polymer papers

Reversible changes in the solid state of HBA/HNA liquid crystalline copolyesters studied by X-ray diffraction

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Real time X-ray diffraction patterns were recorded as a function of heating and cooling cycles using a synchrotron radiation source for copolyesters of 4-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) with monomer ratios 75/25, 58/42 and 30/70. The angular positions of the two main interchain X-ray diffraction reflections 1 1 0 and 2 0 0 were obtained at temperatures below the melting point with a powder diffractometer, and the unit cell dimensions of the copolymers were measured. For the 30/70 and 58/42 compositions the cell dimensions vary linearly and reversibly with temperature. For the 75/25 copolymer the cell dimensions show a clear bend with temperature, which can be associated with a transformation from an orthorhombic to a quasi-hexagonal phase. It is further shown that at higher temperature the dimensions of the D_{110} and D_{200} coherently diffracting domains increase while the scattering intensity of the diffraction peaks decreases with temperature. These changes are reversible with temperature. Results are discussed in terms of partial melting of smaller crystallites contributing in a reversible manner to the occurrence of a mobile high temperature quasi-hexagonal phase.

(Keywords: liquid crystalline copolyesters; WAXS; unit cell thermal variations; solid–solid phase transition; crystalline coherence length)

INTRODUCTION

The series of copolyesters from 4-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) has been receiving considerable scientific attention, both from the basic and the applied points of view. HBA/HNA with composition 75/25 is marketed by Hoechst Celanese under the trade name Vectra. Investigations on these materials have been mainly concerned with mechanical properties of oriented fibres[1–3], thermodynamic[4–6] and thermal[7,8] properties and n.m.r. studies on molecular motion[9]. Their morphology and microstructure have also been investigated by transmission electron microscopy (TEM), scanning electron microscopy (SEM) and small angle X-ray scattering (SAXS)[10–13]. Wide angle X-ray diffraction (WAXS) studies on oriented fibres and tapes have shown non-periodic maxima on the meridian, which have been accurately predicted on the basis of a completely random sequence of monomer units[14,15]. In spite of this random substitution, there is evidence from thermal analysis results and the presence of one *h k l* X-ray reflection which suggests the existence of a crystalline phase at temperatures below the melting point. The cocrystallization mechanisms and the three-dimensional order of such a phase are still a matter of controversy. Windle and co-workers[16,17] have proposed that this phase consists of 'non-periodic layer crystallites' (NPL), which arise from the lateral register of similar but non-periodic sequences of neighbouring chains. Biswas and Blackwell[15] assume, on the other hand, a model that requires only a limited chain register at one point in a sequence and takes no account of differences between monomers or chain sense.

There have been several previous studies of changes in the X-ray diffraction patterns with temperature of the HBA[18–22] and HNA homopolymers[23]. In the case of HBA/HNA copolymers most of the results reported only make reference to the WAXD study of annealed samples examined at room temperature[4,24]. However, in a recent paper, Hanna and Windle[25] have reported a detailed X-ray study of the low molecular weight copolymer, specially in the mid-range of composition during annealing at high temperature. These authors show that annealing of the room temperature metastable pseudo-hexagonal phase leads to a transformation into the orthorhombic phase and suggest a model to account for this phase transformation.

In the present paper, particular attention will be focused on the temperature dependence of the interchain equatorial reflections of non-oriented HBA/HNA materials. In addition, an analysis of the integral breadth of these reflections is also reported. It should be

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emphasized that all the experiments were performed at temperatures well below the melting temperature (T_m) in order to account only for changes occurring in the solid state.

MATERIALS AND TECHNIQUES

Three copolymers prepared from HBA and HNA were supplied by the Hoechst Celanese Corporation, in the form of pellets. The monomer ratios (HBA/HNA) were 75/25, 58/42 and 30/70. Samples in the form of films 0.25 mm thick were produced by compression moulding in a hot press at a temperature 20°C above the melting point of each copolymer and subsequently quenched. In most cases a small degree of planar orientation could not be avoided. Transmission X-ray diffraction patterns (WAXS) of the compression-moulded materials, with the X-ray beam perpendicular to the film surface, were instantly obtained as a function of temperature using the synchrotron radiation source in the polymer beam-line at Hasylab, Hamburg. Scattering patterns were recorded every 20 s, using a position-dependent linear detector. X-ray diffractograms in the reflection mode, as a function of temperature, were also recorded in a Rigaku vertical goniometer attached to a Rigaku high power X-ray generator with rotating anode (Ni-filtered CuKα radiation) using 40 kV and 140 mA. Samples were held at each temperature for about 1 h, which includes thermal stabilization and recording time. Scans were made in the angular range of 17–24° (2θ) at a goniometer speed of $1°\ \mathrm{min}^{-1}$, using a time constant of 1. The full scale number of counts per second varied between 8×10^3 and 10^4. For the determination of the unit cell dimensions the 1 1 0 and 2 0 0 diffraction peaks were used. The experimental profiles of both reflections were fitted to Lorentzian curves using the computer program SIGMAPLOT version 4.0. For the correction of instrumental broadening effects, a sample of silicon was used which exhibited an integral breadth of $\delta\beta_{ins}=1.4\times10^{-3}$ Å^{-1}.

The size of the lattice coherence values D was directly calculated from the integral breadth $\delta\beta$ of each reflection assuming the existence of lattice distortions in the crystallites[26]. This assumption yields D values which are about 20% larger than those directly calculated from $1/\beta$.

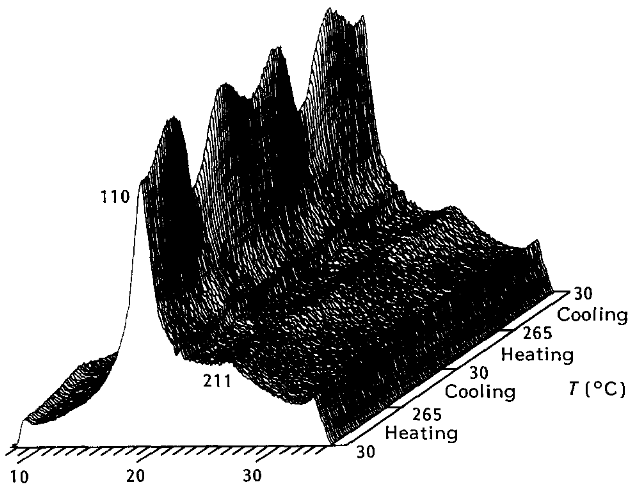

Figure 1 Real time X-ray diffraction patterns of the 75/25 polyester as a function of heating and cooling cycles

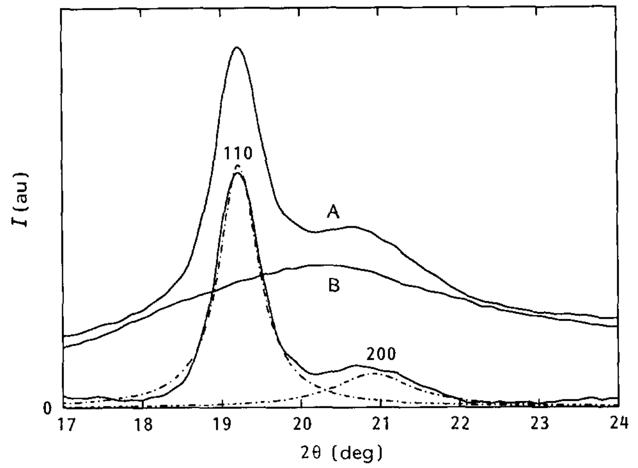

Figure 2 Experimental X-ray profile of the 30/70 copolymer measured at 30°C (curve A) and of the molten polymer (curve B). Subtraction of both curves and the separation of the 1 1 0 and 2 0 0 reflections are shown at the bottom of the figure

RESULTS

Figure 1 shows a series of real-time WAXS patterns of a 75/25 copolyester as a function of two successive heating–cooling cycles, between room temperature and 265°C. The melting temperature of the compression-moulded sample is 290°C. Each heating or cooling cycle is characterized by a maximum in intensity of the strong peak due to the 1 1 0 reflection, as well as by a loss of intensity of the 2 1 1 peak at high temperature. These reflections are referred to an orthorhombic unit cell[24,25]. The small peak at ~21.5° is an electronic artifact. The same reversible behaviour of the scattered intensity, on heating and cooling, is observed for the other two copolyesters investigated.

Data in *Figures 2–8* were obtained with the X-ray diffractometer, which has much better angular resolution than the polymer beam-line at Hasylab, Hamburg. Thus, the angular resolution of the goniometer permits the separation of the overlapping 1 1 0 and 2 0 0 reflections at each temperature. *Figure 2* shows, as an example, the experimental profile (curve A) of the copolyester with a monomer ratio of 30/70 at 30°C. The profile from the amorphous halo (curve B) was adjusted from the scattering intensity of the polymer melt. After subtraction of the amorphous contribution, a least-square computer program fitted the experimental profile to two Lorentz functions corresponding to the two diffraction peaks (bottom of the figure).

From the position of these reflections, the temperature variation of the a and b lattice constants of the orthorhombic unit cell for the investigated copolyesters was derived (see *Figure 3*). These parameters are directly related to the average distance between adjacent molecular chains. For the sake of comparison, the values for the HBA homopolymer taken from reference 19 are also included in *Figure 3*. During the first heating cycle there is a linear variation of the a and b parameters, i.e. a nearly constant thermal expansion coefficient α is obtained for the three copolymers. The unit cell expands more significantly along the a-axis than along the b-axis, where the expansion coefficient is one order of magnitude smaller. The thermal expansion coefficients α_a for the 30/70, 58/42 and 75/25 copolymers are respectively 3×10^{-4}, 2.5×10^{-4} and $1.5\times10^{-4}\ \mathrm{K}^{-1}$. On cooling, the behaviour of the HBA-rich copolymer, 75/25, differs from

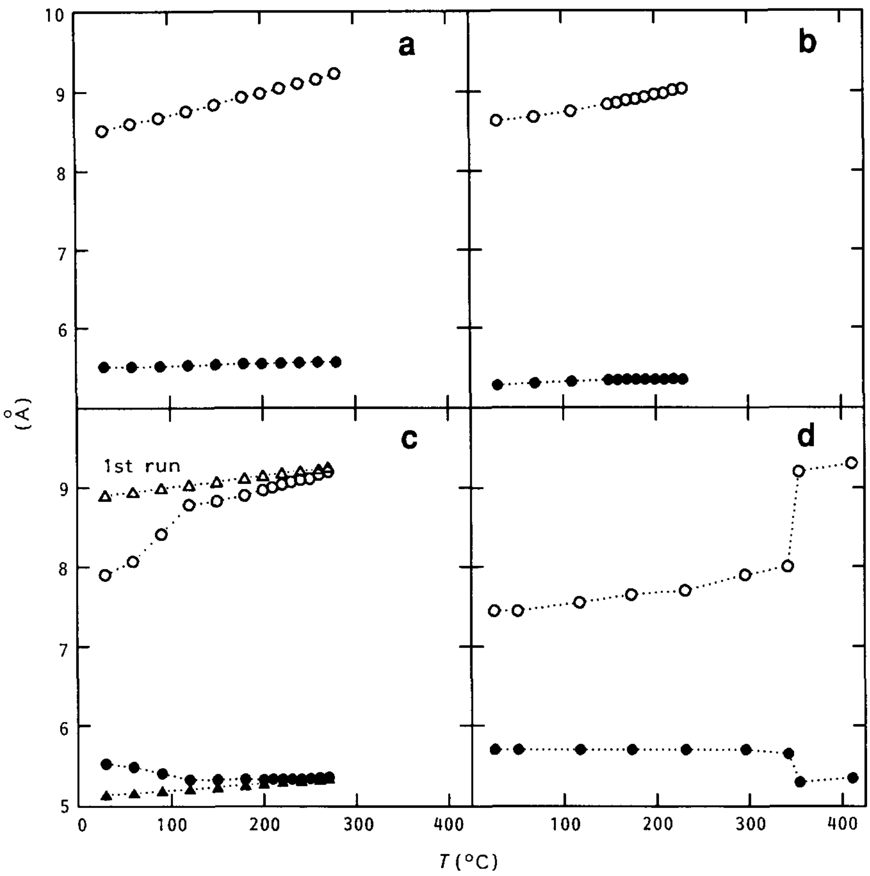

Figure 3 Variation of the *a* (open symbols) and *b* (solid symbols) lattice constants as a function of temperature for various HBA/HNA compositions: (a) 30/70; (b) 58/42; (c) 75/25; (d) 100/1

that of the other two compositions. The *a* and *b* dimensions of the latter two copolymers are reversible with temperature upon heating and cooling during the successive temperature cycles. On the contrary, for the 75/25 copolymer the thermal variation of the lattice constants *a* and *b* shows a clear step around 120°C, involving different slopes above and below this temperature. This step-like behaviour becomes reversible in the following heating and cooling cycles. The step change of the unit cell parameters with temperature can be associated with a crystal structure transformation from the orthorhombic to a quasi-hexagonal phase which is related to the gradual merging into a single peak of the 1 1 0 and 2 0 0 reflections (see *Figure 4*). Most interesting is the fact that, upon cooling, the quasi-hexagonal lattice is reversibly transformed into the orthorhombic lattice as revealed by the splitting of the 1 1 0 and 2 0 0 reflections. A similar crystal transformation has been reported for this material in the course of annealing above 230°C and subsequent quenching[24,25].

The integral breadth $\delta\beta$ of the 1 1 0 and 2 0 0 reflections has also been calculated as a function of temperature. From these values, the sizes D_{110} and D_{200} of the domains which coherently diffract in the [1 0 0] or [2 0 0] directions have been derived assuming the occurrence of lattice distortions[26] (*Figure 5*).

Figure 6 illustrates the integral scattering intensity of the 1 1 0 reflections, i.e. the area under the peak, as a function of temperature measured in the diffractometer. In all three cases a maximum can be observed, similar to the results obtained with synchrotron radiation. It is interesting that the temperature reversibility does not seem to be affected by the different timescales of the experiments performed in the synchrotron (~1 h per curve) and the conventional X-ray source (~1 h per point).

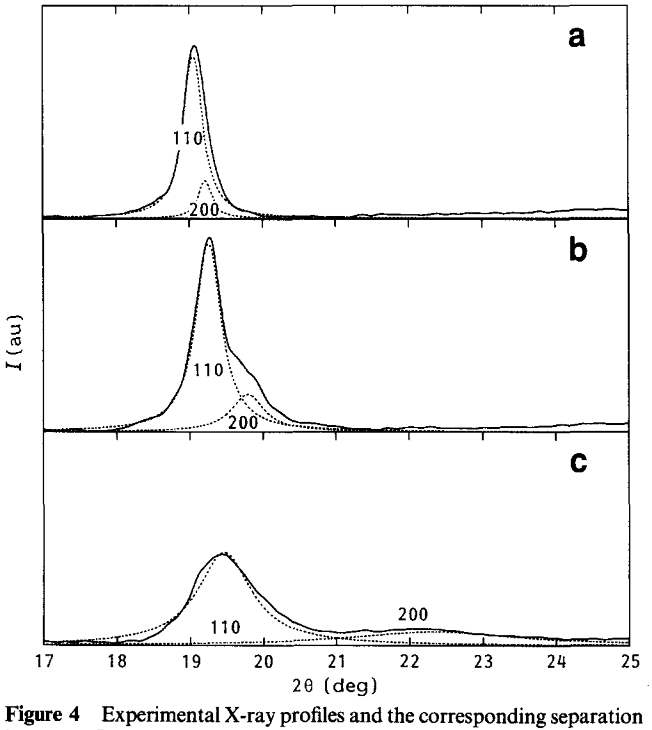

Figure 4 Experimental X-ray profiles and the corresponding separation into two Lorentz curves of the 75/25 copolymer at three different temperatures showing the merging of the 2 0 0 into the 1 1 0 reflection: (a) 260°C; (b) 180°C; (c) 30°C

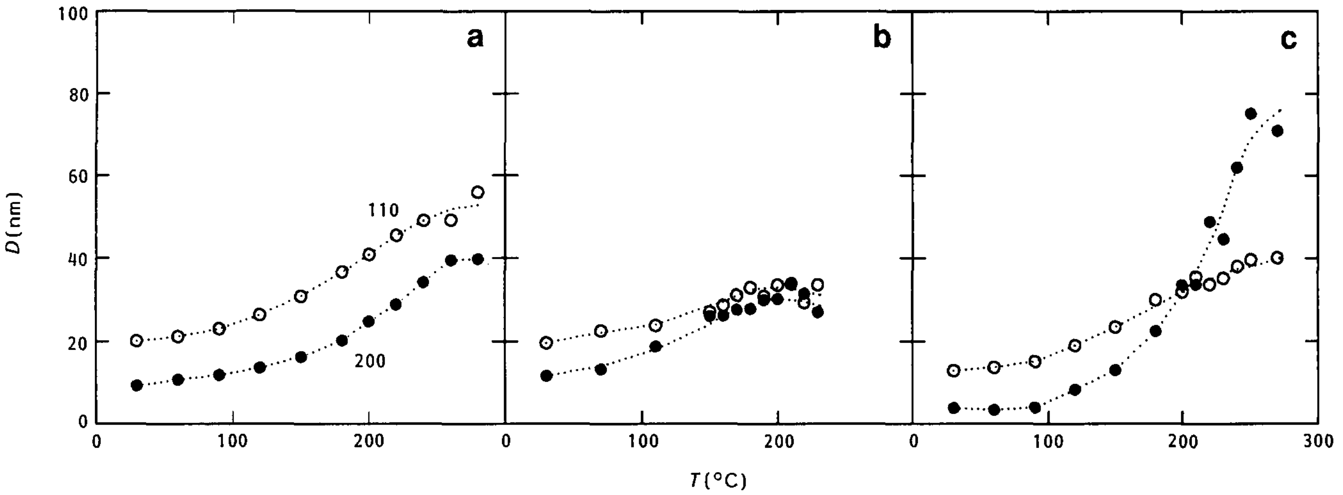

Figure 5 Thermal variation of the crystal length values D_{110} and D_{200} for the three HBA/HNA copolyesters: (a) 30/70; (b) 58/42; (c) 75/25

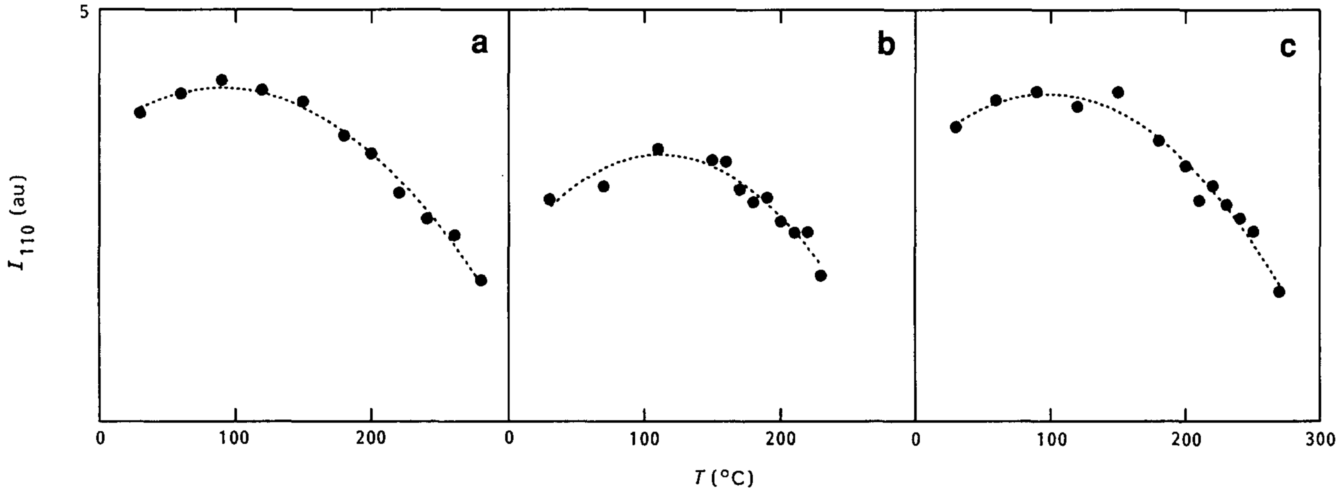

Figure 6 Scattering intensity of the 1 1 0 reflections *versus* temperature for the three HBA/HNA copolyesters: (a) 30/70; (b) 58/42; (c) 75/25

DISCUSSION

A parallel to the step behaviour found for the lattice constants of the 75/25 copolymer can be drawn with the sharp transition obtained at 350°C in the HBA homopolymer (*Figure 3*). In the latter case this behaviour is known to correspond to a first order transition, from an orthorhombic to a pseudo-hexagonal crystal phase (hexagonal phase showing the 2 1 1 orthorhombic reflection), which is defined by a d.s.c. peak[19]. Here, the transformation from orthorhombic to hexagonal resembles that observed in nylon[27] and polyethylene[28] at high temperatures, involving high molecular mobility. This transition entails, in the case of the HBA homopolymer, a multiple rotational twinning of the structure about the *c*-axis, as discussed for condis crystals[19]. In the case of the 75/25 copolymer, there is not such a clear endotherm but rather a wide diffuse endotherm is observed which resembles the Brill transition found in nylon-6,6 from a triclinic to a pseudo-hexagonal phase[27].

The above picture can be further clarified by plotting γ, the angle between the unit cell axes of a quasi-hexagonal

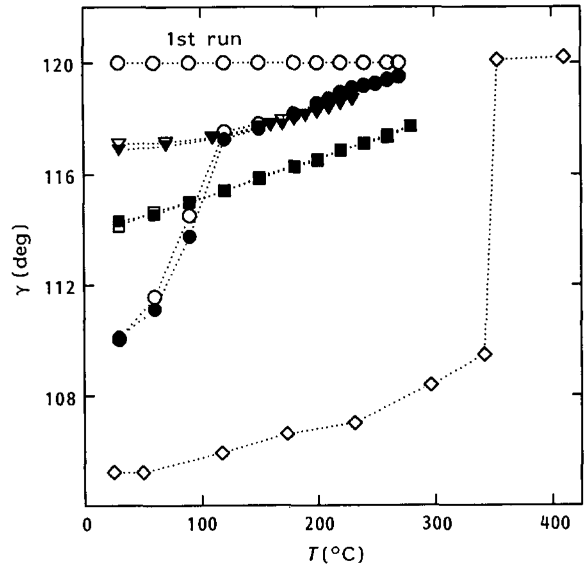

Figure 7 Angle γ of the quasi-hexagonal unit cell as a function of temperature for various HBA/HNA compositions. ○, 75/25; ▽, 58/42; □, 30/70; ◇, 100/1. Open symbols, heating; solid symbols, cooling

lattice, as a function of temperature (*Figure 7*). Again, the two copolymers with the higher HNA content show a reversible linear variation of γ with temperature, whereas in the first heating of the 75/25 copolymer the angle γ takes a constant value of 120°, as in the high temperature phase of the HBA homopolymer. In subsequent heating and cooling cycles there is a sharp change in the slope at 120°C, where after the initial fast growth, a behaviour similar to the first two cases is observed.

It can be concluded that the HBA-rich material, 75/25, is transformed during the initial compression moulding at 290°C to a pseudo-hexagonal phase ($\gamma = 120°$) similar to that found in the HBA homopolymer above 350°C, involving some kind of conformational disorder. By quenching from the melt, the pseudo-hexagonal symmetry is frozen-in at room temperature. The experimental diffraction patterns are first recorded at this point ($T = 30°C$). The pseudo-hexagonal symmetry is present over the first heating cycle; mobility increases with increasing temperature up to 270°C. On cooling slowly to room temperature, the pseudo-hexagonal phase is gradually transformed into a new phase, to be called quasi-hexagonal, because γ is close to but smaller than 120°. The appearance of this new phase resembles the behaviour of the 30/70 and 58/42 compositions above 120°C. Below this temperature a step-wise transformation into an orthorhombic lattice ($\gamma \sim 110°$) is clearly seen. At this point, one may speculate on the possibility of also finding such crystal structure transitions on the latter copolymers. WAXS experiments at subambient temperatures are in progress, which will shed light on this question.

It should be noted that the initial pseudo-hexagonal phase at room temperature is not obtained again unless the temperature is raised above the melting point. Thus, this phase is thermodynamically metastable below the melting point, as pointed out by Hanna and Windle[25].

Figure 8 represents the cross-sectional area ($a \times b/2$) of the molecular rods at room temperature as a function of copolymer composition. Two sets of values can be distinguished: data corresponding to the hexagonal lattice obtained at high temperature and cross-sectional data associated with the low temperature orthorhombic phase. Data of both parent homopolymers HBA[19] and HNA[23] have been included among the latter. From these results, we can conclude that the orthorhombic lattice expands to some extent when different comonomer units are added. This suggests that a certain degree of cocrystallization is present, at least on those crystals which have been formed by rapid cooling.

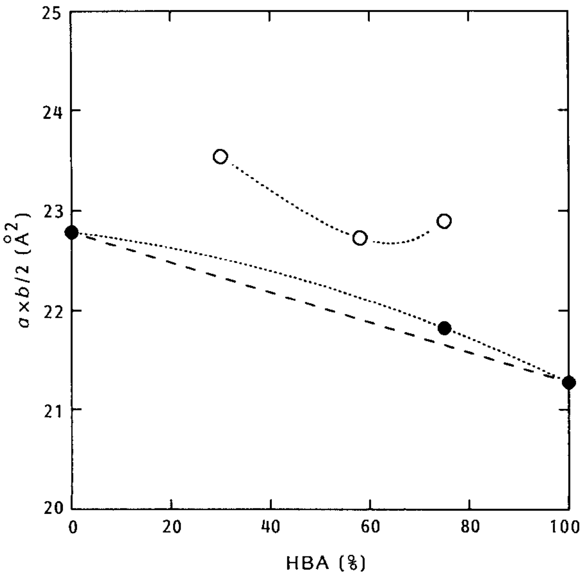

Figure 8 Cross-sectional area of the molecular rods of the HBA/HNA series measured at 30°C as a function of composition: ○, hexagonal; ●, orthorhombic

The domain sizes D_{110} and D_{200} (*Figure 5*) show values between 10 and 80 nm in this temperature range. Typical crystal sizes of approximately 60 nm in the direction normal to the chain axes have been observed by TEM[11]. Although these values are slightly higher than our data, it should be noted that our samples are isotropic while the samples investigated by Spontak and Windle[11] were oriented as a consequence of shear above the melting point. The size and/or perfection of the crystals perpendicular to the molecular chains shows an increasingly sigmoidal behaviour, which seems to reach its maximum near the end of the measured temperature interval. The variation of D_{110} and D_{200} values is also reversible with temperature. This behaviour is a unique feature of these rigid-rod random copolymers. At high temperatures there is, in addition, a decrease in scattering intensity (*Figure 6*) which parallels the continuous increase in the lateral extent of the lattice coherence. The intensity decrease could be explained by partial melting of the most imperfect crystallites which, on average, could also contribute to the increase of the lateral size of the remaining ones. This lateral growth could also be the consequence of the gradual change into a mobile hexagonal phase where the molecular chains adopt a quasi-cylindrical symmetry and thus can be more easily incorporated into laterally growing crystals. On cooling, this symmetry is lost and crystals tend to recover their size as a function of temperature.

CONCLUSION

The aim of this work has been the investigation of the interchain equatorial reflections of isotropic HBA/HNA copolymers as a function of temperature with a view to examining the crystal transformations occurring below the melting point. It is concluded that for the 75/25 copolymer the change from orthorhombic to the quasi-hexagonal structure is associated with a sharp change in the unit cell dimensions with temperature. For the copolymers with lower HBA content such a phase change, if any, may be expected to occur below room temperature.

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