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## Liquid Crystals

Publication details, including instructions for authors and subscription information:

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### Parent homopolymers of liquid crystalline polyesters

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**To cite this Article** Coulter, Patrick D. , Hanna, Simon and Windle, Alan H.(1989) 'Parent homopolymers of liquid crystalline polyesters', *Liquid Crystals*, 5: 5, 1603 — 1618

**To link to this Article:** DOI: 10.1080/02678298908027795

**URL:** <http://dx.doi.org/10.1080/02678298908027795>

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## Parent homopolymers of liquid crystalline polyesters

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A method that combines multi-temperature powder X-ray diffraction and molecular modelling is used to determine the high temperature crystal structures for poly-(*p*-phenylene terephthalate) (PPT) and poly-(*p*-hydroxybenzoic acid) (PHBA). Both have high temperature structures characterized by a degree of rotational disorder. In the case of PHBA there is a distinct high temperature phase above a well defined transition at 350°C, whereas the rotational disorder in 'as polymerized' PPT increases gradually between 370 and 475°C. The interchain packing at high temperatures still maintains phenyl edge to phenyl face correlations and, to some degree, carbonyl carbon to carbonyl oxygen contacts. The findings are relevant to the molecular structure and phase behaviour of liquid-crystalline polyesters as a class.

### 1. Introduction

Thermotropic liquid-crystalline copolyesters were first recognized in the scientific literature as a distinct class of polymeric material in 1976 [1], and have since received considerable attention in both industrial and academic laboratories. Homopolymers poly-(*p*-hydroxybenzoic acid) (PHBA) and poly-(*p*-phenylene terephthalate) (PPT), shown in figure 1, are, in a number of respects, the parent molecules of this class [2].

The two molecules are isomeric and represent two subfamilies of mesogenic polyester [3]: type I (e.g. PHBA) having a 'directionality' and polarity along the chain axis, type II (e.g. PPT) having mirror symmetry in planes perpendicular to the chain axis. Their crystal structures can be expected to indicate the significant intermolecular packing features recurrent throughout the whole family of liquid-crystalline polyesters, and an understanding of the molecular basis of phase behaviour for these homopolymers should provide a platform from which to discuss that of more-complex copolymer systems, with the ultimate ambition of assisting in the design of novel liquid-crystalline polymer formulations.

Despite the seminal character of these materials within the field of liquid-crystalline polyesters, their detailed crystal structures at the atomic scale have not been reported. This is due in part to their intractability, which prevents the drawing of fibres or growth of large single crystals and so limits X-ray diffraction to one dimensional, powder techniques. We have recently developed an approach to solving the crystal structures of intractable polymers and have applied it to PPT at room temperature [4]. The method involves modelling the experimental X-ray powder diffraction of a polymer, using molecular models derived from a well-researched knowledge of the intra- and intermolecular conformational preferences of the component moieties. It is extended here to investigate some of the structural and dynamic changes that occur on the molecular scale as PPT and PHBA are heated towards their degradation temperatures.

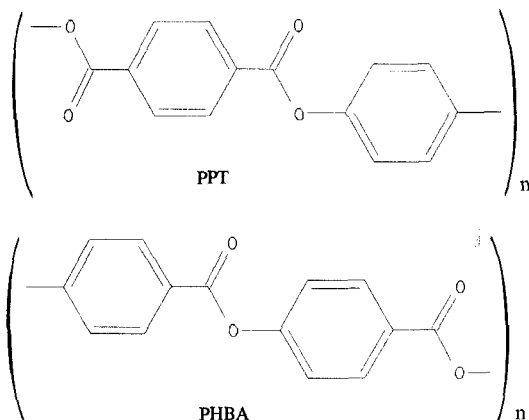


Figure 1. Poly-(*p*-phenylene terephthalate) (PPT) and poly-(*p*-hydroxybenzoic acid) (PHBA).

## 2. Multi-temperature powder X-ray diffraction

### 2.1. Method

X-ray ( $\text{Cu-K}_\alpha$ ) measurements were carried out using a Siemens D500 diffractometer fitted with a Braun position sensitive detector and a modified Anton Paar TTK temperature stage. PHBA was supplied by Carborundum (tradename Ekonol), and PPT by I.C.I. Advanced Materials. Samples were prepared by sprinkling the powder on to a silicon single crystal plate which was specially cut to avoid any Bragg reflections. The temperature was determined by a combination of thermocouples positioned behind and at the surface of the sample and internal temperature standards. Above  $300^\circ\text{C}$  the temperature was accurate to within  $10^\circ\text{C}$ , and below  $300^\circ\text{C}$  to within  $5^\circ\text{C}$ . The temperature stability was better than  $\pm 1^\circ\text{C}$  for the duration of the scan above  $300^\circ\text{C}$ , and better than  $\pm 0.2^\circ\text{C}$  below  $300^\circ\text{C}$ .

The diffraction pattern of the PPT sample shows a number of low angle reflections (below  $7^\circ 2\theta$ ), which have been ascribed to a small fraction of low molecular weight, oligomeric crystals [4].

### 2.2. Results

Figures 2 and 3 show the changes in powder diffraction of PPT and PHBA upon heating from  $25^\circ\text{C}$  to  $470^\circ\text{C}$ . From  $25^\circ\text{C}$  up to  $350^\circ\text{C}$  both materials show two intense reflections to which the indices 1 1 0 and 2 0 0 have been assigned [4–6]. Both show a progressive shift of the 2 0 0 reflection to lower angle (i.e. dominant expansion of the  $a$  unit cell dimension) over this range. Upon heating PHBA through  $350^\circ\text{C}$  there is a clear, and well documented [5, 6], phase transition to what can be described as a 'pseudo-hexagonal' phase. This description is applied because the merging of 2 0 0 and 1 1 0 reflections suggests a hexagonal crystal symmetry, yet the presence of a 2 1 1 reflection at  $2\theta \approx 27^\circ$  betrays orthorhombic symmetry, albeit with a  $\sqrt{3}$  relationship between the  $a$  and  $b$  cell dimensions. At about  $430^\circ\text{C}$  the 2 1 1 reflection disappears, leaving a truly hexagonal structure.

In contrast to the high temperature diffraction of PHBA, that of PPT shows a discontinuity in the rate of shift of the 2 0 0 reflection to lower angle at  $370^\circ\text{C}$ . This process is accompanied by loss of some reflections, for example 0 1 1 at  $2\theta = 17.5^\circ$ ,

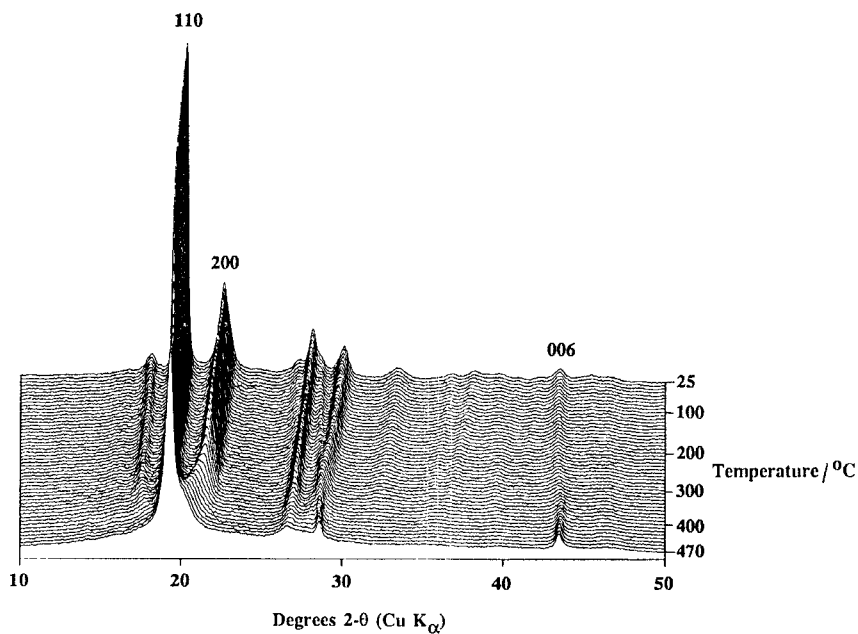


Figure 2. Multi-temperature powder X-ray diffraction of PPT, heating from 25°C up to 470°C.

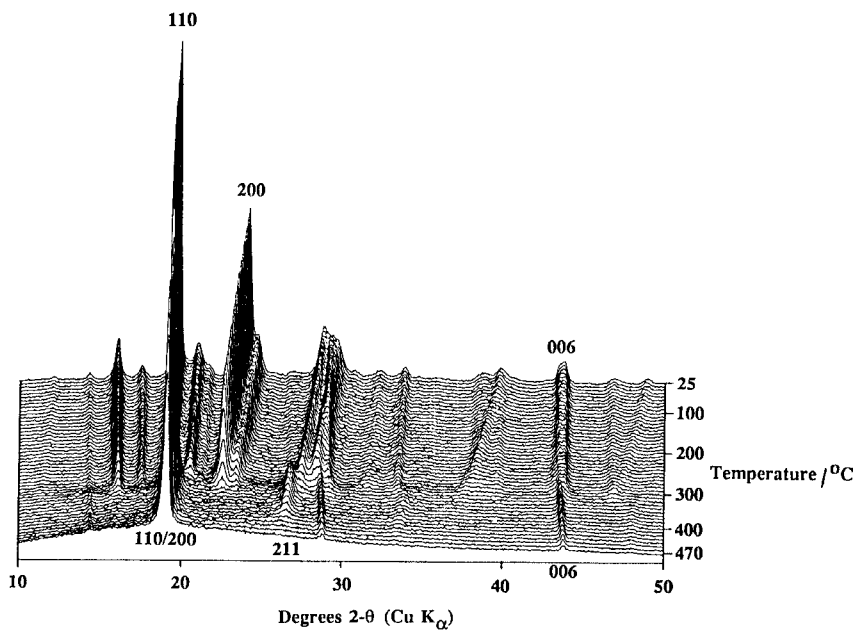


Figure 3. Multi-temperature powder X-ray diffraction of PHBA, heating from 25°C up to 470°C.

and leads to the eventual merger of the 110 and 200 reflections around 475°C. The transitional process here follows a pattern similar to a second order phase change.

The approach adopted to explain these observations is to find molecular models that satisfy the diffraction at the higher temperatures. The time-averaged molecular structure is thus determined and provides a framework within which to make inferences about the molecular motion and the nature of the transitions.

### 3. Structural modelling using powder X-ray diffraction

#### 3.1. Method

All diffraction simulations and structural plots were generated using an in-house polymer molecular modelling system, OSCA. Aspects of the system concerned with diffraction are described elsewhere [4].

#### 3.2. PPT

We have recently solved the structure of PPT at room temperature [4] (see figure 4(a)), showing that it crystallizes in the monoclinic,  $P2_1$ , a space group with cell parameters  $a = 7.98$ ,  $b = 5.33$ ,  $c = 12.65$  Å,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 98.98^\circ$ , and that the principal intermolecular packing features are phenyl edge to phenyl face and carbonyl carbon to carbonyl oxygen contacts. This structure forms an appropriate basis from which to attempt solutions for high temperature structures of PPT.

The unit cell parameters of PPT at 350°C could not be determined by least squares refinement alone, because the overlap of key reflections made it impossible to assign their diffraction angles accurately. The unit cell parameters were therefore determined by a judicious combination of least squares refinement and the fitting of simulated diffraction data to experiment. The structural solution (see figure 4) at this temperature is merely a 'hot' version of the room temperature structure. The mean atomic deviations, as determined from crystallographic temperature factors applied to the simulation, have increased from 0.32 to 0.50 Å in the  $a$  and  $b$  crystallographic directions and remained at 0.05 Å in the  $c$  direction. The new unit cell ( $a = 8.34$ ,  $b = 5.50$ ,  $c = 12.65$  Å,  $\alpha = \gamma = 90^\circ$ ,  $\beta = 98.55^\circ$ ) has expanded principally along the  $a$  crystallographic axis and, sterically consistent with this, the mean torsion angle for the  $O_{\text{ester}}-C_{\text{phenyl}}$  bond (which is directly related to the angle between the planes of consecutive phenyl rings along a polymer chain) has increased from 67° to 70°.

The increase in the  $a$  cell dimension and in the angle between consecutive phenyls can be explained as a product of two temperature dependent factors, the first of which was alluded to in [6] concerning the same phenomenon in PHBA. First, as the libration of phenyls around their 1,4 axes (or indeed of benzoate moieties, the  $O_{\text{ester}}-C_{\text{phenyl}}$  backbone bond being by far the most flexible [7]) increases with temperature, so the volume occupied by the chains is expected to become increasingly cylindrical and there will therefore be a tendency towards hexagonal packing. To achieve this the  $a$  cell dimension must expand to  $\sqrt{3}$  times the  $b$  dimension. Secondly, the intramolecular rotational energy well for the  $O_{\text{ester}}-C_{\text{phenyl}}$  bond is anisotropic, having a minimum around 60–70° but increasing less sharply to higher angle than to lower angle [7]. Thus, increasing libration of this bond with temperature should increase its mean torsion angle.

At 475°C all attempts to model the unit cell contents as an even 'hotter' room temperature structure proved unsuccessful. In particular the 011/011 reflection,

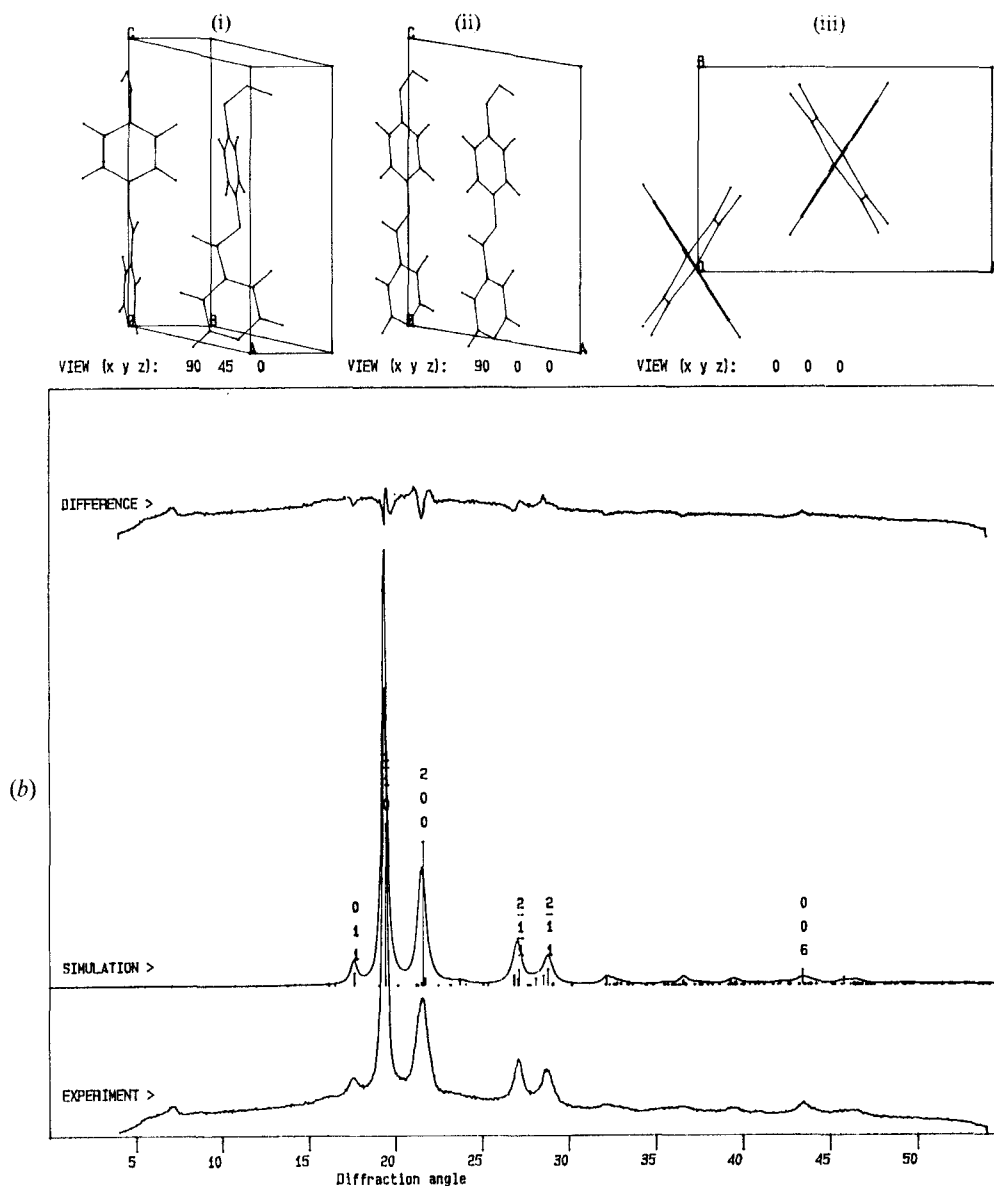


Figure 4. (a) Three views of the crystal motif of PPT at room temperature. (i) A generalized view, demonstrating phenyl edge to phenyl face and carbonyl oxygen to carbonyl carbon 'bonding'. (ii) A view from the  $ac$  plane, showing how the monoclinic angle is related to the orientation of ester carbonyls. (iii) A view down the chain axis, demonstrating phenyl edge to phenyl face 'bonding'. (b) Experimental and simulated diffraction for PPT at 350°C, showing a reasonable fit, using the same basic model as at room temperature. Straight lines under simulated peaks represent actual peak positions and their relative integrated intensities before broadening.

characteristic of the structural symmetry at room temperature, has been lost. It was necessary to invoke a 0–180° disorder in the orientation of the PPT moieties around their chain axes. This was effected by starting with the room temperature model, changing to an orthorhombic symmetry, then allowing for a random, 180° rotational degeneracy of the unit cell 'chains' around their chain axes (see figure 5(a)). In terms

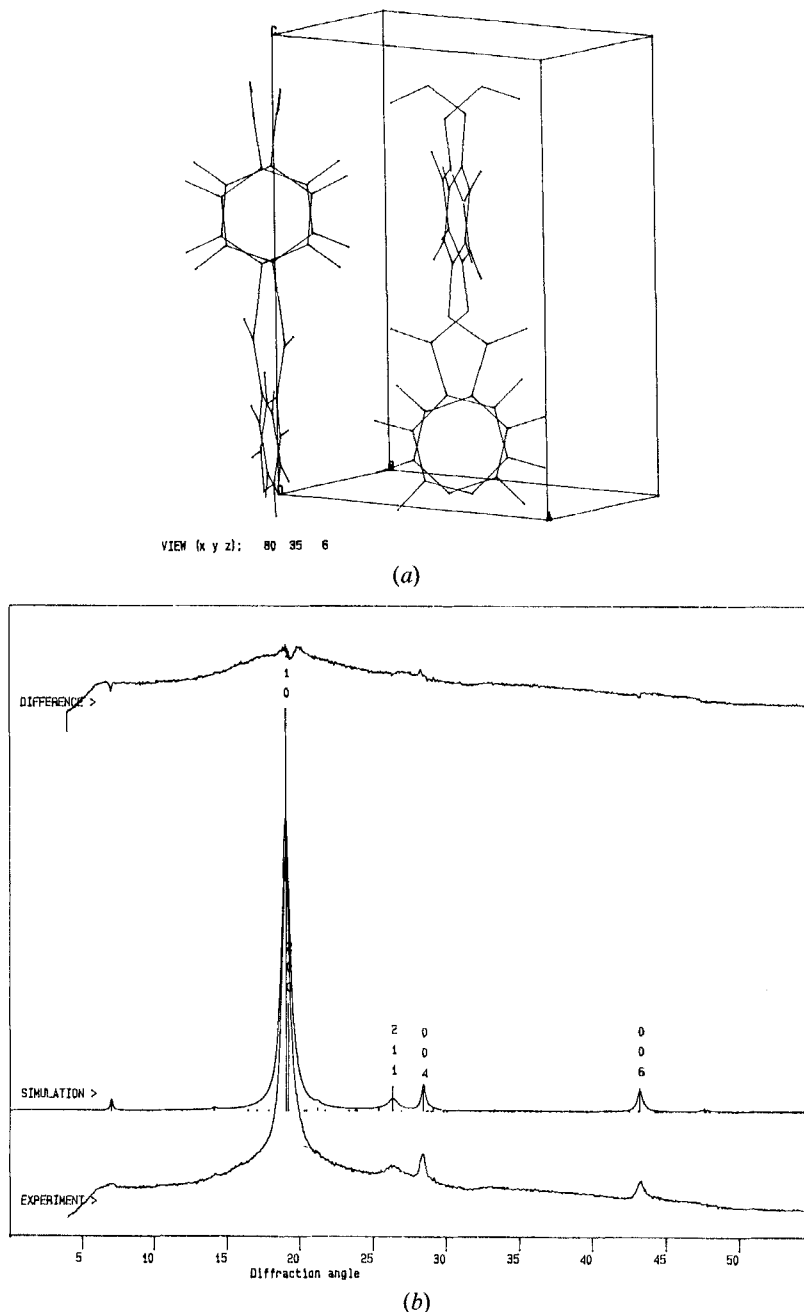


Figure 5. (a) Representation of the disordered model for PPT at 475°C. Note the alternation orientation of ester groups by 180° rotation around the chain axis. (b) Experimental and simulated diffraction for PPT at 475°C, showing a reasonable fit.

of the mechanics of constructing this model for diffraction simulation, each chain in the cell had another related by a 180° rotation about the chain axis superimposed upon it and the contribution of each atom to the diffraction intensity halved. Then, in order to fit the simulated diffraction to experiment (see figure 5 (b)), it was necessary

to refine the unit cell parameters (to  $a = 9.25$ ,  $b = 5.40$ ,  $c = 12.56$  Å,  $\alpha = \beta = \gamma = 90^\circ$ ) and to make two geometrical adjustments to the model. First, a further increase to the  $O_{\text{ester}}-C_{\text{phenyl}}$  bond rotation angle was made (from  $70^\circ$  to  $85^\circ$ ) and, secondly, the chain length needed to be shortened by  $0.09$  Å relative to the  $350^\circ\text{C}$  structure in order to satisfy the position of the  $00l$  reflections. Such 'thermal shortening' is the expected result of increasing polymer chain vibrational freedom. In the structural model the chain shortening was effected by twisting the ester C–O bond  $18^\circ$  out of plane, although it should be emphasized that the choice of this shortening technique was somewhat arbitrary, being just one of a number of shortening mechanisms. The molecular motion along the chain axis necessary for thermal shortening is evidenced by the temperature factor applied in the modelling. From  $25^\circ\text{C}$  to  $350^\circ\text{C}$  the mean atomic displacement along the  $c$  (i.e. chain) axis remained close to  $0.05$  Å, but increased by six times to  $0.31$  Å by  $475^\circ\text{C}$ , whereas the displacement in the  $a$  and  $b$  directions doubled from  $0.50$  to  $0.96$  Å.

In terms of atomic repositioning this disordering has a large effect on ester moieties, but makes little difference to the phenyls because of their two-fold rotational symmetry (see figure 5(a)). There is still, therefore, detectable phenyl edge-face packing correlation at  $475^\circ\text{C}$ , in addition to which carbonyl oxygens and carbonyl carbons maintain an average interaction distance of  $3.6$  Å (cf.  $3.37$  Å at room temperature,  $2.85$  Å for van der Waals contact [8]) in the time-averaged model (see figure 5(a)).

A picture can now be drawn of PPT during the transitional process from  $370^\circ\text{C}$  to  $475^\circ\text{C}$ . At  $370^\circ\text{C}$  an alternative rotational orientation of the ester groups starts to be 'populated' within the existing crystal lattice. By  $475^\circ\text{C}$  the alternative has almost the same population as the original low temperature orientation. The process is accompanied by a progressive shift from monoclinic to orthorhombic symmetry, as the low temperature monoclinicity was caused by the specific orientation of ester groups with respect to the  $ac$  plane (see figures 4(a)(i)), which is lost as the alternative orientation populates (see figure 5(a)).

### 3.3. PHBA

#### 3.3.1. Introduction and chain conformation

It is believed that PHBA exhibits two crystalline phases [9] at room temperature, making the solution of the molecular structures from X-ray powder diffraction additionally complicated. The unit cell for the 'pseudo-hexagonal' phase at  $380^\circ\text{C}$  was determined by least squares refinement, assuming an orthorhombic symmetry ( $\alpha = \beta = \gamma = 90^\circ$ ), to have dimensions  $a = 9.13$ ,  $b = 5.35$ ,  $c = 12.49$  Å. Models for the intramolecular geometry of PHBA were constructed in the same manner as had been done for PPT [4], using the body of structural and conformational information that we have recently compiled on aromatic polyesters [7]. For a crystallographic repeat of two monomer units, there are two low energy conformations for the intramolecular structure of PHBA (see figure 6). Conformer I has an angle of about  $120^\circ$  between the planes of the consecutive ester groups and conformer II an angle of about  $60^\circ$  [10].

#### 3.3.2. Rotational disorder

As with the  $475^\circ\text{C}$  structure of PPT, it was not possible to account for the observed diffraction at  $380^\circ\text{C}$  with a 'single occupancy' of lattice site model, but was necessary



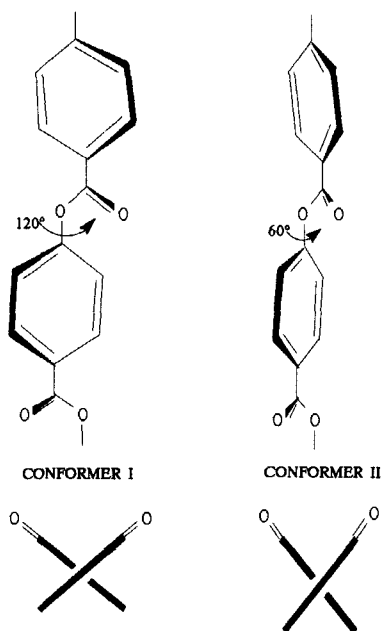


Figure 6. Two low enthalpy conformers of poly-(*p*-hydroxybenzoic acid) and their schematic representations viewed down the chain axis.

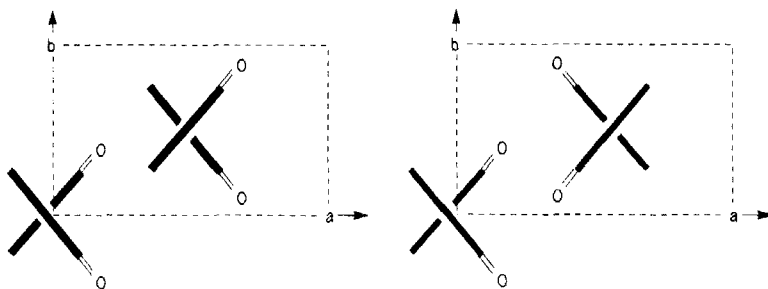


Figure 7. Schematic representation of crystal motif, viewed down the chain axis, for two single occupancy models of the 'pseudo-hexagonal' phase of PHBA, showing phenyl rings (bold lines) and orientation of ester carbonyls.

to generate 'multiple occupancy' models of higher inherent symmetry, so as to account for the small number of observed reflections. Figure 7 shows two schematic single occupancy models. The simulated diffraction of both models show too many reflections. However, by allowing the chains in these models to adopt a random  $180^\circ$  rotational degeneracy (see figure 8(a)), in a similar manner to the  $475^\circ\text{C}$  model for PPT (see §3.2), a much better fit can be obtained (see figure 8(b)). Consistent with rotational disorder of this type is the substantial mean atomic displacement,  $0.67 \text{ \AA}$ , in the *a* and *b* cell axis directions and somewhat smaller displacement,  $0.28 \text{ \AA}$ , in the *c* (i.e. chain axis) direction determined for the model. The model uses conformer I of PHBA, but a similar result can be obtained by employing conformer II, as its atoms can be made to occupy similar positions (see figure 8(c)). The repeat distance for conformer I is intrinsically shorter than that of conformer II by about  $0.07 \text{ \AA}$ , and so in theory it should be possible to distinguish between them crystallographically by measuring the experimental  $00l$  reflections. In practice, however, the rather small

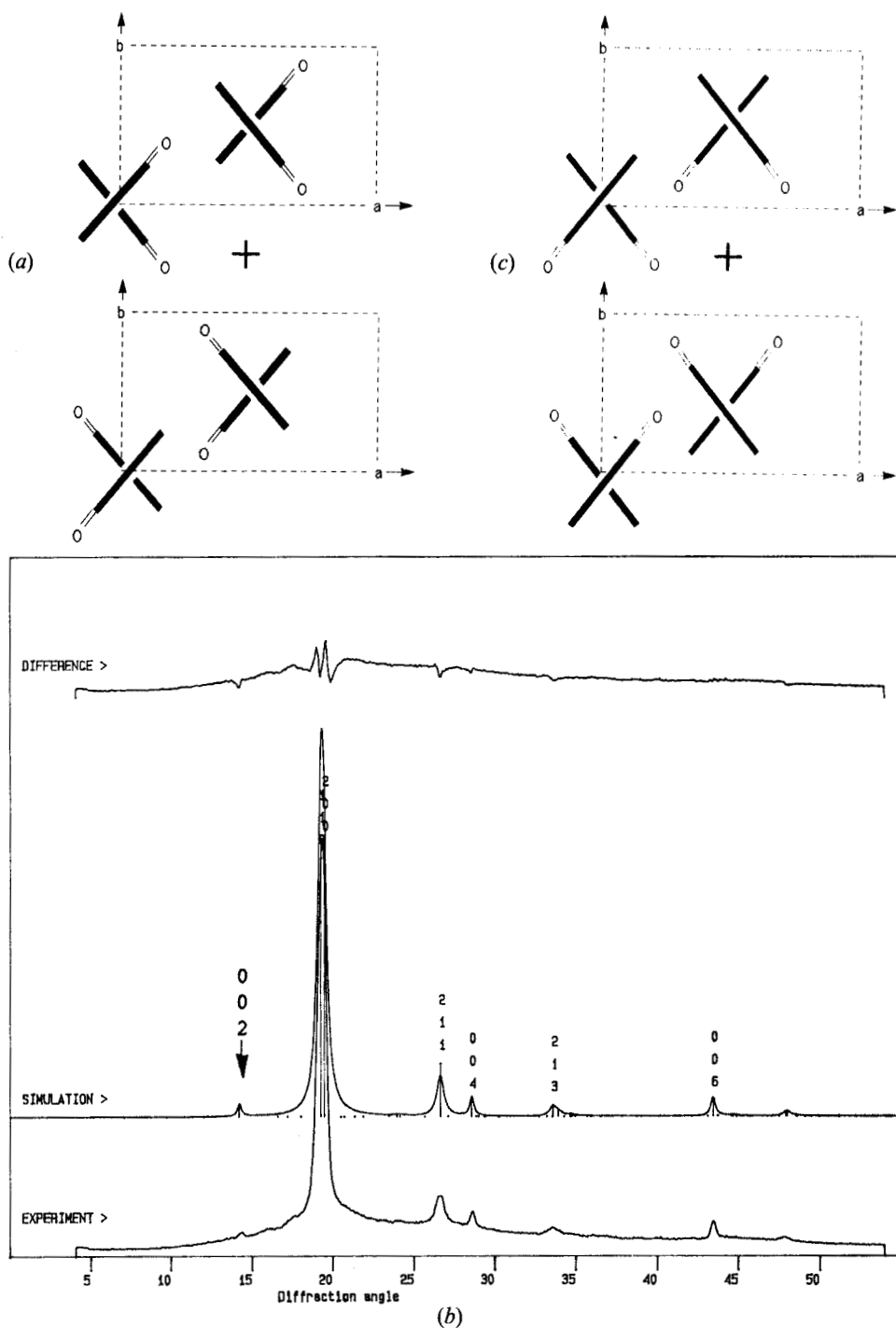


Figure 8. (a) Schematic representation of a double occupancy model motif for the 'pseudo-hexagonal' phase of PHBA. Note that the edge of one phenyl always neighbours the face of another and vice versa. (b) Powder diffraction simulation for this model, showing that it satisfies all the observed reflections and gives a reasonable fit to the 380°C experimental data. (c) Representation of a crystal motif, featuring conformer II of PHBA. Note that this model places phenyl and ester moieties in fundamentally similar positions to the model for (a) and so gives very similar diffraction to (b).

length difference and the unknown extent to which 'thermal shortening' is taking place make this a poor basis for structural differentiation. In the following, conformer I is always used, but it should be borne in mind that conformer II could be employed to achieve very similar results in situations where the 180° rotation degeneracy is applied. Indeed, as there is only a very small ( $< 0.75 \text{ kcal mol}^{-1}$ ) intramolecular energy barrier between the two conformers [7], there may well exist a random jumble of the two at any one moment in this phase. The key interchain structural features of the successful model with either PHBA conformation or a random jumble of the two is the preservation of axial register (i.e. phenyl next to phenyl and ester next to ester), and the preservation of phenyl edge to phenyl face order. The interaction of carbonyl carbon with carbonyl oxygen appears to be of less significance, there being a mean interaction distance of about 3.9 Å in the model compared with a van der Waals contact distance of 2.85 Å [8].

### 3.3.3. *Edge-face versus face-face*

In order to test the model and its implications, other possible types of correlation and additional degeneracies were tried. If, instead of packing phenyls edge to face as in figure 8, they are packed face to face as in figure 9, then the fit between simulation and experiment is clearly poor. The 2 1 1 reflection does not appear but unwanted  $hkl$  reflections (notably 1 1 1 and 1 1 3) do. Strong 1 1 0, 2 0 0 and 2 1 1 peaks in the absence of 1 1 1, 2 1 0 and 3 1 1 are indicative of a body centred cell for which the reflection rules, ( $h + k + l = \text{even integer}$ ) pertain. The intermolecular conformation dictates that benzoate moieties should be disposed to one another at an angle of 60–120° along the chain. A consequence of the body centred arrangement is that the moieties will be packed edge-face on planes perpendicular to the  $c$  axis. Face-face packing on these planes would imply a C centred unit cell for which 2 1 1 is a forbidden reflection ( $h + k$  required to be an even integer). If random face-face edge-face packing of phenyls is permitted (i.e. a combination of models in figures 8(a) and 9(a)), the symmetry becomes near to truly hexagonal and the simulated diffraction (see figure 10) takes on the appearance of the hexagonal ( $> 430^\circ\text{C}$ ) phase. These observations establish the importance of the phenyl edge to phenyl face interaction in the 'pseudo-hexagonal phase'.

### 3.3.4. *Chain directionality*

In the successful model (see figure 8) the two chains in the unit cell had the same polarity and so it may be called an 'up-up' model. Figure 11 shows an analogous 'up-down' model which is clearly a bad fit. However, a random 'up or down' model (see figure 12) gives a reasonable fit. The principal differences in the simulated diffraction for this model from that of the 'up-up' model are slightly weaker 2 1 1 and 2 1 3 reflections, and the absence of the 0 0 2 reflection. Indeed, the presence of this weak reflection in the experimental diffraction suggests, therefore, that at least some of the crystals conform to the 'up-up' model. A qualitative comparison of the simulated-experimental difference plots for the two models (see figures 8(b) and 12) reveals that for reflections where the 'up-up' model is too intense (0 0 2, 2 1 1 and 2 1 3) the 'up or down' model is too weak. It is tempting, though not compelling, to suggest that the 'pseudo-hexagonal' phase consists of two crystal forms, an 'up-up' and an 'up or down'. Such a proposal is consistent with the evidence that room temperature samples of PHBA cooled from the 'pseudohexagonal' phase contains two crystal forms [9, 11].

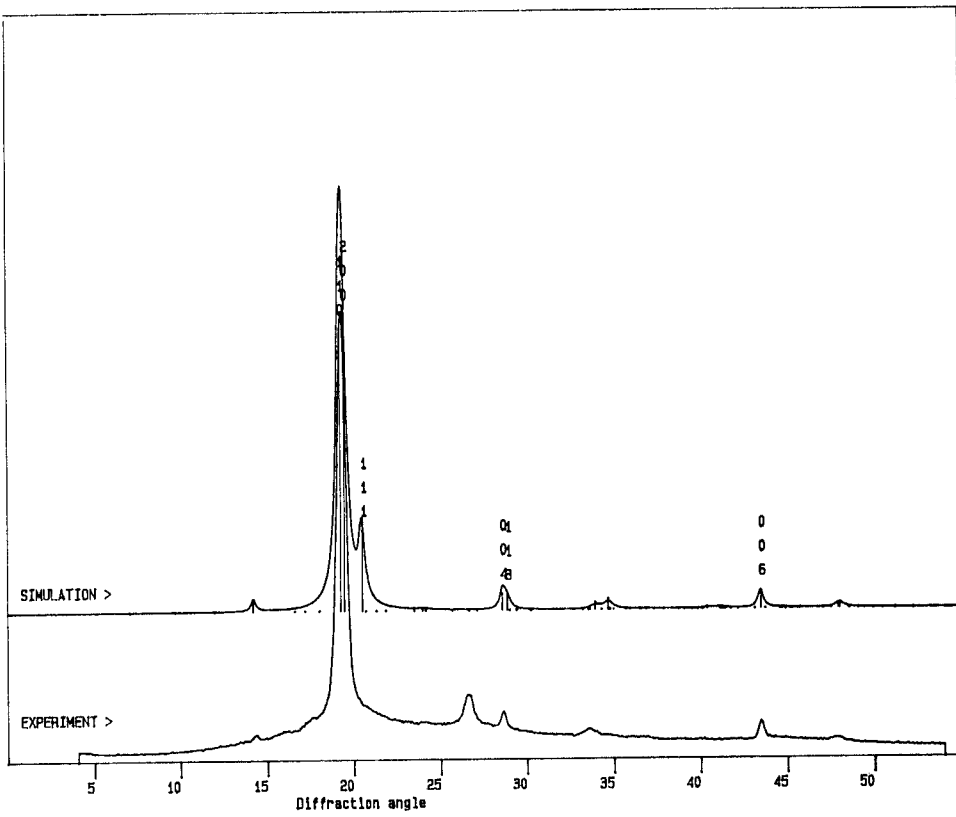
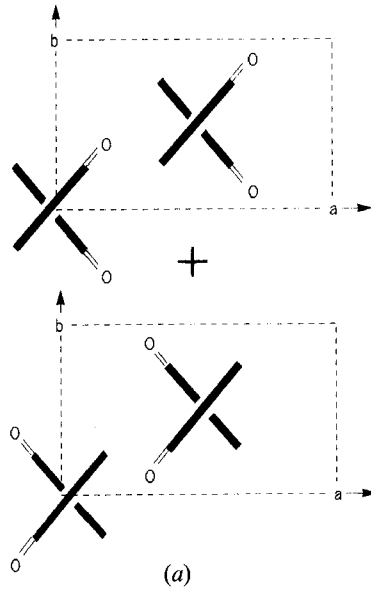


Figure 9. (a) Representation of a PHBA model analogous to that of figure 8 (a) but having phenyls packed face to face instead of edge to face (b) Powder diffraction simulation for this model, showing that it gives a poor fit to experimental data at 380°C.

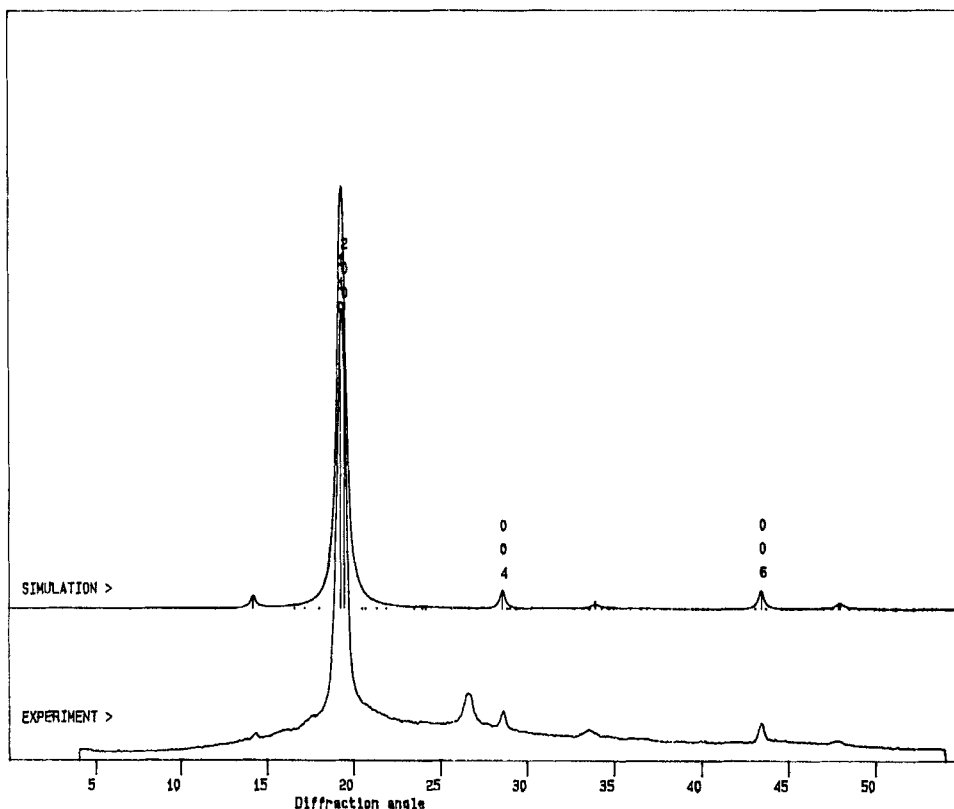


Figure 10. Powder diffraction simulation for a near-hexagonal model (combination of figures 8(a) and 9(a)) which has random face-face and edge-face correlation. Note the absence of the 211 peak and, indeed,  $hkl$  reflections in general.

### 3.3.5. Rotational twinning

While the structural model for PHBA between 350 and 430°C shown in figure 8 successfully accounts for the observed diffraction, it does not explain the reasons for the 'pseudo hexagonal' structure. That is, why the structural contents of a unit cell showing non-hexagonal symmetry (as demonstrated by the occurrence of a 211 (orthorhombic) reflection) should pack with their chain axes on a hexagonal net. An explanation of this packing has already been presented in terms of a dynamic rotational twinning model [6], in which the hexagonal shape of the cell (equivalent to  $a/b$  (orthorhombic) being equal to  $\sqrt{3}$ ) is stabilized by its ability to accommodate  $\pm 60^\circ$  rotational variants of the structure without readjustment of the relative positions of the chain axes.

The transition of the pseudo hexagonal phase to hexagonal above 430°C, which results in the loss of the 211 reflection is accounted for, in the modelling performed here, in terms of simple thermal libration of the ester and phenyl units which suppresses 211 more rapidly than 110 because the former is at a higher diffraction angle. The rotational twinning model, in which the 211 reflection decays when the twin planes normal to the chain axis become sufficiently closely spaced, is more specific in that it is implying that the phenyl-phenyl correlations *along* the chain acquire a  $\pm 60^\circ$  degeneracy before the interchain edge to face phenyl correlations are

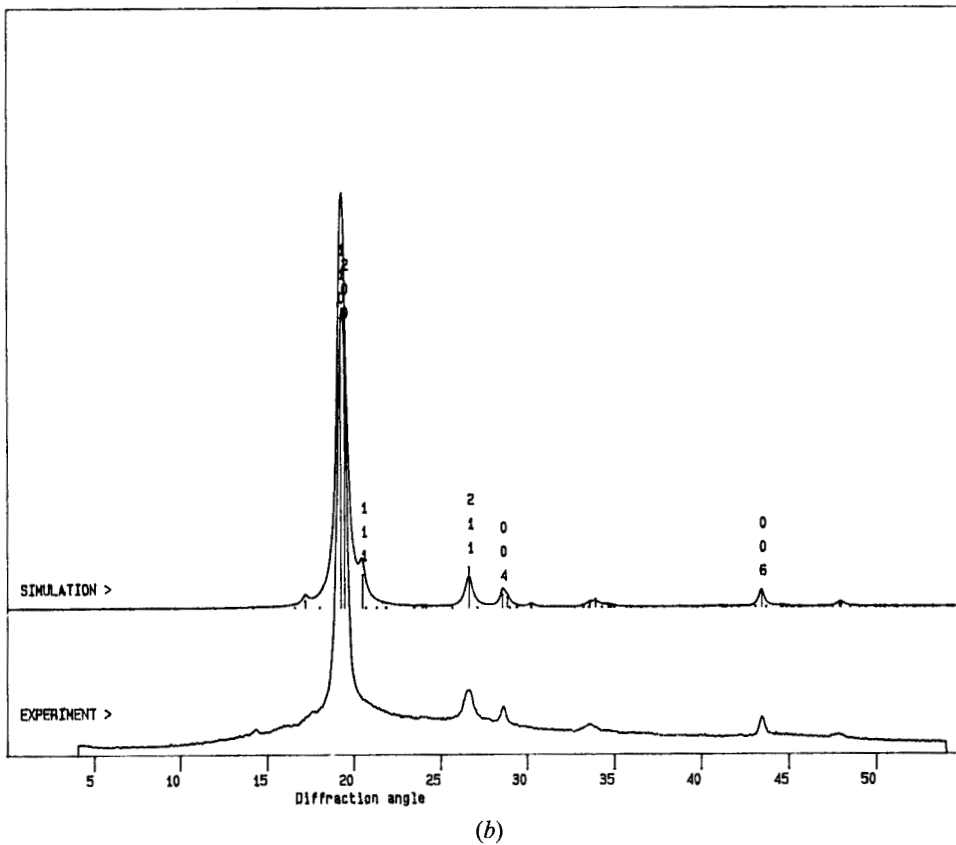
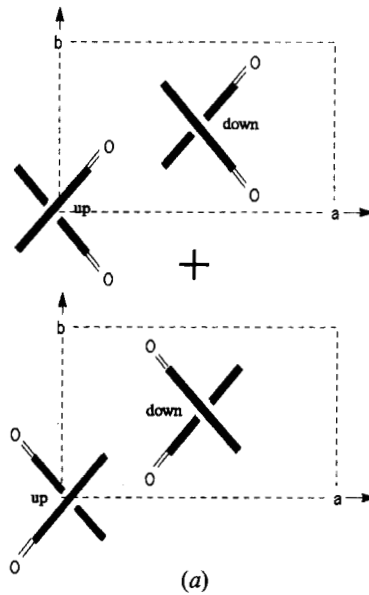


Figure 11. (a) Schematic representation of PHBA model analogous to that of figure 8 (a), but having one chain of the motif oriented 'up' and one 'down' instead of both 'up'. (b) Powder diffraction simulation for this model, showing prominent unwanted reflections such as 111.

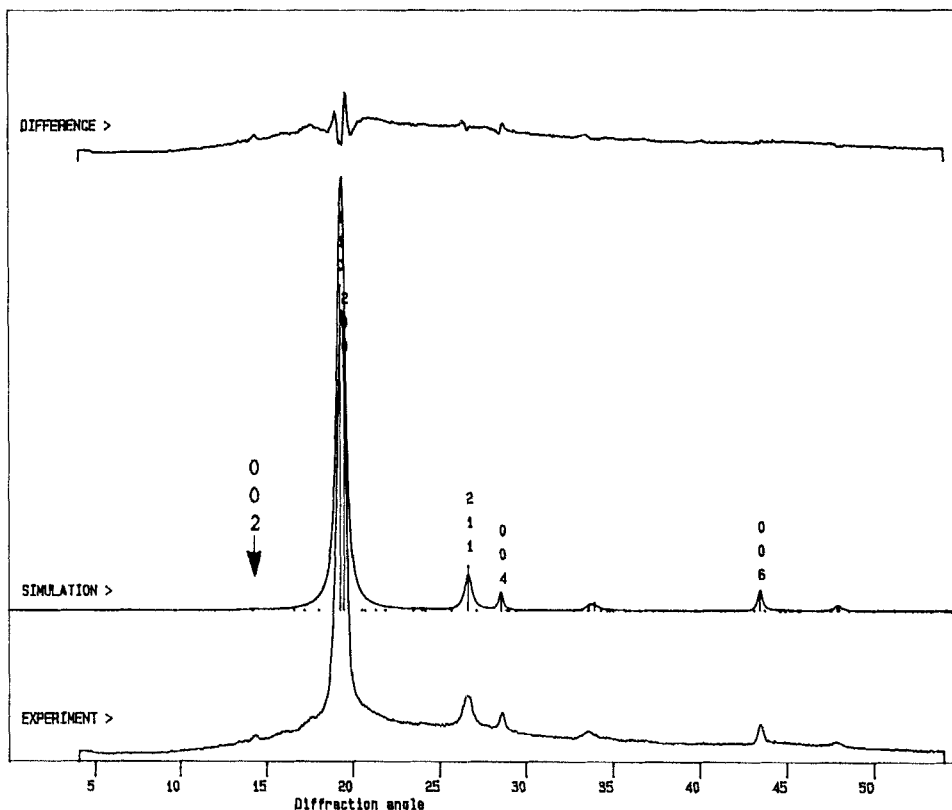


Figure 12. Powder diffraction simulation for a model analogous to that of figures 8 (*a*) and 11 (*a*) but with the option for either chain in the motif to be randomly 'up' or 'down'. Except for the significant absence of a 002 reflection the model provides a reasonable fit to experiment.

lost. The diffraction modelling carried out so far, while consistent with this model, is not able to distinguish it from one of more general libration.

### 3.3.6. Summary for PHBA structures

In conclusion, the 'pseudo-hexagonal' phase has a 180° rotationally degenerate, dynamically disordered structure. The remaining intermolecular ordering is dominated by electrostatically favourable interactions, notably phenyl edge to phenyl face and, to a lesser degree, carbonyl carbon to carbonyl oxygen contact. At least some of the 'pseudo-hexagonal' material has net chain directionality, i.e. it contains regions of crystallites with an electric dipole. Above 430°C PHBA assumes a hexagonal structure and the coupled orientation of consecutive, intramolecularly bonded benzoate moieties is lost. In respect of chain packing the 'pseudo-hexagonal' phase bears a resemblance to the so-called smectic E phases of small molecule thermotropic liquid crystals, while the hexagonal phase has some similarity to a smectic B-phase [12].

## 4. Implications for the family of liquid-crystalline polyesters

There are two issues concerning liquid-crystalline polyesters about which the above work is keenly instructive. Firstly, it demonstrates the important intermolecular

interactions in aromatic polyesters and their persistence at high temperatures. Phenyl edge to phenyl face (type A) and carbonyl carbon to carbonyl oxygen (type B) interactions [4] have been found to be dominant in a number of aromatic ester oligomer single crystals [13] and in PPT at room temperature. While both types of interaction are electrostatically favourable and, theoretical and experimental studies attest in particular to the strength of benzene edge-face bonding [14]. The work presented here shows that type A interactions persist up to at least 430°C in PHBA and 475°C in PPT. A lesser significance is attached to type B interaction in the high temperature phases. It should be noted that phenyl moieties are more dominant in the X-ray diffraction patterns than esters, making precise definition of mean ester orientation and atomic deviation less certain.

We believe, therefore, that type A and B contacts will be dominant in controlling the intermolecular structure of aromatic polyesters and copolyesters that permit them. The strengths of these intermolecular bonds will influence phase transition temperatures, as well as certain mechanical properties such as axial compressive strength.

Secondly, the existence of a stable, crystalline phase, containing elements of rotational disorder, was demonstrated for both materials. This provides evidence to make the assertion that stiff chain polymers can enable structures that are rotationally disordered around their chain axes to some degree, yet nevertheless crystalline in the X-ray diffraction sense. It is also likely that such structures will recur across a wide range of linear aromatic polyesters and copolyesters. In the case of PPT and PHBA the disordering 'agent' is heat, however it appears that rotational disorder can also be encouraged by the presence of comonomer units. In this way an analogy can be drawn between comonomer and heat as structurally disruptive forces. An implication of this analogy is that it should be no surprise to find the existence of a pseudo hexagonal crystalline phase, as a common feature of liquid crystal random copolyesters at room temperature. A good example may be the (*p*-hydroxybenzoic acid)-(2,6-hydroxynaphthoic acid) copolymers, materials whose unexpected crystalline properties have attracted substantial interest [15].

We acknowledge financial support from SERC and ICI.

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