The influence of temperature on the structure of poly(2,6-hydroxynaphthoic acid)

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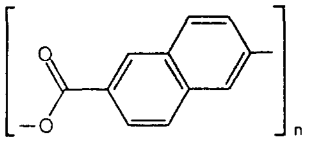
The structure of poly(2,6-hydroxynaphthoic acid) (PHNA) is studied as a function of temperature using X-ray diffractometry. Similarities are observed between its behaviour and that of poly(1,4-hydroxybenzoic acid) (PHBA), including a high temperature transition to a pseudo-hexagonal rotator phase, which has been commented on previously. There are, however, striking differences between the two polymers, most notably the presence of a melt phase in PHNA, above 440°C, which displays ordering similar to that observed in smectic liquid crystals. The phase observed in PHNA at a given temperature depends on thermal history so that, for example, the room temperature orthorhombic phase reported by Mühlebach *et al.* is seen only after annealing, while the temperature of the transition to the pseudo-hexagonal phase decreases from 395°C, in our as-polymerized samples, to 300°C or lower, after heat treatment. The unit cell determined for the pseudo-hexagonal phase of PHNA has similar *a* and *b* parameters to those in the corresponding phase of PHBA. Implications of these findings for the structures of the copolymers of PHBA and PHNA are discussed.

(Keywords: poly(2,6-hydroxynaphthoic acid); smectic liquid crystal; rotator phase; X-ray diffractometry)

INTRODUCTION

The subject of this paper is the structure of poly(2,6-hydroxynaphthoic acid) (PHNA):



a polymer which hitherto has received much less attention than the related polyester poly(1,4-hydroxybenzoic acid) (PHBA)[1-5]. 2,6-Hydroxynaphthoic acid (HNA) has been used primarily as a comonomer with other more linear monomer units, such as 1,4-hydroxybenzoic acid (HBA), as a means of disrupting crystallization and so encouraging the formation of liquid crystalline mesophases. Indeed, copolymers of HBA and HNA (the B–N copolymers) have been marketed by several companies for applications requiring high strength or resistance to solvents[6]. However, PHNA is interesting in its own right, displaying a range of different phases including, at high temperatures, a melt phase with ordering resembling that of a smectic liquid crystal[7].

The similarity between the behaviour of PHBA and PHNA has already been noted[8]. However, this similarity is superficial, for when examined closely, the structure and phase stability of PHNA exhibits several particular aspects which reflect the different structure of the monomer.

The presence of a relatively stable high temperature melt phase in PHNA would suggest the possibility of producing oriented samples. Unfortunately, there are technical difficulties involved with working at such high temperatures (~450°C) and, so far, although we have succeeded in melt shearing the material, the degree of orientation so produced has been very poor. We have been unable to draw fibres as yet, but this is the subject of on-going research. For this reason, we will limit our discussions to the unoriented powder, as supplied.

The study of PHNA forms part of a much larger project to try to understand the nature of molecular packing in the B–N copolymers. By studying the end members of the copolymer series, i.e. PHBA and PHNA, it is hoped to elucidate the main rules governing the packing of the molecules in both the crystalline and liquid crystalline phases of the copolymers.

EXPERIMENTAL

The polymer was supplied in the form of a powder by Hoechst-Celanese, and was made by a polycondensation reaction employing a high temperature heat transfer medium in a process analogous to that used commercially for the production of PHBA[9]. Throughout this paper, reference will be made to heat-treated or annealed samples of PHNA. These were produced by heating at an average rate of 1°C min^{-1} up to 425°C whilst taking diffraction scans, holding there for 15 min, and then cooling at 1°C min^{-1} to room temperature. The term as-polymerized is used to refer to the material as supplied.

X-ray diffractometry was carried out using a Siemens D500 θ–θ vertical reflection diffractometer, using Cu Kα

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radiation and a Braun position-sensitive detector. Temperature control was achieved using a modified Anton Paar TTK temperature stage controlled by an Acorn BBC B+ microcomputer, which maintained and ramped the temperature according to a pre-programmed temperature profile. The nominal sample temperature was monitored using a type K thermocouple positioned behind the sample, and calibrated by incorporating copper powder particles in the polymer sample, and comparing measured lattice parameters with published values for a range of temperatures. By this method, the sample temperature was known to within ±5°C above 300°C and within ±2°C below that temperature. This calibration was necessary because, in X-ray reflection geometry, the sample is heated by thermal conduction from elements behind the mount. The temperature stability using the computer controller was better than ±1°C above 300°C and usually better than ±0.2°C below 300°C, for the duration of each diffraction scan. However, since diffraction scans were taken at preset temperatures, transition temperatures as measured by this method are only quoted to the nearest 5°C. In order to minimize problems of degradation, samples were kept under nitrogen for the duration of the high temperature experiments.

Differential scanning calorimetry (d.s.c.) was performed on a Perkin Elmer Delta Series DSC7 machine.

RESULTS

Thermal history

The diffraction pattern of PHNA depends on the thermal history of the sample. Thus, the diffraction pattern of as-polymerized PHNA at room temperature differs significantly from that of an annealed sample (*Figure 1*). It is clear that, in *Figure 1*, although the same principal reflections are seen in both patterns, they differ in position before and after the heat treatment. *Table 1* gives details of peak positions and peak widths for the two patterns. The degree of crystallinity is difficult to determine accurately in poorly ordered systems where crystalline peaks are very broad, but within experimental errors appears to be the same in both traces, at ~50%.

The effect of thermal history is also reflected in the d.s.c. data. *Figure 2* shows d.s.c. traces for two samples of the as-polymerized material, during several heating cycles. *Table 2* details peak positions and enthalpies. It can be seen that the first heating cycle differs from subsequent cycles in that the temperature of the first endotherm (at ~395°C) in the as-polymerized materials drops by almost 100°C in later cycles. The endotherm at 300°C in second and subsequent heating runs is very broad, extending over more than 50°C, and in some cases appears more as a change in gradient rather than a peak. The gradual nature of this transition is also observed by

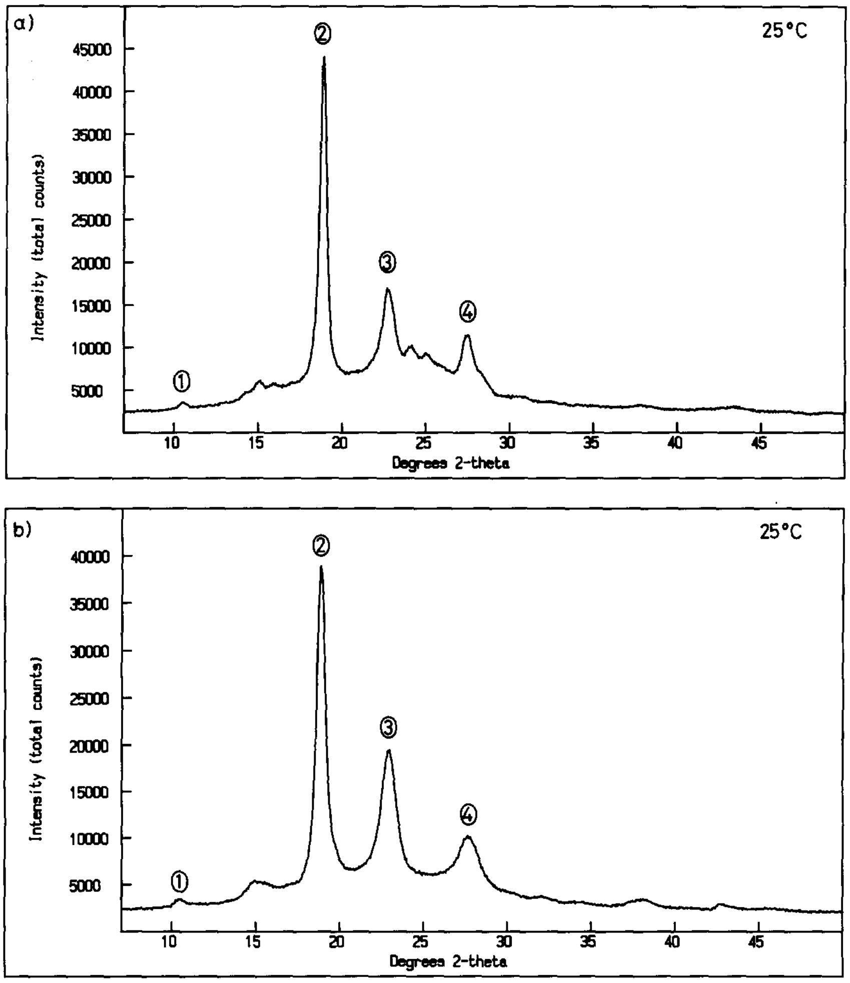


Figure 1 X-ray diffraction patterns of (a) as-polymerized PHNA and (b) annealed PHNA measured at room temperature (25°C), indicating a structural change on annealing. Principal peaks are labelled 1–4. The labels correspond to those used in *Table 1*

X-ray diffraction. Subsequent heating cycles do not differ qualitatively from the second, although exact peak positions and enthalpies may vary slightly. We have not observed an endotherm at 338°C, as described by Mühlebach *et al.*[8], which may be a consequence of different methods of sample preparation.

The endotherms labelled in *Figure 2* may be attributed to different phase transitions in the light of the X-ray data to be described below. The peak marked (i) in the first heating cycle is a transition to a high-symmetry orthorhombic phase which will be referred to as a pseudo-hexagonal phase, for reasons to be discussed. Those marked (ii) indicate the corresponding transition in the heat-treated material. The peaks marked (iii) are transitions to a melt phase, which appears to show liquid crystalline order, and the temperature of this transition is approximately the same in all heating cycles.

As-polymerized material

The powder diffraction pattern of as-polymerized PHNA is shown in *Figure 3* for a range of temperatures between 25°C and 425°C, equivalent to the temperature range of the d.s.c. scans in *Figure 2*. The most noticeable feature of *Figure 3* is a transition at around 400°C to a phase of high symmetry with few diffraction maxima (*Figure 4*) that resembles the high temperature diffraction pattern of phase III of PHBA[4]. Phase III of PHBA has recently been shown to be body centred orthorhombic, with the ratio of cell lengths a:b very close to $\sqrt{3}$, so that a primitive hexagonal cell is possible[1,2]. The term pseudo-hexagonal is commonly used to describe similar phases which occur in highly ordered smectic liquid crystals, and the term will be applied here to the high temperature solid phase of PHNA. The diffraction pattern at 425°C (*Figure 4*) may also be indexed according to an orthorhombic cell, with cell parameters

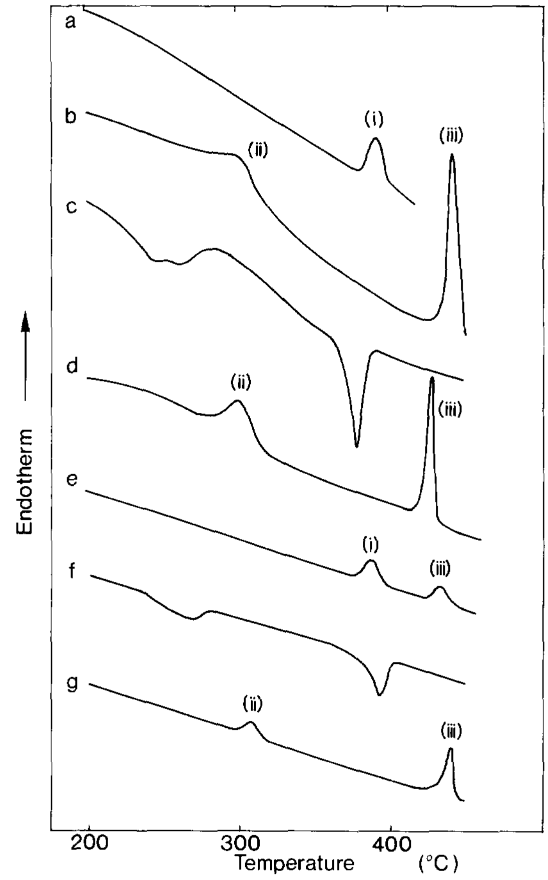


Figure 2 D.s.c. scans for two samples of as-polymerized PHNA over several heating and cooling cycles. Peaks labelled (i), (ii) and (iii) are explained in the text. A standard heating and cooling rate of 20°C min^{-1} was used unless stated otherwise. (a) Sample I, first heating cycle. Heating was arrested before melting occurred: the furnace was switched off and the sample allowed to cool freely. (b) Sample I second heating and (c) cooling cycle. (d) Sample I, third heating cycle. (e) Sample II first heating and (f) cooling cycle. (g) Sample II second heating cycle

Table 1 The effect of thermal history on the peak positions (2θ) and widths ($\Delta 2\theta$) of the room temperature (25°C) diffraction pattern of PHNA

	Peak 1		Peak 2		Peak 3		Peak 4	
	2θ(°)	$\Delta 2\theta$(°)	2θ(°)	$\Delta 2\theta$(°)	2θ(°)	$\Delta 2\theta$(°)	2θ(°)	$\Delta 2\theta$(°)
As-polymerized	10.52	0.40	18.88	0.47	22.79	0.92	27.49	0.72
Annealed	10.48	0.66	18.89	0.64	22.94	1.05	27.72	1.32
Recrystallized	10.62	0.75	18.84	1.03	21.49	1.50	27.58	2.50

The peak numbers refer to *Figures 1* and *7*. The as-polymerized row refers to the material as-supplied. The annealed sample was cooled at 1°C min^{-1} from the pseudo-hexagonal phase, while the recrystallized sample was cooled at the same rate from the melt phase. Cu Kα radiation was used. The peak widths quoted are full widths at half maximum values

Table 2 D.s.c. peak positions and enthalpies for two samples of PHNA corresponding to the traces shown in *Figures 2a–f*

		$T_{\text{C-PH}}$ (°C)	$\Delta H_{\text{C-PH}}$ (J g^{-1})	$T_{\text{PH-M}}$ (°C)	$\Delta H_{\text{PH-M}}$ (J g^{-1})
Sample I	(a)	392	11.5	–	–
	(b)	298	–	443	14.8
	(c)	248	−17.4	382	−19.4
	(d)	296	13.2	432	22.3
Sample II	(e)	394	9.5	433	8.9
	(f)	280	–	392	−21.4
	(g)	304	14.6	438	23.5

For sample I, heating was stopped before the melt phase was reached in the first heating run (a), and the sample allowed to cool freely. In all other cases heating and cooling were performed at 20°C min^{-1}. $T_{\text{C-PH}}$ and $\Delta H_{\text{C-PH}}$ are, respectively, the temperature and enthalpy change of the transition from the room temperature crystal phase to the pseudo-hexagonal phase. $T_{\text{PH-M}}$ and $\Delta H_{\text{PH-M}}$ are the melting temperature and melting enthalpy of the pseudo-hexagonal phase. Enthalpies were not calculated in some cases where the peak was too broad to allow accurate measurements of $a = 9.26$, $b = 5.69$ and $c = 16.59$ Å (all ± 0.01 Å). The indices are marked on the figure. The shoulder on the 110 peak is the 200 reflection, which moves closer to the 110 peak position as the unit cell becomes closer to hexagonal on increasing the temperature. All peaks satisfy the selection rule $h + k + l$ even, consistent with an orthorhombic I (body centred) lattice.

A minor structural change can be seen at ~205°C (*Figure 3*) in which a small peak appears at ~20°2θ and the intensity of the peak at ~15°2θ diminishes. Attempts to index the reflections above and below 205°C on the basis of orthorhombic unit cells have been unsuccessful, and indicate the likelihood of both phases possessing monoclinic symmetry. However, since this has not yet been demonstrated conclusively, and is the subject of further work, we shall refer to them simply as low-symmetry phases. There is some precedent for the formation of a monoclinic phase in this class of linear aromatic polyester, since the related polymer poly(p-phenylene terephthalate) (PPT) was recently reported to possess a monoclinic unit cell[5]. A further complication which should be borne in mind is the possible coexistence of two phases, as has been observed in PHBA below 350°C[4]. The origin of the two phases in PHBA has not yet been determined but may be due to some crystals having parallel stacking and others having anti-parallel stacking of the polymer chains (the polarity of the polymer chain being determined by the orientation of the ester dipoles). The phase transition at 205°C is reversible, provided that the sample does not enter the pseudo-hexagonal phase.

Heat-treated material

The room temperature annealed structure, formed by cooling slowly (1°C min^{-1}) from the pseudo-hexagonal phase (*Figure 1b*), can be indexed by an orthorhombic unit cell with lattice parameters $a = 7.75$, $b = 5.90$ and $c = 16.86$ Å (all ± 0.01 Å). The cell must contain two polymer chains, each of two monomer unit length, i.e. a total of four monomer units. The exact arrangement of atoms within the cell has yet to be determined. *Figure 5* shows the effect of increasing temperature on this new structure. The orthorhombic phase transforms to pseudo-hexagonal at ~300°C, compared with 400°C for the as-polymerized material. Above 400°C, the diffraction pattern appears identical to the as-polymerized pattern at the same temperature. There is a very weak reflection at ~15.5°2θ, which is indexable as 010 in the

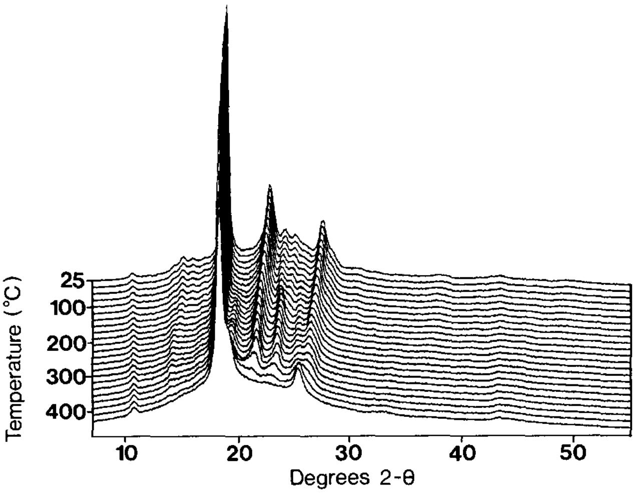


Figure 3 X-ray diffraction scans of as-polymerized PHNA for temperatures between 25°C and 425°C. Note the phase transition at 400°C, and the minor structural modification at 205°C

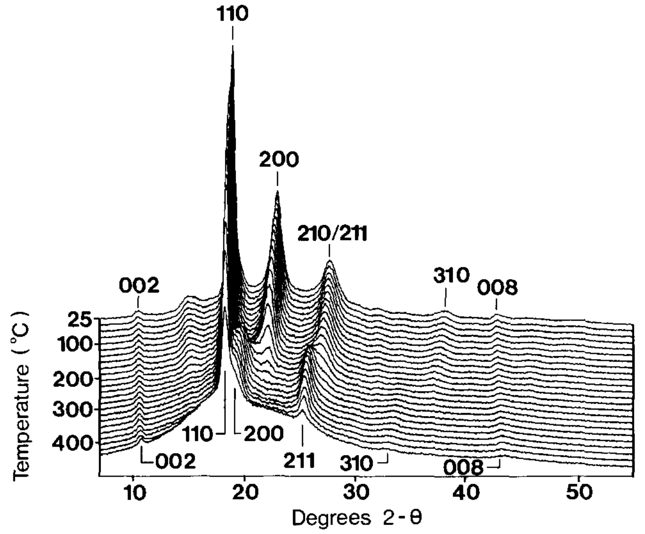


Figure 5 X-ray diffraction scans of annealed PHNA for temperatures between 25°C and 440°C. The orthorhombic structure is indexed above the diagram, while the pseudo-hexagonal structure is indexed below

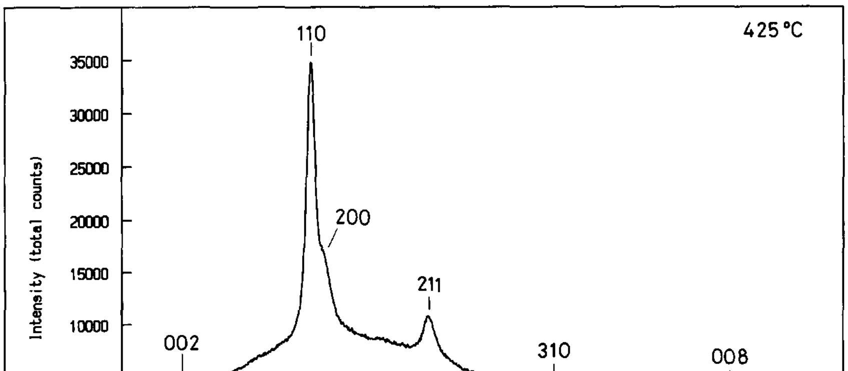


Figure 4 X-ray diffraction pattern of the pseudo-hexagonal phase of PHNA at 425°C. Indices of principal reflections are marked

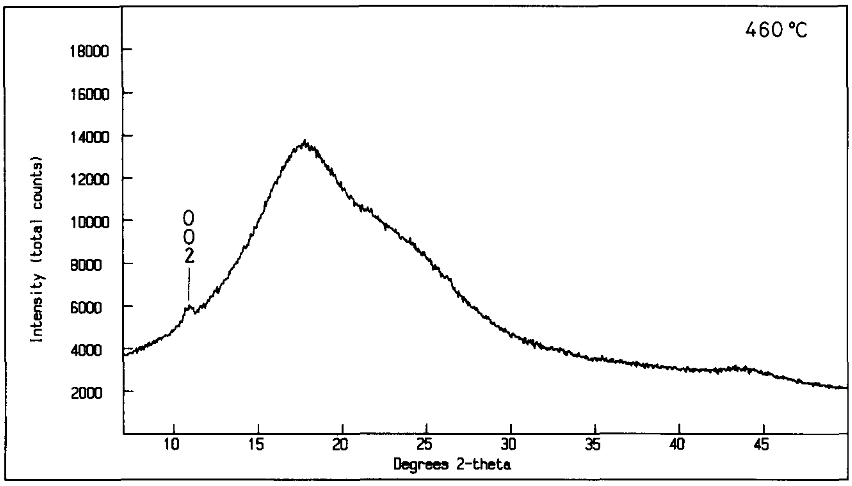


Figure 6 X-ray diffraction pattern of the liquid crystalline melt phase of PHNA at 460°C. Note the sharp reflection at 10.9°2θ, labelled 002

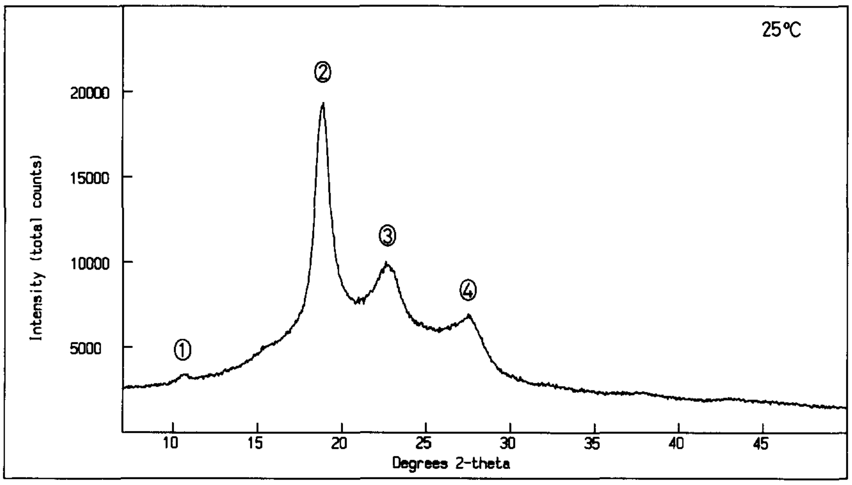


Figure 7 X-ray diffraction pattern of recrystallized PHNA at 25°C. The peak numbers refer to *Table 1*

pseudo-hexagonal unit cell. This reflection, which disappears above 400°C, and is not consistent with an *I* lattice, may be associated with the continued presence of a small fraction of the low-symmetry as-polymerized material. Alternatively, it may indicate the presence of a small amount of a second crystalline component.

The pseudo-hexagonal phase melts completely by 445°C and *Figure 6* shows the melt diffraction pattern at 460°C. The material does not flow freely at this temperature, but resembles soft putty, being readily deformed for example by shearing with a razor blade. The diffraction pattern of the melt is intriguing in that, although the main interchain peaks 110 and 211 have been replaced by amorphous halos, the 002 peak remains sharp up to the highest temperatures attained (480°C). The presence of this strong meridional maximum suggests the existence of smectic-like liquid crystalline order in the melt. At 480°C the 002 reflection is diminished in intensity, which seems to be associated with thermal degradation of the sample. On slow cooling (1°C $\min^{-1}$) a sample which has been taken into the melt at 445°C but not given time to degrade, the pseudo-hexagonal phase reappears at 330°C, and the orthorhombic at 205°C. Both phases are superimposed on a large amorphous background and appear poorly ordered in that the crystalline peaks are very broad (see *Figure 7* and *Table 1*). On re-heating, the orthorhombic to pseudo-hexagonal phase transition occurs at 205°C, but the pseudo-hexagonal phase does not melt until 430°C. A summary of the phases and transition temperatures observed by X-ray diffractometry is given in *Figure 8*.

DISCUSSION

Room temperature phases

Since PHNA is not molten at the temperature of synthesis ($\sim$350°C), it seems reasonable to assume that crystallization occurs during the polymerization reaction, and that the structure formed is that observed when the as-polymerized material is heated to 350°C.

At first sight the production of an orthorhombic phase on heat treatment might be considered to be an example of annealing to form a more ordered structure. However, closer examination (*Table 1*) shows that the diffraction peak widths are broader in the orthorhombic case than in the as-polymerized low-symmetry case, indicating that the orthorhombic phase is less well ordered. Peak broadening may be caused by lattice distortions or crystallite size effects, both of which could be implicated here.

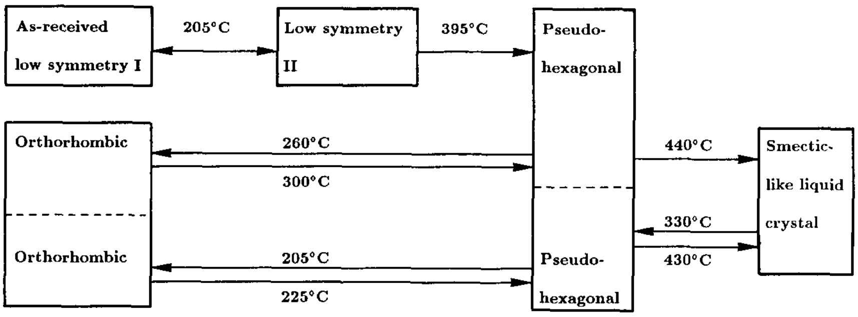


Figure 8 Summary of the phase transitions observed in PHNA using X-ray diffractometry

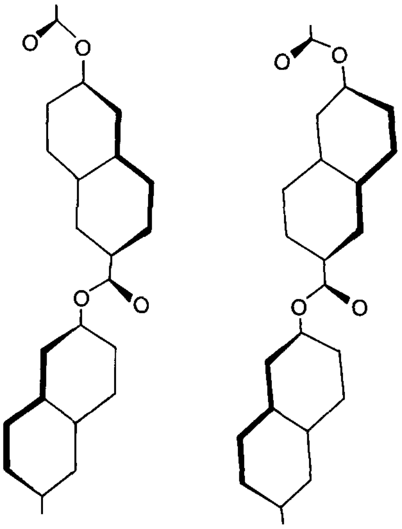


Figure 9 Two possible extended chain conformations of PHNA. In each case the conformation will repeat every two monomer units in the polymer crystal

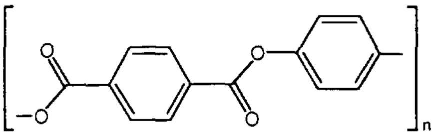
One possible explanation for the formation of the orthorhombic phase from the original low-symmetry phase may concern conformational disordering of the PHNA chains. There are several possible conformations that will produce an extended PHNA chain (*Figure 9*), and it is suggested that the as-polymerized crystals consist of a single extended chain conformation, whereas the more disordered orthorhombic phase may contain a mixture of two or more different conformers, of similar energy. The only way to form the as-polymerized phase again would be if all the chains switched back into the same conformation. The poorer packing resulting from the presence of several conformations would lead to a more distorted lattice of higher symmetry.

Another explanation for the peak broadening is that transformation twinning is likely to occur on cooling from the high symmetry pseudo-hexagonal phase to the lower symmetry orthorhombic phase, resulting in many small, differently oriented crystal domains being formed, compared with the large crystals that would form on polymerization.

A third possibility is that the polar PHNA chains are initially all pointing in the same direction within a crystallite, i.e. a parallel configuration, but that annealing results in a random antiparallel arrangement, perhaps by a process of interdiffusion between adjacent crystallites. Such a random configuration would necessarily be less well ordered. Also, the possibility that polymerization continues during annealing, thus disrupting the crystallinity, should not be overlooked. Unfortunately, the currently available powder diffraction data are not of sufficiently high quality to discriminate between the different explanations for peak broadening, and further work involving fibres or single crystals is required.

The orthorhombic phase appears metastable with respect to the low-symmetry phases, since the transition from orthorhombic to pseudo-hexagonal occurs at 300°C whereas the low-symmetry to pseudo-hexagonal transition is at 400°C. It is assumed that the orthorhombic phase will be the phase most likely to be seen after processing of the polymer, since processing usually involves high temperatures. It is thus no surprise that this phase is seen in the B–N copolymers[7,10] where disruption of crystalline order tends to favour the higher symmetry of the orthorhombic cell.

A similar disordering phenomenon has also been observed in PPT:



and may be due to the same cause. The diffraction patterns before and after annealing are shown in *Figure 10*. Once again some peaks are observed to broaden and shift in position and others appear or disappear. Both polymers are the subject of continuing investigation.

Thermal expansion

The thermal expansion behaviour of heat-treated PHNA resembles that of PHBA, with most thermal expansion being concentrated in the 100 direction in the unit cell (*Figure 11*). At the orthorhombic to pseudo-hexagonal phase transition, there is a jump in both the a and b values, with the a parameter increasing markedly, while the b value decreases. No step is observed in the value of the c parameter. There is a volume increase associated with the phase transition of $\sim 6.5\%$ on entering the pseudo-hexagonal phase. Once in the pseudo-hexagonal phase, no further change is observed in the b cell parameter, while the a parameter continues to expand. However, the ratio $a{:}b$ always remains $< \sqrt{3}$. *Figure 11* also shows the expansion behaviour of PHBA for comparison. The similarities between the two polymers, both in terms of the phases observed and the molecular structure, lead us to suggest a similar model for chain packing within the unit cell to that of PHBA[1,2]. We suggest that the polymer molecules are oriented with the chain direction parallel to the c-axis of the cell, with the planes of the naphthalene rings at a shallow angle to

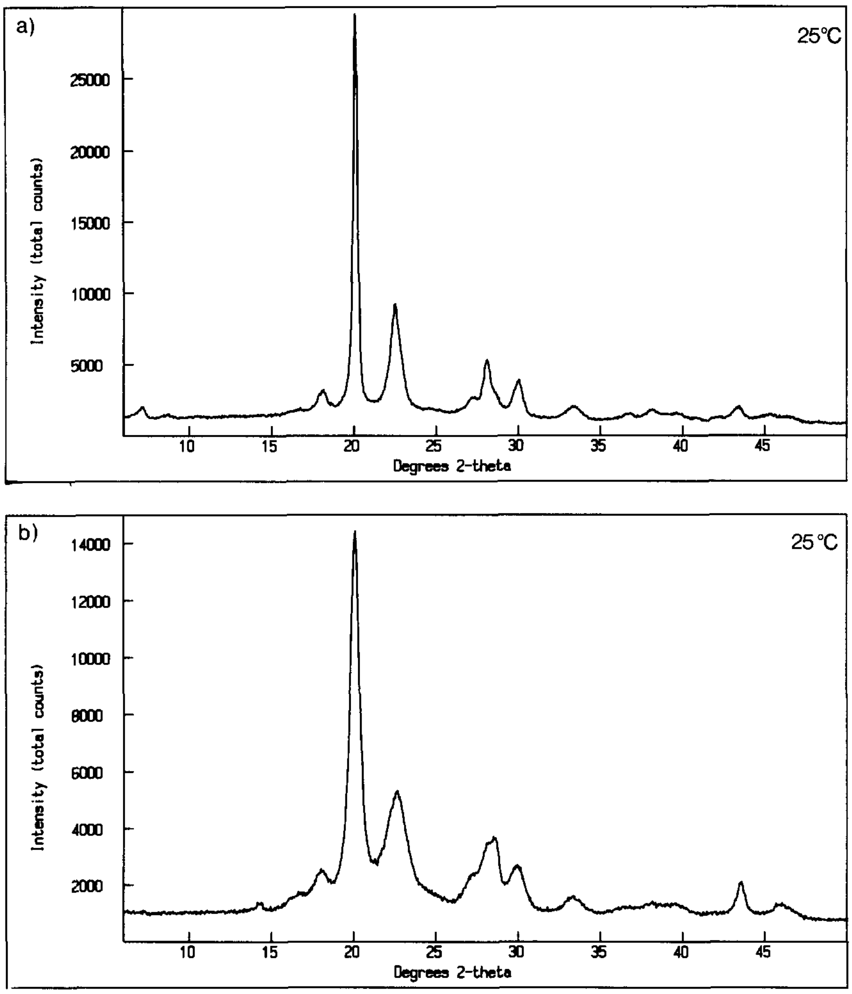


Figure 10 X-ray diffraction patterns of (a) as-polymerized PPT and (b) annealed PPT, showing a structural change on annealing. The anneal consisted of slowly heating the sample (at an average rate of 1°C min^{-1}) to 480°C, waiting for 10 min, and then cooling to room temperature at the same rate

the 100 planes, such that the increase in rotational motion of the naphthalene rings about their 2,6 axes, which will occur on heating, will lead to expansion normal to these planes (*Figure 12*).

The *c* dimension shortens gradually throughout the temperature increase, more rapidly as the melt phase is approached. Such shortening is clearly a consequence of thermal motions acting on an extended chain molecule, and is expected to become more marked as the free volume between the chains increases due to the expansion of the crystal.

It is interesting to note that at the highest temperature reached before melting (440°C) the *a* parameters of PHBA and PHNA are equal (~9.3 Å) and the *b* parameters differ by only 5%. Such close values might be expected to have important consequences for molecular packing in the B–N copolymers. Indeed, pseudo-hexagonal crystalline phases have been observed by X-ray diffraction across the entire compositional range of the B–N copolymers[7,10], suggesting that the formation of this crystalline phase is facilitated by the similar packing dimensions of the two homopolymers at high temperatures.

Pseudo-hexagonal phase

There is good reason to suppose that the pseudo-hexagonal phase is a mobile rotator phase, similar to that encountered in PHBA. Dielectric and n.m.r. studies of PHBA have shown that the occurrence of the pseudo-hexagonal phase is closely associated with an increase in rotational freedom of the ester groups about the polymer chain axis (crystallographic *c*-axis)[9,11], which must derive from an increase in the number of conformations accessible to the chain at higher temperatures. The onset of rotational motion of the benzene rings in PHBA, albeit at frequencies many orders of magnitude less than that associated with free libration, is observed at ~120°C, and thus is not a direct cause of the orthorhombic to pseudo-hexagonal phase transition.

Similar behaviour is observed in studies of naphthalene-rich B–N copolymers[12], with the onset of naphthalene ring motion occurring at higher temperatures than benzene ring motion. The exact temperatures involved depend on the molar composition of the copolymer. One reason for the lower mobility of the naphthalene rings may be that the 2,6 axes of the rings are not coaxial with the polymer chains, which results in crankshaft rotations. Although, to the authors' knowledge, no n.m.r. studies have yet been published on the PHNA homopolymer, it seems reasonable to expect corresponding behaviour in PHNA to that observed in PHBA and the B–N copolymers.

The fact that the pseudo-hexagonal phase is more correctly described by an orthorhombic lattice is

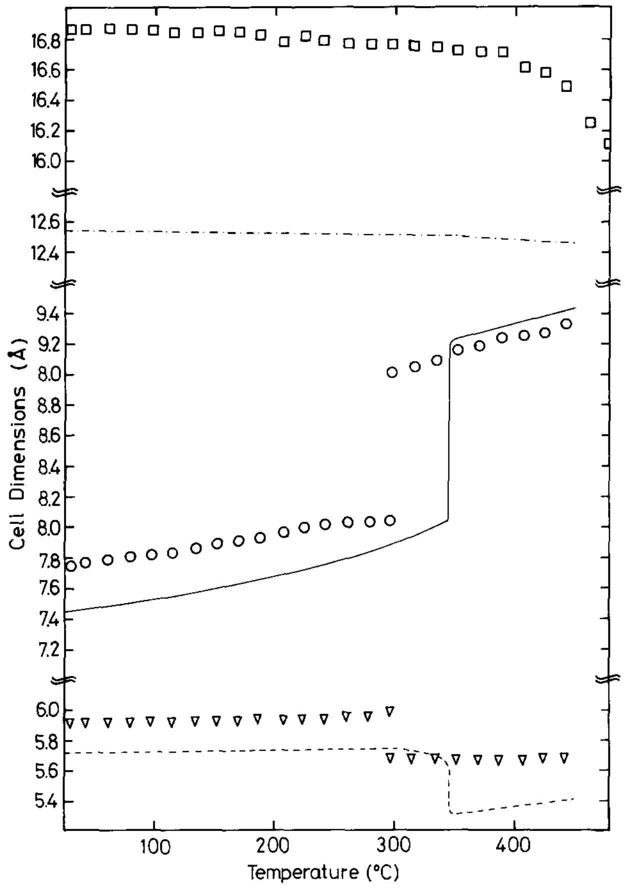


Figure 11 The variation of PHNA unit cell parameters with temperature, from 25°C to 480°C: (○) *a*; (▽) *b*; (□) *c*. The cell parameters of PHBA (as given in ref. 1) are also shown for comparison: (—) *a*; (– –) *b*; (–·) *c*

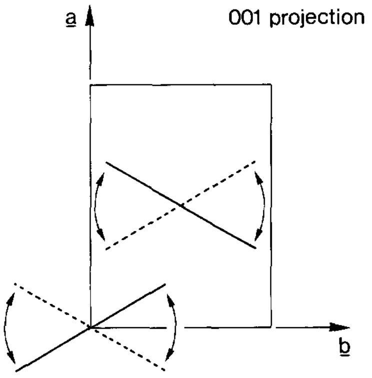


Figure 12 Schematic representation of the (001) projection of a unit cell of PHNA to illustrate the origin of the large coefficient of thermal expansion observed parallel to the *a* direction. The solid lines represent the planes of naphthalene rings at fractional height zero in the *c* direction, while the broken lines represent naphthalene rings at height $\frac{1}{2}$. The ester groups are not shown

indicated by the fact that the 200 reflection does not coincide exactly with the 110 reflection. In addition, the orthorhombic equivalent of a hexagonal lattice is the orthorhombic *C* lattice, for which the reflections must satisfy $h + k$ even, whereas the observed reflections actually satisfy $h + k + l$ even, suggesting an orthorhombic *I* lattice, as mentioned above.

The presence of *any hkl* reflections is also important for it indicates that, although the naphthalene rings are rotating, there are still specific long-range orientational correlations between neighbouring rings, both on adjacent chains and along the same chain. In particular, it is thought that the planes of the naphthalene rings must lie close to planes of the {211} form in the crystal to account for the relatively large structure factor of the 211 reflection compared with other *hkl* reflections. Specifically, this reflection must arise from a combination of the preferred conformations of the polymer chain, which determine the dihedral angles between adjacent aromatic groups along the chain, and a combination of packing constraints and dipole interactions which favour edge-face contacts between aromatic groups on adjacent chains. The matter has been discussed at some length in connection with PHBA in two previous papers[1,5].

The rotation of naphthalene groups about their 2,6 axes will be far from free: the lack of space in the unit cell will necessitate co-operative rotations of groups of chains which will mesh together like arrays of tiny molecular gear wheels, thus rotating the entire unit cell and forming rotational twins, as has been suggested for PHBA[1]. Such twinning will require only minor distortions to the unit cell, since the cell parameters of the pseudo-hexagonal cell are very close to those required for a truly hexagonal cell. In the case of PHBA, the decrease in intensity of the 211 reflection with temperature is attributed to a proliferation of differently oriented twins of decreasing size that gradually result in a single disordered hexagonal structure. However, in the present case we see only a slight decrease in the intensity of the 211 reflection (compared to the 110 reflection) before the onset of melting occurs.

Liquid crystalline melt

The most significant feature of the melt-phase diffraction pattern of PHNA (*Figure 6*) is the presence of a sharp maximum at ~10.9°2θ. This peak is in almost the same position as the 002 reflection in the pseudo-hexagonal phase and is of similar shape and intensity. Another maximum corresponds to the pseudo-hexagonal 008 reflection, but is much broader in the melt phase. The presence of these maxima suggests that there is some retention of longitudinal register between the polymer chains in the melt, but that it is far from perfect. The molecular registration will propagate laterally forming a layered structure, in which the layers consist of a single monomer unit from each chain (*Figure 13*). This type of structure closely resembles a smectic liquid crystal phase. In particular, if the layers were perpendicular to the molecular axes, it would resemble a smectic *A* (S_A) phase.

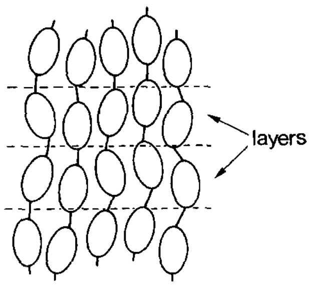


Figure 13 Schematic diagram to illustrate the origin of the layer formation in PHNA. The monomer units are represented by ellipses. The diagram shows a section cut perpendicular to the layers

The accepted model of a S_A phase[13] consists of rigid mesogenic units arranged into layers with their long axes perpendicular to the layers. Our case differs from this in that although the long axes of the polymer chains are still perpendicular to the layers, the layers are formed from the monomer units, which in isolation would not be expected to be mesogenic due to their low aspect ratio. For this reason we hesitate to classify our material as a smectic phase, but will refer to it as smectic-like, because it shares some of the principal characteristics of a S_A phase.

The layers are not well defined; hence we observe only one sharp inter-layer diffraction peak. The position of the peak gives a *d*-spacing of 8.12 Å which is slightly shorter than the extended length of the monomer unit derived from the orthorhombic cell of 8.43 Å. This shortening is thought to be a consequence of the greater torsional freedom in the polymer chain at higher temperatures, which allows the monomers to twist away from the chain axis and so shorten the molecule. Such behaviour is again analogous to the S_A phase in which the layer spacing is normally slightly less than the length of the mesogenic molecule[13].

A previous report[8] has suggested, on the basis of optical microstructures, that the melt phase is, in fact, nematic. However, the nematic textures were observed in samples that had been sheared in the melt and then quenched, and so could not be said to represent equilibrium conditions. Whilst it is true that a nematic phase could produce the low angle (inter-layer) peak that has been observed, it would correspond to an unsampled layer line on the fibre pattern and would be extremely smeared to the high angle side. The 002 peak we observe is almost identical to that in the lower temperature crystalline phases, being neither asymmetric nor particularly broad, thus reaffirming our smectic classification.

The remainder of the diffraction pattern of the liquid crystalline phase (*Figure 6*) can also be seen to derive from that of the pseudo-hexagonal phase (*Figure 4*). The main amorphous peak in *Figure 6*, at $\sim 18°2\theta$, corresponds quite closely to the position of the pseudo-hexagonal 110 reflection, and is thus taken to reflect a disordering of the inter-chain packing. There is an amorphous shoulder in *Figure 6* corresponding to the pseudo-hexagonal 211 peak position which implies that there is still some degree of orientational correlation between the naphthalene rings, as described in the pseudo-hexagonal case, but that it is now very short range.

It seems probable that the conformational disorder introduced into the polymer by entering the liquid crystal phase reduces the perfection of the crystallites that may form easily on cooling. It is also apparent that the disordering is more marked the longer the sample is held in the liquid crystal phase. This is demonstrated by the fact that the orthorhombic to pseudo-hexagonal phase transition occurs at $\sim$300°C in d.s.c. samples that were held in the melt for <5 min, but at $\sim$200°C in X-ray samples that remained in the melt phase for nearly an hour.

Under equilibrium conditions, PHBA has not been observed to possess a melt phase, but has been shown to retain chain registration up to 480°C, by virtue of the fact that the $00l$ reflections remain sharp[1,2]. Thus it appears that HNA and HBA both possess a strong tendency to segregate into layers, which may have important implications for the nucleation of crystallites in the B–N copolymers. If both monomer units show a tendency to form layers, then it is easy to envisage a situation in the copolymer melt in which adjacent layers may contain either benzoate or naphthoate units, which on cooling would form non-periodic layer crystallites[14], which are believed to be responsible for the observed levels of crystallinity in the B–N copolymers[15,16].

CONCLUSIONS

The behaviour of PHNA at high temperatures has been studied and compared, where appropriate, to that of PHBA. The main similarity between the two polymers is that both form a high symmetry pseudo-hexagonal rotator phase. The *a* and *b* lattice parameters in the two rotator phases are very similar, which perhaps explains why similar phases are also observed across the entire compositional range of the B–N copolymers. Thermal history plays an important rôle in determining which phase is observed at a given temperature in PHNA, but not in PHBA.

The most significant finding is that PHNA forms a melt above 440°C which appears structurally similar to a liquid crystalline smectic *A* phase. The formation of this phase may have important consequences for structure formation in the B–N copolymers, and is the subject of further investigation.

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