

# The rôle of crystallinity in the deformation of main-chain liquid-crystalline copolyesters

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## Abstract

The importance of crystallinity in the deformation processes of main-chain liquid-crystalline copolyesters is examined. Two materials are studied: one a copolymer of hydroxybenzoic acid (HBA) with 2-hydroxy-6-naphthoic acid (HNA); the other a copolymer of HBA with isophthalic acid (IA) and hydroquinone (HQ). In both cases it is observed that the transverse compressive yield stress and modulus of the polymer are optimised by annealing at about 20°C below the melting temperature. In the case of the copolymer containing HBA and HNA, it is found that deformation of unannealed samples results in a pronounced loss of crystallinity. However, the effect is less marked in annealed samples, and the crystallinity is found to recover after modest annealing close to the glass transition temperature. In both polymers, evidence is found for a stress-induced solid-state phase transition, which may be similar to the martensitic phase transition proposed for polyethylene. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Liquid-crystalline polymer; Deformation; Yield stress

## 1. Introduction

It is well known that the theoretical Young's moduli of many linear polymers can rival that of steel, at least in the direction of the chain axes [1–4]. While, in conventional polymers, poor molecular orientation makes such high performance difficult to realise, in liquid crystalline polymers (LCPs), orientation parameters<sup>2</sup> greater than 0.9 are easily obtained [5], making them the target of commercial as well as scientific interest. The first commercial LCP was introduced by DuPont in 1965 under the trade name of Kevlar™. Modern formulations of Kevlar™ have a tensile modulus of about 185 GPa [2] (cf. Steel ~210 GPa). However, unlike lyotropic LCPs such as Kevlar™, thermotropic LCPs, which are melt processible, are of more relevance to the production of mouldings or extrudates [2,5–10].

Many thermotropic LCPs have been synthesised, but their mechanical properties are often not especially good at

elevated temperatures. For example, copolymers of HBA and HNA show a 75% drop in tensile modulus on heating from room temperature to 150°C [11], while copolymers of HBA with IA and HQ show an 85% loss of stiffness over a similar temperature interval [9]. The tensile properties of thermotropic LCPs may be improved by heat treatment, and the optimal annealing temperature is typically found to be between 10 and 30°C below the melting point [12]. In fact, while this treatment leads to a dramatic improvement in tensile strength and elongation at break, it has much less impact on the modulus. For example, Yoon quotes 270°C as the optimum heat treatment temperature for copolymers of HBA and HNA [13]. After annealing for several hours, he observes an increase in tensile strength by a factor of between 3 and 4. Under the same conditions, the tensile modulus increases by only about 10% [12,14]. The increase in tensile strength is generally attributed to molecular weight growth during annealing [12,13,15], whereas the modulus is thought to depend primarily on the degree of molecular orientation [16]. However, in the absence of any change in the molecular orientation, it is likely that improvements in the modulus may also be due to localised structural rearrangements accompanying the heat treatment.

While the extreme anisotropy of the molecular arrangement in LCP fibres is beneficial for tensile properties, it is generally detrimental to the compressive properties. The

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<sup>2</sup> The orientation parameter,  $P_2$ , is defined as  $P_2 = \langle [3 \cos^2(\theta) - 1] / 2 \rangle$  where  $\theta$  is the angle between the polymer chain axis and the fibre axis.

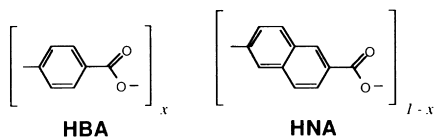
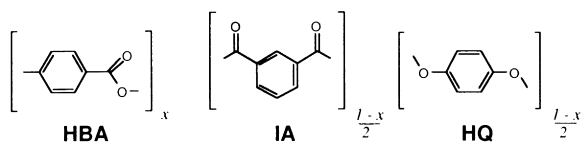
(a) BN ( $x = 0.75$ )(b) BIQ ( $x = 0.36$ )

Fig. 1. (a) The BN copolymer system, consisting of 75 mol% hydroxybenzoic acid (HBA) units and 25 mol% hydroxynaphthoic acid (HNA) units. (b) The BIQ copolymer system, consisting of 36 mol% HBA units, 32 mol% isophthalic acid (IA) units and 32 mol% hydroquinone (HQ) units.

absence of covalent bonding *between* the polymer chains results in low shear strength and shear modulus and consequently poor performance in compression. In some systems, compressive strengths have been found to be less than 10% of their tensile counterparts [2]. This is a severe drawback if LCPs are to be used in mechanically demanding applications or, for example, in light-weight composite structures. The interchain interactions will be especially weak in random copolymers, in which the registration between adjacent polymer chains is poor. Thus, the presence of any crystallites would be expected to have an important

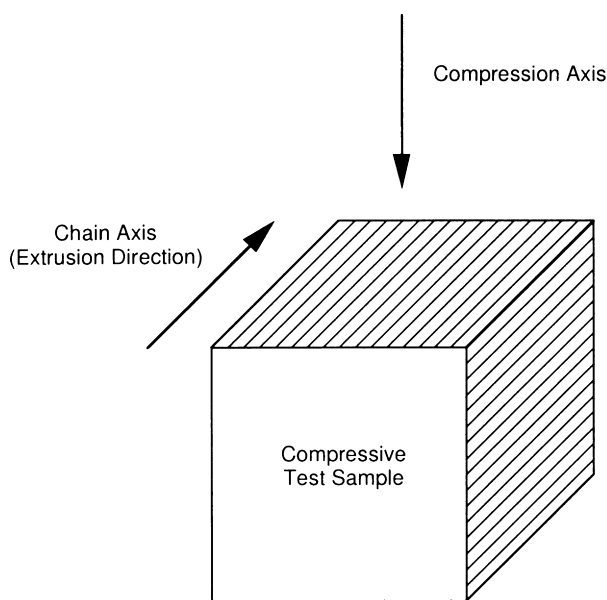


Fig. 2. Schematic representation of the compressive testing geometry used in this study.

influence on the compressive mechanical properties of these polymers.

The aim of the present paper is to explore this possibility, by examining the relationship between the compressive mechanical properties and the degree and perfection of crystallinity in two thermotropic liquid crystalline copolyesters. The materials studied are both copolymers of hydroxybenzoic acid, in one case with 2-hydroxy-6-naphthoic acid, and in the other with isophthalic acid and hydroquinone. The effect of the annealing temperature on the compressive yield stresses and moduli of the two polymers is examined, as well as the effect of compression on the degree of crystallinity and the crystal structures observed in the two systems.

## 2. Experimental

### 2.1. Materials

The materials under investigation are two wholly aromatic thermotropic liquid crystalline copolyesters, known as BN and BIQ, which were supplied by ICI Advanced Materials Division. BN consists of residues of *para*-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) (see Fig. 1a), while BIQ is synthesised from residues of *para*-hydroxybenzoic acid, isophthalic acid (IA) and hydroquinone (HQ) (Fig. 1b). The composition of the BN material was 75 mol% HBA and 25 mol% HNA and the BIQ composition was 36 mol% HBA, 32 mol% IA and 32 mol% HQ. The approximate molecular weights were 20,000 for BN, and 35,000 for BIQ. The BN and BIQ materials were supplied in the form of rods, approximately 6 mm in diameter and 400 mm long, extruded under elongational flow.

### 2.2. Sample preparation

The specimens tested were rectangular cuboids with faces cut parallel and perpendicular to the extrusion direction. Dimensions were typically 5 mm on each side. A low speed diamond saw was used to prepare the specimens. This allowed sectioning of the rods with a high degree of precision and low damage. All specimens were additionally polished with 1200 grade carbon paper. After mechanical testing, samples were prepared for X-ray analysis by further polishing on grinding wheels to a thickness of 1.5 mm. Tests showed that this procedure did not affect the crystallinity of the remaining material.

### 2.3. Annealing

The annealing routine comprised of maintaining the samples at a constant temperature in an air circulating oven for 6 h, followed by a slow cool. Sample dimensions were measured before and after annealing. Dimensional stability was found to be excellent, except for samples annealed for prolonged periods within 20°C of the melting

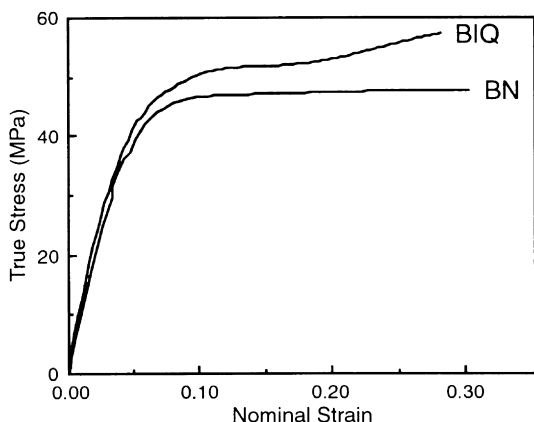


Fig. 3. Transverse stress–strain behaviour of BN and BIQ extrudates tested in compression at  $0.20 \text{ min}^{-1}$  and  $20^\circ\text{C}$ . The compression axis is perpendicular to the extrusion direction.

point. For these samples, there was a small volume expansion ( $\sim 1.5\%$  for BN and  $\sim 2.5\%$  for BIQ) which may be due to degradation.

#### 2.4. Mechanical testing

The mechanical properties of BN and BIQ were investigated using uniaxial compression. The method consisted of placing the specimens between parallel, polished plates, applying a compressive strain and measuring the resultant stress. The specimens were tested in a transverse direction, i.e. perpendicular to the extrusion direction (see Fig. 2). Testing in compression offers several advantages over the more widely used tensile test method. Firstly, very small specimens may be examined, which would be too small to be gripped effectively in tension. Secondly, the occurrence of kinking and localised deformation bands makes the measurement of true stress values difficult in tensile tests; it is much easier to define the area undergoing deformation in a compressive test. Finally, compression also helps to

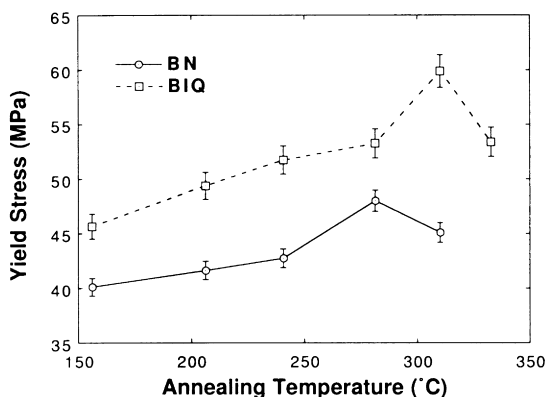


Fig. 4. Influence of annealing temperature on the compressive yield stresses of BN and BIQ extrudates. All samples were annealed for 6 h at the temperature specified.

suppress premature fracture, which sometimes intervenes before the onset of yielding during tensile tests.

The uniaxial compression procedure, although simple and practical, has some drawbacks too. The choice of specimen shape for compressive testing is inevitably a compromise between the attainment of mechanical stability and the reduction of frictional end effects to an insignificant level. Ideally the specimen should be parallel sided, with the axial dimension (i.e. the dimension parallel to the compression axis) long compared with the lateral dimensions. However, if the axial dimension is too long, buckling occurs. Tests using standard PMMA specimens indicate that the optimum aspect ratio of the sample lies between 1.0 and 2.0 [17]. In the present work, the aspect ratio was limited by the shape and size of the extruded rods to be in the range 0.9–1.1, but extensive testing indicated that the reproducibility of the results was satisfactory.

Specimens were compressed using an ESH hydraulic testing machine fitted with a 5 kN load cell. The strain rate used was  $0.20/\text{min}$ , and all samples were compressed at room temperature, unless otherwise indicated. For temperatures below  $60^\circ\text{C}$  a thin film of PTFE was used as a lubricant. Strain was recorded using strain gauges arranged so as to eliminate the effect of rig bending. Displacement measurements were accurate to within 0.5%.

#### 2.5. X-ray measurements

Wide-angle equatorial X-ray diffraction patterns were obtained from aligned samples using a symmetrical-geometry transmission diffractometer with monochromatic  $\text{CuK}\alpha$  radiation [18,19]. Percentage crystallinities were estimated from the diffractometer traces by comparing the areas of the crystalline and amorphous components, after first removing the background scattering, in a method similar to that of Blundell [20].

#### 2.6. Differential scanning calorimetry

Differential scanning calorimetry was carried out using a Perkin–Elmer DSC7 machine, calibrated using indium and zinc standards.

### 3. Results

#### 3.1. Effect of annealing on compressive yield stress and modulus

Typical stress–strain curves for samples of BN and BIQ, tested in compression using the geometry of Fig. 2, are shown in Fig. 3. Both materials show the onset of yield at a nominal strain of around 0.08, with clearly defined plateau regions, which give the yield stress. The influence of annealing temperature on the compressive yield stress of BN and BIQ at room temperature is shown in Fig. 4. Both materials showed an increase in yield stress with increasing annealing

Table 1

Comparison of the compressive mechanical properties and crystallinity of unannealed samples of BN and BIQ with those resulting from optimum annealing conditions

Sample:	Compressive yield stress (MPa)	Compressive modulus (GPa)	Crystallinity (%)
BN unannealed	41.2 ± 0.7	1.05 ± 0.04	21 ± 2
BN annealed (6 h at 265°C)	48.0 ± 0.8	1.20 ± 0.05	23 ± 2
BIQ unannealed	46.1 ± 1.2	0.97 ± 0.05	–
BIQ annealed (6 h at 290°C)	60.1 ± 1.5	1.20 ± 0.06	10 ± 2

temperature, with some improvement apparent when annealing at temperatures as low as 200°C. As expected from previous studies [13], annealing at about 20°C below the melting point, as defined by the peak of the melting endotherm on the DSC trace, produces the largest increase in the yield stress. The melting temperatures defined in this way are 289°C for BN and 308°C for BIQ. BIQ samples annealed at 290°C showed a mean yield stress of 60.1 MPa, which is around 32% greater than the yield stress of the unannealed material (see Table 1). For BN samples annealed at 265°C, the mean yield stress improved by 14% to 48.0 MPa.

The variation of the compressive elastic modulus with annealing temperature for BN and BIQ is shown in Fig. 5. The general trend is similar to that observed for the compressive yield stress. There is a maximum increase of about 15% in the modulus of each material. Thus, for BN, the relative increases in yield stress and modulus brought about by annealing are comparable, whereas for BIQ the increase in yield stress is more than double the corresponding increase in modulus. In both materials, annealing resulted in a tendency to fracture in the post-yield region, at strains greater than about 20%. The dominant mode of failure was shear, in a plane parallel to the extrusion axis.

### 3.2. Effect of deformation on crystallinity

Fig. 6 shows the equatorial transmission diffraction patterns from unannealed BN samples compressed at

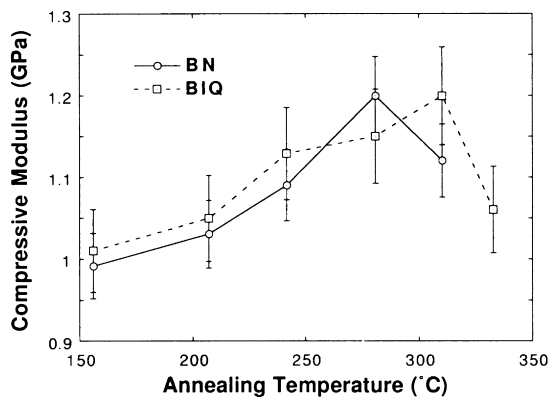


Fig. 5. Influence of annealing temperature on the compressive moduli of BN and BIQ extrudates. All samples were annealed for 6 h at the temperature specified.

room temperature to strains of 0, 30 and 50%. The most striking feature of the patterns is the broadening of the main peak, at about  $2\theta = 19.5^\circ$ , which occurs on deformation. At first sight, the broadening appears to be accompanied by a loss of crystallinity, which, for the sample strained to 50%, is almost complete. However, a more careful analysis reveals that the total crystallinity, as determined by subtraction of the amorphous part of the diffraction curve, is less seriously affected. The crystallinity values and diffraction peak widths are summarised in Table 2.

Interestingly, annealing the deformed BN samples at temperatures below, but close to the glass transition temperature, usually quoted as between 100 and 120°C [11], re-establishes the disrupted crystallinity, as can be seen in Fig. 7. This figure shows the equatorial diffraction pattern from an unannealed BN sample which was compressed to 30% strain, and subsequently annealed at 90°C for 1 h. The trace is very similar to that obtained prior to deformation (see Fig. 6a). This type of behaviour was also observed by one of us (S.H.) when preparing

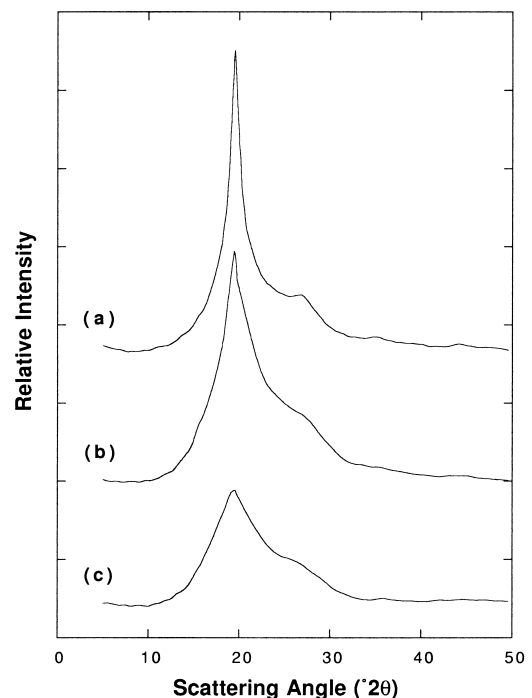


Fig. 6. Equatorial diffraction patterns obtained from unannealed BN samples, deformed to compressive strains of: (a) 0%; (b) 30%; and (c) 50%.

Table 2

The effect of deformation on the crystallinity and widths of the principle diffraction peak (i.e. the interchain peak at  $2\theta = 19.5^\circ$ ) of unannealed and annealed BN. The peak widths quoted are full widths at half maximum height. The annealed samples were held at  $265^\circ\text{C}$  for 6 h. The crystallinity measurements at 50% strain are less reliable than the other measurements, due to the extreme broadening of the main diffraction peak, which makes it difficult to subtract the amorphous halo accurately

Total strain (%)	Unannealed samples		Annealed samples	
	Crystallinity (%)	Peak width $2\theta$ ( $^\circ$ )	Crystallinity (%)	Peak width $2\theta$ ( $^\circ$ )
0	$21 \pm 2$	$1.9 \pm 0.1$	$23 \pm 2$	$1.8 \pm 0.1$
30	$19 \pm 2$	$4.4 \pm 0.1$	$22 \pm 2$	$1.8 \pm 0.1$
50	$12 \pm 4$	$6.2 \pm 0.1$	$19 \pm 2$	$2.4 \pm 0.1$

powdered samples of BN by filing extruded pellets [21]. The filed material appeared to be non-crystalline on initial examination, but crystalline diffraction peaks appeared after warming for a few minutes to about  $60^\circ\text{C}$ .

The effect of deformation on annealed samples of BN is shown in Fig. 8. The equatorial diffraction patterns are given for a sample annealed at  $265^\circ\text{C}$  for 6 h, and then deformed at room temperatures to strains of 30% and 50%. The diffraction scans show two important characteristics. Firstly, the disruption of crystallinity resulting from the deformation is much less pronounced than for the unannealed specimens (see Table 2). The sample with 30% strain is relatively unaffected by the deformation process, and even at 50% strain the main diffraction peak does not broaden dramatically. Secondly, there is a new diffraction maximum at about  $2\theta = 16^\circ$ , which will be discussed below.

The BIQ samples behave in a similar manner to the BN samples on deformation, except that the effects are less pronounced because of the lower crystallinity. Fig. 9 shows the equatorial diffraction traces from an unannealed BIQ sample, both before and after the application of a 30% compressive strain. There is very little difference between the two scans, which show only trace amounts of crystallinity. However, the effect of deformation is seen more clearly in the annealed samples. In Fig. 10 equatorial diffraction traces are shown for a sample of BIQ, annealed at  $290^\circ\text{C}$  for 6 h and then deformed to 30% strain. The

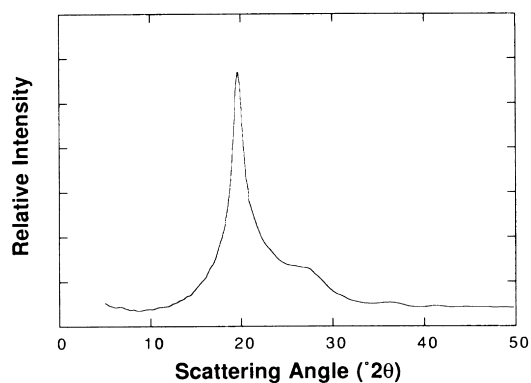


Fig. 7. Equatorial diffraction pattern from a BN sample deformed to a compressive strain of 30% and subsequently annealed at  $90^\circ\text{C}$  for 60 min.

relatively indistinct crystalline peaks make it difficult to comment reliably on changes in crystallinity resulting from deformation. Nevertheless, some loss of crystalline order is apparent. However, the most striking feature of the deformed annealed sample, is the enhanced prominence of the first diffraction maximum at  $2\theta \sim 16^\circ$ .

#### 4. Discussion

As indicated above, both BN and BIQ show an increase in their compressive yield stresses and moduli following annealing, peaking at about  $20^\circ\text{C}$  below the DSC melting temperatures. Any improvement in the transverse compressive properties could originate from two sources: increasing interchain interactions and loss of orientation due to retraction. (It should be remembered that while loss of orientation is detrimental to tensile properties it may well be beneficial to compressive ones.) However, the relative insensitivity of the tensile modulus of thermotropic LCP fibres to heat treatment suggests that the degree of orientation is largely unaffected by the annealing process. This has been verified by orientation measurements taken from wide-angle X-ray diffraction patterns. The orientation parameter,  $P_2$ , in samples taken from the centres of the extruded rods, is found to be unchanged by annealing at  $20^\circ\text{C}$  below their melting points, at around 0.52 for BN and 0.39 for BIQ. Additionally, micrometer measurements of samples before and after annealing indicated excellent dimensional stability for both BN and BIQ. The change in dimensions following annealing were generally found to be less than 0.5%. This has been confirmed in a study of the retractive behaviour of BN and BIQ, which is described elsewhere [17]. Hence, we would expect loss of orientation to have only a minor effect on mechanical properties in the present case.

The changes in the wide-angle X-ray diffraction pattern of BN resulting from annealing, which may be seen by comparing Fig. 6a with Fig. 8a, are usually interpreted in terms of a transition from a meta-stable pseudo-hexagonal structure to a more ordered and stable orthorhombic one [21–23]. An analogous, but reversible, phase transition is observed in the parent homopolymer poly(*para*-hydroxybenzoic acid) (PHBA), between a low temperature orthorhombic phase and a high temperature pseudo-hexagonal

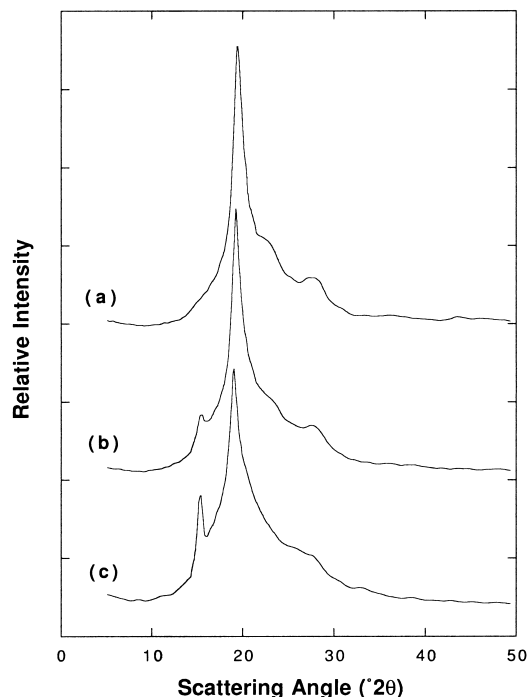


Fig. 8. Equatorial diffraction patterns obtained from annealed samples of BN, deformed to compressive strains of: (a) 0%; (b) 30%; and (c) 50%. All samples were annealed for 6 h at 265°C. Note the appearance of a new reflection at  $2\theta = 15.5^\circ$ .

phase [24,25]. In the case of BIQ, appropriate annealing induces crystallinity, which is thought to be associated with the segregation and crystallisation of the IA-HQ residues [26–29].

Thus, it appears likely that the observed enhancements in the compressive yield stresses and moduli of BN and BIQ are due to an increase in three-dimensional ordering and crystalline perfection as a result of annealing, although the exact nature of the ordering is different in the two cases. A similar finding has been reported by Zhang et al. [30], who

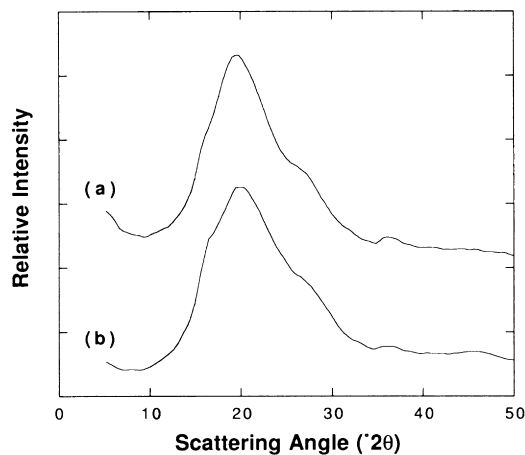


Fig. 9. Equatorial diffraction patterns obtained from unannealed BIQ samples deformed to compressive strains of: (a) 0%; (b) 30%.

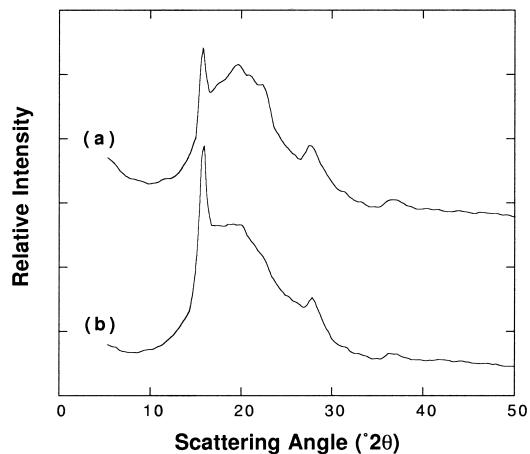


Fig. 10. Equatorial diffraction patterns obtained from annealed BIQ samples deformed to compressive strains of: (a) 0%; (b) 30%. Both samples were annealed for 6 h at 290°C.

showed that the introduction of a small proportion of side branches into the BN system disrupted the crystallinity and reduced the shear modulus compared to the unbranched systems. A corollary to this is that the deterioration in properties for samples annealed too close to the DSC melting point is probably associated with partial melting of the crystallites. The increase in yield stress may well be related to an increase in crystal thickness, which could be consistent with the dislocation theory of yield in polymers, developed by Young [31].

The proportionately greater improvement of the yield properties of BIQ, as compared with BN, may be attributable either to the larger increase in percentage crystallinity of the BIQ resulting from the heat treatment, or alternatively may be related to the different type of crystals that are forming. Since the mechanical properties must also depend on the molecular packing in the non-crystalline matrix, it is difficult to draw any firm conclusions on the matter. In either case, if we assume that the annealing process leads to an improvement in intermolecular interactions, then the yielding process must depend on the ease with which polymer chains can slip past each other sideways, i.e. in a direction perpendicular to the chain direction. This has important implications for the formation of new crystalline phases, as discussed below.

Interestingly, thermal treatment is also an important factor in the development of the tensile properties of aramid fibres such as Kevlar™. In this case it appears that annealing promotes small axial chain displacements, which permit the formation of regular hydrogen-bonding between the highly oriented molecules [32]. However, the short heat treatment of a few seconds is to be contrasted with the extensive times, of the order of a few hours, necessary to promote significant increases in the moduli of thermotropic LCP fibres. The tensile yield mechanism in the aramid systems is then related to the rupturing of these interfibrillar hydrogen bond networks.

#### 4.1. Effect of deformation on crystallinity

It is generally accepted that crystallites in semi-crystalline polymers undergo structural changes as a consequence of yielding [33]. The currently accepted mechanism of large-scale plastic deformation of semi-crystalline polymers involves the sliding and tilting of lamellae, which break into blocks of folded chains and subsequently reform into a fibre structure [34,35]. However, two other mechanisms have been suggested: Bowden and Young [36] postulated that yielding in semicrystalline polymers, and polyethylene in particular, involves the thermal activation of screw dislocations, while Flory and Yoon [37] proposed a partial melting and recrystallisation mechanism for the deformation process. It is interesting to consider whether similar mechanisms may operate in liquid crystalline polymers during compressive plastic deformation.

As shown in Table 2, there is a decrease in the level of crystallinity, and an associated broadening of the principal crystalline diffraction peak, when compressing as-received samples of BN to strains of 30% or more. The peak broadening may be due to a reduction in mean crystallite size, an increase in paracrystalline disorder, or a combination of the two factors. The overall picture appears to be one of distortion and possible fragmentation of crystallites, with the total volume fraction of ordered regions approximately halving. Similar structural changes, including loss of crystallinity, have been demonstrated in conventional semi-crystalline polymers as a result of yielding [38].

The recovery of crystallinity at temperatures close to, but below,  $T_g$  indicates that the yielding process does not cause a wholesale destruction of the crystallites. From the low temperatures required to recrystallise, it would appear likely that very localised rearrangements are needed for the crystals to re-form. Indeed, DSC measurements on the deformed samples give very similar enthalpy changes for the melting and subsequent crystallisation processes, suggesting that the damaged crystals are able to relax back to their original structure on the time scale of the heating cycle of the DSC. The lack of any discernible recrystallisation exotherm on initial heating suggests that the process occurs over a broad temperature range. These results suggest that the shearing of crystals, in a direction normal to the chain axes, disrupts the crystalline order most significantly, and is probably not accounted for in terms of discrete active slip planes, as in most crystals. It maybe that the shear strain rotates the aromatic groups around the chain axes sufficiently to disrupt the local crystalline order.

The difference in behaviour of the annealed samples of BN compared to the unannealed ones, is most likely to be due to the change in crystal structure on annealing. As was indicated above, annealing of BN induces a phase change from a pseudo-hexagonal structure to an orthorhombic arrangement. The orthorhombic crystallites have a higher packing density and are thus likely to be more resistant to the post-yield deformation than the pseudo-hexagonal ones.

#### 4.2. Stress-induced phase transition

The appearance of a new reflection at  $2\theta \sim 16^\circ$  in the X-ray diffraction patterns of both BN and BIQ is highly suggestive of the formation of a new crystalline phase. In BIQ, the reflection is seen in as-annealed samples, but is enhanced on deformation. In BN, on the other hand, the reflection only appears on deforming the annealed samples, suggesting that, in this case at least, it may be associated with the more highly ordered orthorhombic crystalline phase. Furthermore, the similar position of the new peak in both deformed BN and BIQ samples indicates that it may be associated with the common HBA component, and may be due to a similar type of transformation in both materials.

On the basis of electron diffraction studies, Leiser [24] describes two orthorhombic phases for PHBA, Phases I and II, which have different cell parameters, and which are related through a shearing of the unit cell. In powder diffraction patterns from PHBA, Phase I is observed to be the majority component. However, the most intense reflection belonging to Phase II is the (020) reflection which occurs at  $2\theta = 15.9^\circ$ . It is tempting, therefore, to try to associate the  $15.9^\circ$  peak from Phase II of PHBA with the ca.  $16^\circ$  peak found in compressed samples of BN and BIQ, which contain substantial proportions of HBA monomers. It should be noted that no mechanically induced transformation between Phases I and II has been observed in samples of PHBA, although there has been a report of a transition following high temperature annealing [39]. However, the possibility of such a shear-induced phase transition would appear to be much greater in a copolymer, owing to the smaller size of the crystallites that will be present.

There are analogies between the suggested behaviour of BN and BIQ, and the deformation of bulk polyethylene perpendicular to the chain direction, i.e. the loading geometry used in this work. In polyethylene, the appearance of extra reflections in both X-ray and electron diffraction patterns, indicates the occurrence of a stress induced phase transition to a monoclinic phase. In fact, Young and Bowden [40] have demonstrated, using X-ray measurements *during* deformation, that the shear induced transformation from orthorhombic to monoclinic phases in polyethylene corresponds closely to the martensitic transformation mode described by Bevis and Crellin [41]. Unfortunately, in the present case, the samples have a uniaxial orientation before and after deformation, so that it is not possible to establish any geometric relationship between the as-received and stress-induced phases.

A definitive conclusion regarding the appearance of the  $16^\circ$  maximum is not possible here. However, there appears to be strong evidence in favour of the formation of a new phase, in both BN and BIQ, which may be related to Phase II of PHBA, and which forms through a stress-induced martensitic transition.

## 5. Conclusions

It is clear from the studies of the yield behaviour of both BN and BIQ that the transverse compressive yield stress is optimised by annealing at temperatures about 20°C below the melting point. It would appear likely that the improvements in yield stress are a direct consequence of the improvement of crystalline order that occurs during such anneals, rather than being linked to any changes in the molecular orientation of the samples. The effect is more evident in BIQ than in BN, which is probably due to the lower crystallinity of the BIQ samples prior to annealing.

Deformation of unannealed samples of BN appears to result in distortion and local loss of internal order in the crystallites. It seems likely that the disruption occurs on a very local scale, since the crystallite structure is recovered through low temperature anneals, below the glass transition temperature. Yielding of the annealed BN samples does not result in the same level of crystalline disruption, suggesting that the orthorhombic crystallites in annealed BN are more resistant to deformation than their pseudo-hexagonal counterparts. However, it does cause a crystal–crystal transformation giving a new X-ray peak at  $2\theta \sim 16^\circ$ . In the case of the BIQ samples, the peak corresponding to a second phase appears on annealing, but it is intensified by the shear deformation. The new peaks may be related to Phase II of PHBA, which is the common and majority component of the two copolymers.

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