	0.4143
H7	0.0592	−0.3959	0.2171

Table V
Refined Parameters for the Models of Poly(HBA)

	$P2_12_12_1$	$P2_1$	$Pbc2_1$
ϕ_1, deg	−38.9 (2.8)	7.8 (3.3)	−5.2 (2.3)
ϕ_2	38.0 (2.8)	47.3 (4.3)	55.2 (4.6)
ϕ_1'	−38.9 (2.8)[a]	2.1 (0.7)	5.2 (2.3)[a]
ϕ_2'	38.0 (2.8)[a]	−50.7 (1.4)[a]	−55.2 (4.6)[a]
θ, deg	88 (8)	127 (14)	119 (15)
s, Å	0.44 (0.02)	0.0[a]	0.0[a]
B	46.5	33.5	43.1
R[b]	0.21	0.16	0.18

[a] Nonrefineable defined by symmetry operations. [b] $R = [\sum ||F(\text{obsd})| - |F(\text{calcd})||]/\sum |F(\text{obsd})|$.

value and repeated the refinement. This resulted in only small changes in the refined structure: for example, the torsion angles changed by less than 2° and θ by less than 5°. Similarly, since the 110 reflection contains most of the observed intensity, it is possible that this could unreasonably dominate the refinement. When we omitted this reflection for the data set and rerefined the structure, we obtained the same result apart from a few small changes in the torsion angles and other refineable parameters. All subsequent refinements therefore continued to be based on the unmodified intensity data.

A reasonable alternative to the $P2_12_12_1$ structure is one that has a 2_1 screw axis parallel to and halfway between the chains, which now have the same sense. We therefore refined the structure in which the unit cell contains two parallel dimers with monoclinic space group $P2_1$ (c unique). The torsion angles ϕ_1, ϕ_2, and ϕ_1' are independent refineable parameters, along with θ, which defines the orientation of both chains about their long axes; s is no longer a variable, as a consequence of the 2_1 axis between the chains.

The final $P2_1$ structure had $R = 0.16$, and the values of the refineable parameters are listed in Table V. It can be seen that the chain conformation has changed significantly from that in the $P2_12_12_1$ structure, and the torsion angles are close to those in the model compounds and polymers in Table II. In terms of the X-ray agreement, the improvement in the R value is not significant,[24] in view of the limited data. However, the new structure is superior in that the intrachain bad contact of the $P2_12_12_1$ structure is relieved due to the large value of ϕ_2. The distances between ester oxygen and the ortho hydrogen are 2.37 and 2.38 Å for the two independent residues.

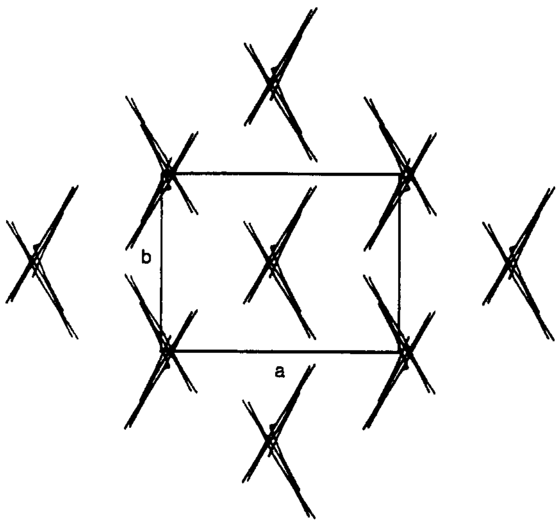


Figure 5. ab projection of poly(HBA) refined with $Pbc2_1$ symmetry.

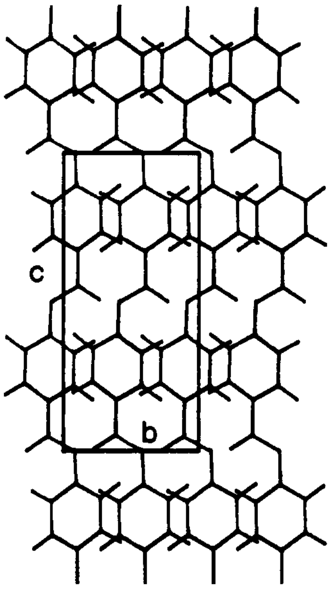


Figure 6. bc projection of poly(HBA) refined with $Pbc2_1$ symmetry.

Table VI
Fractional Atomic Coordinates of Poly(HBA) Refined with $Pbc2_1$ Symmetry

atom	X	Y	Z
O1	0.0395	0.0851	−0.0025
C1	−0.0242	−0.1111	0.0476
C2	−0.0112	−0.1052	0.1661
C3	0.0858	0.0860	0.3271
C5	0.0133	−0.0942	0.3876
C6	−0.0714	−0.2800	0.3373
C7	−0.0836	−0.2855	0.2265
O2	−0.0849	−0.2723	−0.0009
H3	0.1298	0.2206	0.1694
H4	0.1516	0.2304	0.3662
H6	−0.1277	−0.4201	0.3842
H7	−0.1494	−0.4299	0.1875

When we examine the refined $P2_1$ model, we can see that the center and corner chains are approximately related by a b glide plane passing though $a = 1/4$. In addition, a small rotation of each chain about its axis would result in contiguous residues being related by an approximate c glide in the bc plane. Thus the $P2_1$ structure is close to the orthorhombic structure $Pbc2_1$. A structure with this space group was refined in the same way as those above: the refineable parameters are ϕ_1, ϕ_2, θ, B, and K. The final R value was 0.18, and the model is shown in Figure 5. The atomic coordinates are in Table VI, and the refined parameters are given in Table V. The refined torsion angles are similar to those for the $P2_1$ model: the main change is the orientation of the chains (i.e., θ) to conform to the $Pbc2_1$ space group. The O1···H7 distance is 2.57

Å, very similar to 2.61 Å for this distance in phenyl benzoate. The high values of B, the isotropic temperature factor, reflect the distortions inherent in packing random copolymer chains.

In converting from $P2_12_12_1$ to $P2_1$ symmetry, we changed the polarity of adjacent chains from parallel to antiparallel. The copolyester fibers are drawn from a nematic melt, which presumably contains a 50/50 mixture of up and down chains. While segregation to form domains of parallel or antiparallel chains may occur, it is difficult to see what the driving force would be for such segregation, since any defects due to changes in chain sense would be small compared to those inherent in packing random copolymer chains. When we retain the refined parameters of the $P2_1$ structure and simply reversed the polarity of the ester groups on one chain to produce an equivalent antiparallel model, then R increased only to 0.18 (from 0.16). Thus the data are not sensitive to chain polarity, and we cannot decide between parallel, antiparallel, or random polarity packing.

Although we have refined a poly(HBA) model, we stress that the structure proposed is for the annealed 75/25 copolymer. Our model is closest to the $Pbc2_1$ space group and appears to be similar to that proposed for poly(HNA) by Ianelli et al.[15] The data are insufficiently sensitive to determine the polarity of adjacent chains. The chain conformation is very similar to that seen for the model compounds phenyl benzoate and the copolyester poly(phenyl phenylene terephthalate) and is consistent with theoretical predictions.

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