Polymer Vol. 37 No. 25, pp. 5667–5680, 1996

0032-3861/96/$15.00 + 0.00

S0032-3861(96)00427-2

Crystallization of thermotropic liquid crystalline HBA/HNA copolymers

H. C. Langelaan* and A. Posthuma de Boer†
Department of Polymer Technology, Faculty of Chemical Technology and Materials Science, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands
(Received 11 August 1995; revised 20 March 1996)

The crystallization behaviour of random copolymers based on *p*-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) is reviewed. First a summary is given of what is known about the structure and thermal transitions of the constituent homopolymers. Next the crystallization behaviour of HBA/HNA copolymers is described starting with the glass transition, after which the two crystallization processes that have been found in these copolyesters are treated. The crystallization of the HBA/HNA copolymers will be compared to the crystallization of similar random copolymers that are not liquid crystalline. Two models have been proposed to describe the solid state of the HBA/HNA copolymers: the non-periodic layer (NPL) model and the paracrystalline lattice (PCL) model. In the NPL model, ordered domains are formed by the lateral register of similar but non-periodic sequences of neighbouring chains, whereas in the PCL model ordered domains are formed by the presence of conformational correlations between adjacent monomers without explicit sequence matching. The two models are compared in view of the experimental observations about the structure and the morphology of the crystallized material. This review ends with some conclusions. Copyright © 1996 Elsevier Science Ltd.

(Keywords: HBA/HNA copolymers; crystallization; random copolymers)

INTRODUCTION

Liquid crystalline polymers (LCPs) show liquid crystalline order in solution (lyotropic LCPs) or in the melt (thermotropic LCPs) because of the rigid character of the molecules. In main-chain LCPs the rigid groups are part of the polymer chain, while in side-chain LCPs they are attached to a (flexible) polymer backbone. The properties of side-chain LCPs have been reviewed by McArdle[1]. This paper will concentrate further on the properties of main-chain LCPs and, in particular, on *p*-hydroxybenzoic acid/2-hydroxy-6-naphthoic acid (HBA/HNA) copolymers.

From a technological point of view, main-chain LCPs are interesting materials because the orientability of the molecules facilitates the production of very strong products. Lyotropic LCPs have a melting point which is above their decomposition temperature, and they can only be processed from a solution. Lyotropic LCPs find a still growing application in strong fibres. The reduced melting point of thermotropic LCPs gives them the advantage of melt processability. Because of their excellent flow properties and dimensional stability they are very well suited for the injection moulding of complex shapes, e.g. in electronic appliances. The strength and stiffness of thermotropic LCPs, however, are lower than those of lyotropic LCPs because the reduction in melting point is at the expense of the strength of the molecules or the amount of crystallinity. The melting point of intractable polymers can be lowered by increasing the transition entropy and/or decreasing the transition enthalpy. This can be achieved by[2]:

- the introduction of flexible parts into the molecules;
- the introduction of elements which decrease the linearity of the molecules;
- (random) copolymerization with another monomer that hinders crystallization;
- the addition of flexible side-chains, which act as an 'internal solvent'.

The polymers thus obtained are still fairly rigid and can show a liquid crystalline order in the melt since their melting point is below the decomposition temperature. The thermodynamics of the formation of mesophases has been reviewed by Keller and Ungar[3].

A well known class of thermotropic LCPs is the random copolyesters of HBA and HNA, which are commercially available from Hoechst-Celanese under the trademark Vectra, type A. The homopolymer of HBA is highly crystalline and cannot be processed using conventional techniques. Random copolymerization with HNA units disrupts the three-dimensional packing of the HBA units, but the extended chain conformation is maintained. HBA/HNA copolymers form a nematic structure in the melt.

It is expected that the crystallization of (semi-)rigid molecules such as thermotropic LCPs differs from the extensively described crystallization of flexible polymers such as poly(ethylene) or poly(ethylene terephthalate) (PET) (see, for example, Mandelkern[4]). The crystallization of the latter can be fast because then the overall

---

* Present address: ATO-DLO, Bornsesteeg 59, PO Box 17, 6700 AA Wageningen, The Netherlands
† To whom correspondence should be addressed

chain conformation hardly changes: crystallization only affects the local conformation of the polymers. Due to the reduced flexibility, crystallization of semi-flexible and rigid molecules requires large translations of the molecules. The reduced flexibility also limits the movements of the chain as soon as an appropriate sequence is built in into a crystallite. For these reasons and the additional effects of copolymerization, it is expected that the degree of crystallinity in HBA/HNA copolymers is low.

The crystallization behaviour of HBA/HNA copolymers has been studied extensively, but the nature of molecular order in these thermotropic LCPs is still not understood properly. Different points of view exist on, for example, the nature and the width of the glass transition, the (co)crystallization mechanisms and the three-dimensional order of the crystalline phase. Measurements have shown that the amount of crystallinity in these copolymers can be considerable: depending on the composition and the thermal history, the reported values range between 15 and 25%, but values as high as 60% have also been mentioned[5].

The crystallization of HBA/HNA copolymers has been reviewed by Ambrosino and Navard[6]. Since then, a considerable amount of literature on this subject has been published. New insight has been gained into the similarity between the behaviour of the copolymers and their constituent homopolymers. Also, the models describing the solid state structure are now more developed. In the present review we summarize what is now known about the crystallization behaviour of the HBA/HNA copolymers. A brief review is given of the crystallization behaviour of the homopolymers because of the similarity of their structure with that of the copolymers. The thermal transitions of the copolymers are also described. The structure and morphology of the formed crystallites are discussed, as well as the models that have been proposed to describe the crystalline structure. The final section recapitulates the crystallization behaviour following from the observations described in the previous sections, and gives the conclusions of this literature study.

STRUCTURE AND THERMAL TRANSITIONS OF POLY(HBA) AND POLY(HNA)

It is well known that the crystallization behaviour of copolymers is governed by the structure of the constituent homopolymers[7]. This section reviews what is known about the structure and the thermal transitions of the homopolymers of HBA (PHBA) and HNA (PHNA). Although the results of the measurements are highly influenced by the preparation method, the thermal history and the molecular weight of the sample, they can be summarized as follows.

The HBA homopolymer displays two transitions detected by d.s.c.: one around 340°C and another around 430°C. At room temperature, HBA packs in an orthorhombic unit cell with the dimensions $a = 7.52$ Å, $b = 5.70$ Å and $c = 12.49$ Å, having two chains per unit cell with a 2_1 screw axis parallel to the chain axis[8–10]. In samples of low degree of polymerization another variation is found[8], with a unit cell with $a = 3.77$ Å, $b = 11.06$ Å and $c = 12.89$ Å.

With increasing temperature the unit cell expands predominantly along the a axis[11] with an expansion coefficient of about $1.5 \times 10^{-4}\,K^{-1}$. The reason is that the increasing molecular motion about the 1,4-axis with increasing temperature leads to an expansion normal to the (100) plane where the phenylene rings initially lie. Compared to the a axis, the expansion along the b and c axes is negligible. N.m.r. and dielectric measurements revealed that all rings undergo rapid flipping motions at 300°C, but the carbonyl groups remain fixed[12–14]. The (reversible) transition at 340°C is accompanied by a stepwise expansion of the a and b axes, enabling jumping motions of the entire unit including the carbonyl groups. This results in a stepwise increase of the dielectric constant. At this transition the 200 and 100 wide-angle X-ray diffraction (WAXD) reflections merge, suggesting hexagonal symmetry. The presence of the 211 reflection, however, betrays orthorhombic symmetry. At 380°C the unit cell parameters are $a = 9.2$ Å, $b = 5.3$ Å and $c = 12.4$ Å[8,15].

The transition at 340°C has been described as a crystal/crystal transition[16], a crystal/condis crystal transition[11,17] or a crystal/plastic-crystal transition[18,19]. Most recent papers suggest that this transition is a crystal/smectic (E) transition[13–15,19]; different results have been found by Liu and Geil[20,21]. Above this transition a rotationally degenerate, dynamically disordered structure is formed in which the chains are still rotationally correlated to each other. The remaining intermolecular ordering is dominated by electrostatically favourable interactions, in particular phenyl-edge to phenyl-face and, to a lesser degree, carbonyl-carbon to carbonyl-oxygen contact. With increasing temperature the correlation between orientations of both inter- and intrachain neighbours is gradually lost, but there is no evidence for the loss of three-dimensional order.

The structure of PHBA above the second transition has been described as nematic[18], but in more recent papers it is concluded from dielectric measurements and still visible meridional reflections that it must be a smectic B phase[13–15,22]. The transition at 430°C, thus, does not involve a change in packing along the chain axis and in chain conformation, but only the loss of long-range orthorhombic coherence in the a–b plane, while the herringbone packing on the hexagonal lattice is preserved locally. The unit cell parameters of this hexagonal structure are $a = 5.40$ Å and $c = 12.45$ Å[13,22].

The behaviour of PHNA, like that of PHBA, is strongly determined by the thermal history of the sample. Two transitions are found in d.s.c. measurements: the first at temperatures around 320°C (for as-polymerized material at 395°C) and the second around 440°C. At room temperature, PHNA is packed in an orthorhombic unit cell with $a = 7.75$ Å, $b = 5.90$ Å and $c = 16.86$ Å, having two chains of two monomer units per cell[19,22,23]. Rutledge and Ward[10] found essentially the same a and b values, whereas the determined c value was 13 Å. The orthorhombic phase of PHNA transforms to a pseudo-hexagonal one at the first transition. From the presence of HKL reflections in this phase it was concluded 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. The lack of space in the unit cell necessitates co-operative rotations of groups of chains. The reported unit cell parameters of

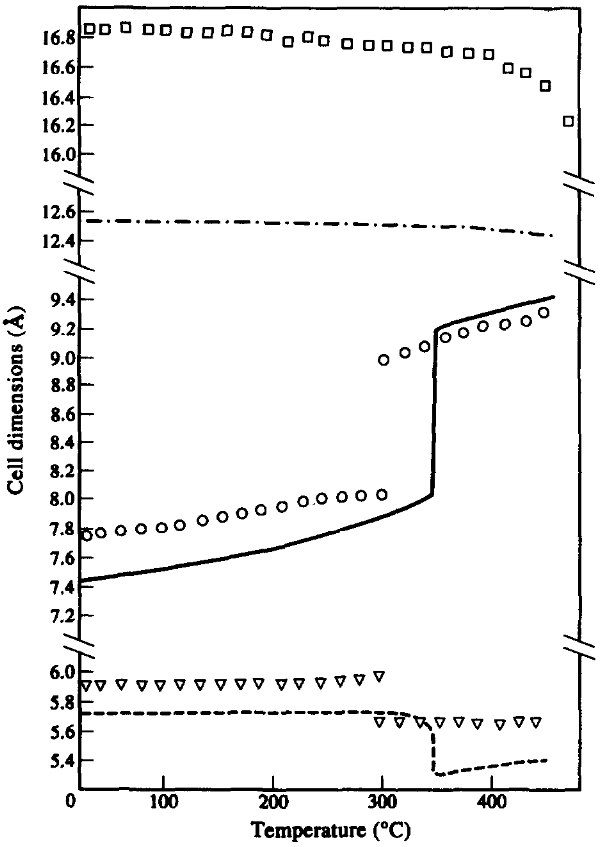

Figure 1 The variation of the unit cell parameters of the HNA homopolymer (O, *a* axis; ▽, *b* axis; □, *c* axis). The corresponding unit cell parameters of the HBA homopolymer are represented by lines. (Reprinted with permission from Hanna and Windle[22])

this pseudo-hexagonal phase at 425°C are $a = 9.26$ Å, $b = 5.69$ Å and $c = 16.59$ Å[22,23]. Above the second transition the main interchain peaks are replaced by amorphous halos, but the 002 peak remains sharp. This suggests the existence of smectic-like order in the melt, most likely a smectic A phase[22,24].

The temperature dependence of the unit cells of PHBA and PHNA is summarized in *Figure 1*. From this figure it is clear that the thermal expansion of PHNA resembles that of PHBA, with most thermal expansion being concentrated in the 100 direction of the unit cell. Apparently, the polymer molecules are oriented with the chain direction parallel to the *c* axis of the cell and with the planes of the phenylene or naphthalene rings at a shallow angle to the 100 planes. An increase in rotational motion with temperature thus essentially leads to an increase of the unit cell along the *a* axis. At the orthorhombic to pseudo-hexagonal phase transition the unit cell expands jumpwise along the *a* axis, while it decreases jumpwise along the *b* axis. In the pseudo-hexagonal phase the unit cell continues to increase along the *a* axis, whereas it remains more or less constant along the *b* axis. It is important to note that at 440°C, when both homopolymers are packed in a pseudo-hexagonal phase, the values of the *a* axes are equal (9.3 Å) whereas the values of the *b* axes only differ by 5%. This close resemblance of the high temperature structures of the two constituent homopolymers may play an important role in the crystallization behaviour of the copolymers.

THERMAL TRANSITIONS OF HBA/HNA COPOLYMERS

This section summarizes the literature concerning the thermal transitions of the HBA/HNA copolymers. There is a short introduction to the usual crystallization behaviour of random copolymers. Next the glass transition in HBA/HNA copolymers is briefly considered. Following this the melting and crystallization behaviour of these copolymers is described. A special part of the melting/crystallization behaviour, the recrystallization of the melt above the nominal melting point, is then treated.

Crystallization of random copolymers

The sequence distribution in HBA/HNA copolymers is completely random, as was established by Mühlebach *et al.*[25] using n.m.r. Economy *et al.*[26] reported the formation of sequences of the alternating copolymer and the two homopolymers at high temperatures due to chemical processes such as interchain transesterification. This change in sequence distribution, however, could not be detected with n.m.r. measurements. A drastic change in sequence distribution at high temperatures is not plausible, because most phenomena are reported to be thermoreversible. The molecular weight of HBA/HNA copolymers, however, may change due to continuing polymerization. This phenomenon has (among others) been reported by Economy *et al.*[18], Yoon[27], Yoon *et al.*[28] and Anwer and Windle[29].

While in graft and block copolymers (not only liquid crystalline), repeating unit-sequences may crystallize because they are sufficiently long to overcome the nucleation barriers, crystallinity in random copolymers can only be induced via isomorphic substitution[7]. The main requirements for isomorphism in macromolecules are chemical similarity, similar size, equal bonding between the atoms, ions and molecules, and similarity in chain conformation. Crystals with a high packing density can allow less volume addition than crystals with a lower packing fraction, e.g. crystals containing helices. Also, high-temperature crystal forms usually have a larger disorder and lower density and can accommodate larger defects. For example, a high-temperature crystal form of the random copolymer of poly(tetrafluoroethylene) and poly(hexafluoropropylene) is stable, a form that permits rather large amounts of mobility[30].

In the case of perfect isomorphic substitution the copolymer is crystalline over the whole concentration range and shows a continuous change in melting temperature from one homopolymer to the other without a minimum or maximum. Since complete matching is rare, most random copolymers display limited mixed-crystal formation. If the foreign units fit less well into the host crystal, they change from substitutional defects to point defects coupled with chain disorder, and finally to amorphous defects. The phase diagram then becomes of the eutectic type with a minimum in the melting point at intermediate compositions. The melting point depression due to copolymerization can be substantial[31,32].

The glass transition in HBA/HNA copolymers

The thermal transitions in HBA/HNA copolymers as a function of the composition have been investigated by CaO and Wunderlich[17]. The glass transition they measured was extremely broad (about 180°C) and decreased only slightly in the mid concentration range. Sauer *et al.*[33] confirmed the presence of a very broad glass transition (50–150°C), using thermally stimulated current and d.s.c. measurements. A broad glass transition was found for all random copolyester LCPs they investigated, while a rather sharp glass transition was found for the structurally homogeneous LCPs (i.e. no copolymers). This supports the hypothesis that the broadness of the glass transition is caused by the structural heterogeneity in the random copolyesters. The anisotropic nature of the glass was found not to influence the broadness of the glass transition, whereas the presence of crystallinity could have an influence, but was ruled out as being the sole factor contributing to the very broad glass transition. Sauer *et al.*[34] found for a similar thermotropic LCP that the step in the heat capacity, ΔC_p, at the glass transition was independent of the amount of crystallinity. They concluded that the glass transition involved both the disordered nematic and the ordered regions of the material. On the other hand, Yonetake *et al.*[35] showed that the glass transition in completely amorphous HBA/HNA films is more pronounced than in films with a higher crystallinity. A critical discussion of the glass transition, however, is beyond the scope of this paper.

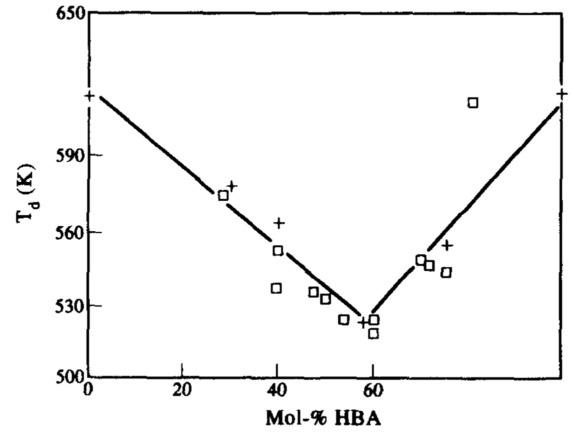

Figure 2 Change of the melting point $T_{m,f}$ of HBA/HNA copolymers with concentration. (Reprinted with permission from Cao and Wunderlich[17])

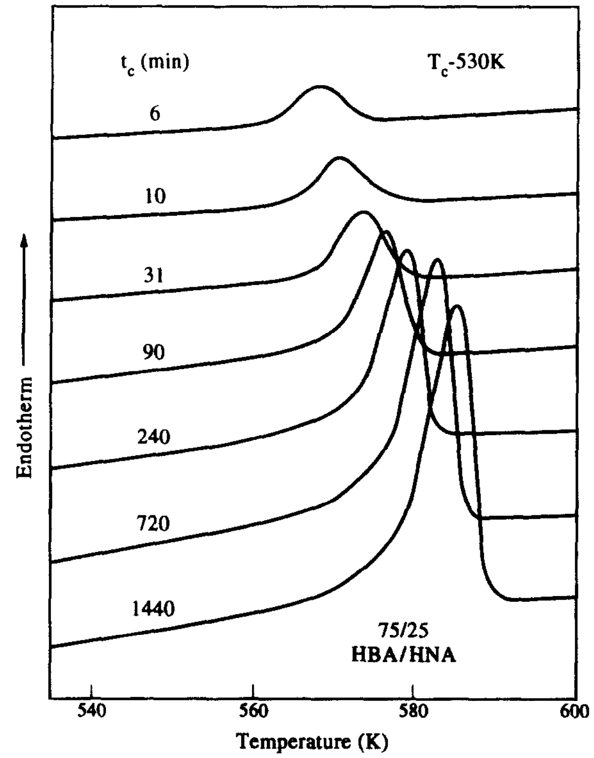

Figure 3 D.s.c. curves of the HBA/HNA 75/25 copolymer after annealing at 257°C (i.e. below $T_{e,f}$) for the indicated time. (Reprinted with permission from Cheng[37])

Melting and crystallization of HBA/HNA copolymers

Crystallization studies demonstrated that two crystallization processes can take place in HBA/HNA copolymers: one slow and the other fast. Each of these processes is associated with a different melting point: $T_{m,s}$ and $T_{m,f}$.

The fast process occurs when the polymer is cooled down rapidly from the nematic melt. It gives rise to an exothermic peak at a temperature $T_{c,f}$. This temperature decreases for higher cooling rates. The position, $T_{m,f}$, and the magnitude of the melting endotherm in the subsequent d.s.c. heating run are not influenced by the previous cooling rate, provided it is high enough[36–38]. This indicates that the crystallization process itself is fast and that the heat transfer to the surroundings is the dominating factor. For the 73/27 copolymer, $T_{m,f}$ is about 280°C. Since nematic melts can be supercooled to a substantial degree, $T_{e,f}$ can be about 60°C lower than $T_{m,f}$.

In *Figure 2*, $T_{m,f}$ is shown as a function of the HBA content. The HBA/HNA copolymer shows a eutectic-like melting diagram, with a minimum in the melting temperature for the copolymer containing 60% HBA. The shape of the melting diagram is indicative for a system showing isodimorphism or limited solubility of the components in the solid state[30]. The low value of ΔH indicates that the mesophase crystallizes to a small degree, but this low level of three-dimensional order is sufficient to fix the polymer chains[17]. The fast crystallization process cannot be suppressed: even at very high cooling rates some crystallinity is present[36].

The 70/30 copolymer crystallizes fast when the cooling rate is higher than $3.2\,\mathrm{K\,min^{-1}}$ [38]. The samples cooled at a rate below $3.2\,\mathrm{K\,min^{-1}}$ showed (in the subsequent heating run) a steady increase in melting temperature and heat of transition with decreasing cooling rate. This can be ascribed to the occurrence of the slow crystallization process. Slow crystallization also occurs in isothermal crystallization experiments. For isothermal crystallization experiments starting from the nematic melt the crystallization temperature can be chosen to be above or below $T_{e,f}$ (the exothermic peak originating from the fast crystallization process). These two distinct situations are described below.

The heating run of samples crystallized isothermally at temperatures above $T_{e,f}$ usually has one endotherm ($T_{m,s}$), originating from the slow process. This is shown in *Figure 3* for samples of HBA/HNA 75/25 crystallized at temperatures above $T_{e,f}$ for different times. $T_{m,f}$ of HBA/HNA 75/25 is located around 560 K and thus is always lower than $T_{m,s}$ in this type of crystallization experiment. The endotherm is characterized by a linear growth of the magnitude of the heat of transition[36] or the transition temperature[37] with the logarithm of the

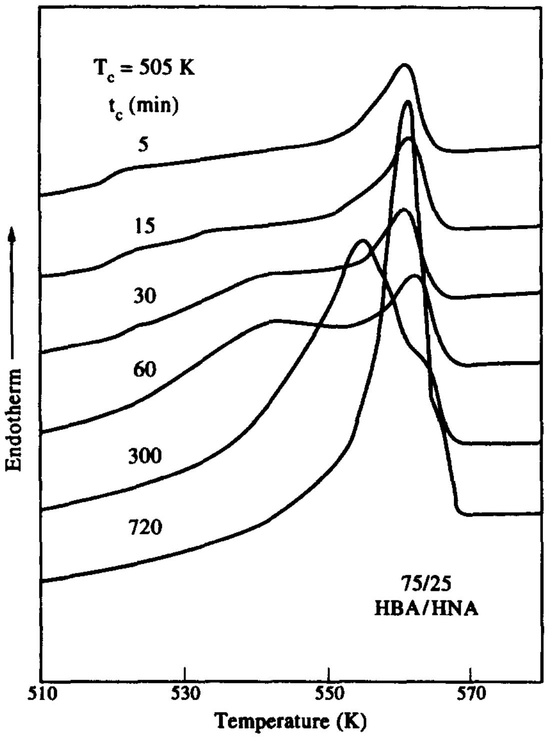

Figure 4 D.s.c. curves of the HBA/HNA 75/25 copolymer after annealing at 232°C (i.e. below $T_{c,f}$) for the indicated time. (Reprinted with permission from Cheng[37])

annealing time. The transition temperature increases faster for higher crystallization temperatures.

In isothermal crystallization experiments below $T_{c,f}$, the melting endotherm originating from the slow crystallization process ($T_{m,s}$) is formed in addition to the one originating from the fast process[36–38]. This is shown in *Figure 4* for the HBA/HNA 75/25 copolymer. Again $T_{m,s}$ increases linearly with the logarithm of the annealing time. This increase is more or less constant for all annealing temperatures. The heat of transition is also linearly dependent on the logarithm of the annealing time, but it increases faster for higher annealing temperatures. For short annealing times, $T_{m,s}$ is lower than $T_{m,f}$. This lower melting point of the more ordered material can be explained by its higher entropy of transition. The position and size of the fast crystallization endotherm remain almost constant (or decrease slightly) with the annealing time. For longer annealing times, $T_{m,s}$ and $T_{m,f}$ become equal; from the moment that both peaks overlap, they shift as one peak to higher temperatures.

$T_{m,s}$ and $T_{m,f}$ also show up in the heating run of samples that are first quenched and then annealed at higher temperatures[36]. A stepwise increase of the annealing temperature leads to a loss of the low-temperature annealing history: $T_{m,s}$ is equal to the location of the melting peak that originates from annealing directly at the higher temperature. This might be due to the fact that crystallites formed at low temperatures are not stable at higher temperatures and new crystallites are formed with a higher melting point.

The Avrami exponent n of the fast process is always 2, which corresponds to rod-like growth from sporadic nuclei[38]. On the other hand, values between 0.2 and 0.8 were calculated for the slow process[37]. An explanation for these low values might be that the crystal growth is restricted by the preceding crystallization: the incorporation of parts of the chains into crystals leads to the fixation of the local orientational order and the local positional order in the remaining nematic regions. Any further crystal growth has to occur via translational and reorientational motions of chains that are attached to other crystals. This decelerates the structure formation as crystallization continues. The slow process is, therefore, self-delaying. The value of the Avrami exponent does not change systematically whether the crystallization temperature is above $T_{c,f}$ or not. Although the existence of the quenched form hampers the growth of the annealed form, the kinetics of the fast and the slow transition process were found to be independent[39].

The presence of two crystallization processes is not restricted to the thermotropic LCPs based on HBA/HNA. Similar phenomena have been reported for a thermotropic LCP consisting of HBA, hydroquinone and carbonyl units[34], a thermotropic LCP based on phenylhydroquinone terephthalate and HBA[40] and for the thermotropic LCP PSHQ10[41]. According to the last authors this may indicate that the underlying mechanisms are independent of the chemical structure and may be an intrinsic property of thermotropic LCPs. The existence of a slow and fast crystallization process, however, is also reported for the random copolymers of polyethylene terephthalate-*co*-adipate, which are not liquid crystalline[30]. The random copolymer character may, therefore, be the origin of the two different crystallization processes.

The values of the enthalpy and entropy of fusion for the LCP copolyesters have been measured by Blundell (at least for the material which crystallized at $T_{m,f}$)[42,43]. These quantities are much lower for LCPs than those usually found for isotropic polymers. The low value of the enthalpy of fusion is related to the low molecular cohesion within the crystals, a result of the presence of many defects. Obviously, there is not such a great difference in the conformational and positional entropy as the nematic melt assumes its crystalline state, since only positional order is added to the already existing local orientational order. Both low values are the result of the stiffness of the molecular backbone.

Recrystallization of the melt

When heated to temperatures just above the crystalline/liquid transition temperature ($T_{m,f}$), the melt of HBA/HNA copolymers is not stable but shows a tendency to recrystallize, thereby forming crystallites with a higher melting point than the initial material. The recrystallization behaviour of HBA/HNA 73/27 (Vectra A900) at high temperatures has been studied extensively in dynamic rheological measurements[44–48] and in capillary flow[49].

This recrystallization originates from the presence of small unmolten crystallites in the melt. The exact melting point of these high-melting crystallites depends on the thermal history of the sample. It cannot be detected with d.s.c., but melting of these crystallites gives a minor second transition in the dynamic moduli, in addition to the normal melting transition. The presence of high-melting crystallites has a dramatic effect on the rheological response of the material. When the as-received LCP is heated to a temperature just above the melting point $T_{m,f}$ (which is the 'normal' melting point of the material), it melts into a nematic liquid only for a limited time since it recrystallizes gradually. This recrystallization is evident from the strong increase in the dynamic moduli or the pressure drop over the capillary as a function of time due to the formation and further growth of the crystals. The recrystallized material has a higher melting point than the initial one. When the material is heated to temperatures above the melting point of the crystallites and subsequently cooled to temperatures just above $T_{m,f}$, no further recrystallization occurs.

Recrystallization thus occurs in the temperature zone between $T_{m,f}$ and the melting point at the high-melting crystallites. In the experiments of Lin and Winter the latter was determined at 297°C. In this temperature zone the rheological behaviour depends on three factors:

- the holding temperature in the melt;
- the preheating temperature;
- the thermal history prior to melting.

In dynamic rheological measurements, recrystallization results in an increase of both G' and G''. The increase of G' is always faster than the increase of G''. A higher measuring temperature results in a decrease of the rate of recrystallization, and at temperatures above 300°C the phenomenon is no longer observed. Eliminating the high-melting crystallites by preheating to 320°C results in stable moduli for measuring temperatures between 280 and 300°C. For lower measuring temperatures the moduli increase with time, but with a rate that is only determined by the depth of supercooling (i.e. the difference between the preheating and the measuring temperature). After preheating between 300 and 320°C, the moduli at 290°C still increase, but slower than for the isothermal measurements. Preheating between 290 and 300°C, on the other hand, results in a greater amount of higher-melting crystallites and, consequently, a faster modulus growth.

Since the amount and melting temperature of the residual crystallites are determined by the thermal history of the sample, pre-annealing of the solid sample influences the course of the recrystallization. Pre-annealing at 240°C was found not to influence the moduli measured at 290°C. The modulus growth is faster after pre-annealing between 250 and 270°C. Pre-annealing above 270°C lowers the rate of recrystallization. This is probably due to the reduction of molecular mobility due to the large amount and size of unmolten crystallites. The time of pre-annealing also influences the measurements.

The recrystallization in the cone and plate geometry is slower than in the parallel plate geometry. The modulus growth is faster for samples that are sheared or elongated because the molecular mobility is then higher due to the flow-induced orientation[46]. The formation of crystallites under the action of shear is also found at temperatures as high as 320°C[50]. At this temperature the wide-angle X-ray scattering (WAXS) pattern of the melt of HBA/HNA 73/27 in the quiescent state consists of a strong diffuse maximum whereas shearing of the sample leads to the development of an additional sharp reflection.

In isothermal capillary flow between 280 and 300°C, recrystallization causes a steady increase of the pressure drop over the capillary. Preheating of the melt results in an initially stable pressure drop followed by a sudden increase. The location of this increase seems to be determined by the product of shear rate and measuring time, i.e. the amount of accumulated strain[47].

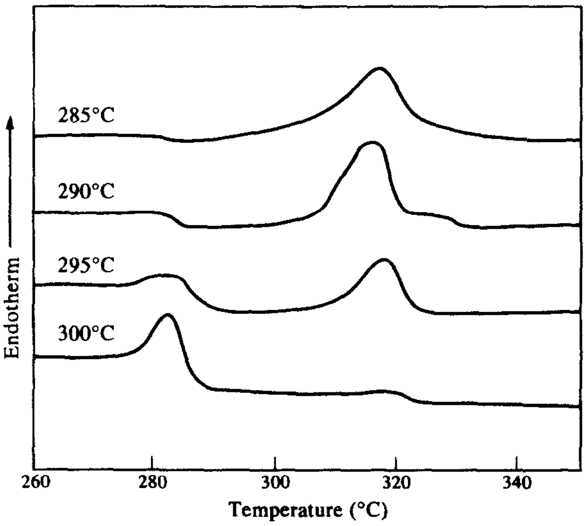

Figure 5 D.s.c. curves of samples which had been annealed at the indicated temperature for 200 min and then cooled. (Reprinted with permission from Lin and Winter[46])

The recrystallized samples of Lin and Winter[44] display two endothermic peaks in a d.s.c. heating run, as can be seen in *Figure 5* for samples recrystallized at different temperatures. One endotherm is located at about 280°C, which corresponds to the melting temperature of the fast crystallized material ($T_{m,f}$), and the other at about 315°C, which is the melting point of the recrystallized material ($T_{m,s}$). $T_{m,s}$ is slightly higher for the samples recrystallized at higher temperatures, due to the slower crystallization resulting in more perfect crystallites. The area under this peak shows a linear increase with time during the first 150 min of recrystallization.

The two endothermic peaks are also observed in the capillary flow experiments of Langelaan *et al.*[49] The shearing inside the barrel of the rheometer was found to promote the increase of the second melting endotherm $T_{m,s}$. Comparison for the same residence time (thus with different amounts of accumulated strain) showed that $T_{m,s}$ is located at higher temperatures for the material sheared at higher shear rates. For the same amount of accumulated strain, however, $T_{m,s}$ of the material extruded at low shear rates is located at higher temperatures than for the material extruded at higher shear rates. The melting behaviour of the extrudates was found not to be influenced much by the capillary length and the entrance angle.

The influence of the thermal history on the amount and melting temperature of the residual crystallites is also clear from the cone and plate experiments of Langelaan and Gotsis[51]. Samples made of as-received granules that were cold pressed into discs at room temperature were stable during the experiments at 300°C. The samples that were pressed into discs at 300°C and subsequently cooled, on the other hand, showed a considerable amount of recrystallization during the measurements at 300°C. Stability in the measurements of these hot-pressed samples was only realized at temperatures above 310°C.

In the experiments of Lin and Winter the modulus growth is thermo-reversible: after heating to 320°C the moduli drop to their initial values, and the behaviour resembles that of a fresh sample. WAXS measurements showed that the meridional maxima do not change during the recrystallization process, which indicates that the origin is more physical than chemical. From the presence of an additional equatorial WAXS reflection, Lin and Winter concluded that the high-melting crystals consist of periodic HBA sequences. This additional reflection is only observed after apparent or partial melting of the material. Annealing in the solid state results in better-ordered and larger high-melting crystallites, but no additional WAXS reflection is observed.

Lin and Winter explain the formation of the high-melting crystals assuming the ordering of matching HBA sequences that grow on the unmolten HBA sequences. Support for this hypothesis is given by the fact that the upper limit of the melting temperature of the crystallites is about 325°C. This temperature roughly coincides with the first transition in the HBA homopolymer, if one takes into account the disturbance in the chain due to the presence of HNA segments. The observed thermo-reversibility indicates that the aggregation of long HBA blocks is not the result of transesterification. Other evidence that matching of HBA sequences plays a role is found in similar measurements of a thermotropic LCP consisting of 60% HBA and 40% PET[52]. Also in this polymer a high-melting crystallite can be formed, accompanied by an additional WAXS reflection. The effects in HBA/PET, however, are less strong than in the HBA/HNA copolymer. This might be due to the lower amount of HBA units in the HBA/PET copolymer or to the lower compatibility of the PET units with the HBA units, which restricts the amount of cocrystallization. According to Biswas[53], however, the extra reflection Lin and Winter mention might be a 200 WAXD reflection which is associated with the lateral packing between the chains and does not relate to the structure along the chain axis. Thus, according to this author, from this reflection no conclusions can be drawn about the sequence distribution along the chain axis. The high-melting nuclei are most likely the small matched sequences expected in the assembly of chains with random sequences.

Schmack and Vogel[54] ascribe the increase of the dynamic moduli in HBA/HNA 72/25 to both chemical and physical changes in the sample. The changes on annealing in their experiments involved the formation of a melting peak at 345°C and a strong decrease of the solubility of the material in pentafluorophenol. Kachidza *et al.*[55] explain the formation of two melting endotherms by a segregation into two different compositions. This process takes place in the already existing crystalline regions and occurs via interchain transesterification. Heating to higher temperatures results in randomization and eliminates the modest bimodal compositional variation. This is clear from the presence of only one endotherm after these measurements. Interchain transesterification may lead to a change of sequence distribution at these high temperatures[26]. A drastic change in sequence distribution, however, is not in agreement with the observed thermo-reversibility of the formation of high-melting crystallites.

The exact nature of the high-melting crystal formation is still not understood. From statistical considerations it is unlikely that the higher melting crystallites consist solely of matched HBA units. It seems more likely that the high-melting crystallites are formed by matching of similar but non-periodic sequences of neighbouring chains.

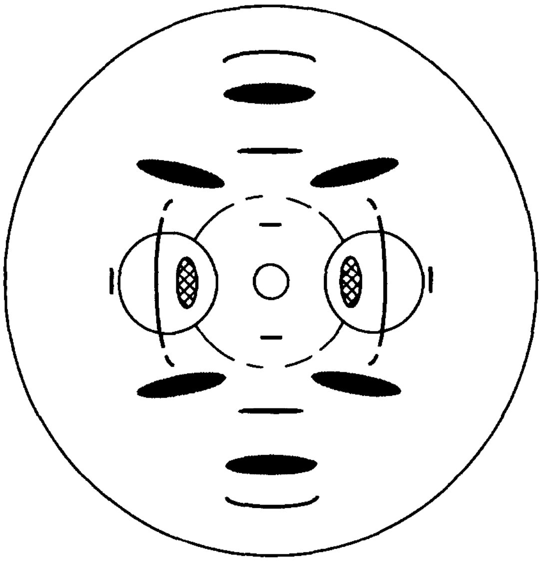

Figure 6 Schematic of the X-ray diagram of melt-drawn fibres of the HBA/HNA 75/25 copolymer. (Reprinted with permission from Gutierrez *et al.*[56])

THE CRYSTALLINE STRUCTURE IN HBA/HNA COPOLYMERS

This section describes the structure of the crystalline material that is formed during the crystallization of HBA/HNA copolymers. The order is described on a molecular level, then a description of the morphology of the crystallized material is given. Following this, the two models that have been proposed to describe the experimental observations of the solid state order in the HBA/HNA copolymers are discussed.

Crystalline structure

The crystallite structure that the HBA/HNA copolymers form depends on the crystallization conditions. An X-ray diagram of as-spun fibres of the 75/25 copolymer is shown in *Figure 6*. The as-spun fibres essentially consist of the fast crystallized form. The diffraction patterns of such fibres of the HBA/HNA copolymers can be described as follows:

- The compositions 75/25, 58/42 and 50/50 give three aperiodic maxima on the meridian; compositions with a higher amount of HNA give four maxima. The maxima on the meridian indicate a high degree of axial order. The position of the first maximum gradually shifts with copolymer composition from 6.36 Å (100% HBA) to 8.52 Å (100% HNA). The maximum at 2.1 Å (corresponding to the third-order reflection of HBA and the fourth-order reflection of HNA, respectively) does not shift on changing the composition. The fact that the meridional maxima are not at a fixed distance indicates that there is no fixed intrachain molecular repeat unit, which is the consequence of the random copolymer character.
- Two or three relatively sharp maxima on the equator and one off-equatorial maximum (between 3.1 and

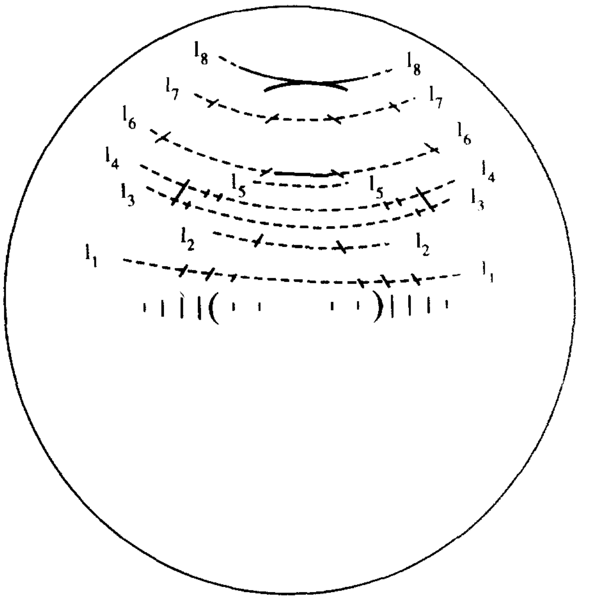

Figure 7 Schematic of the X-ray diagram of the HBA/HNA 75/25 copolymer after annealing for 30 days at 270°C. The layer lines are indicated by the dashed lines. (Reprinted with permission from Cheng[5])

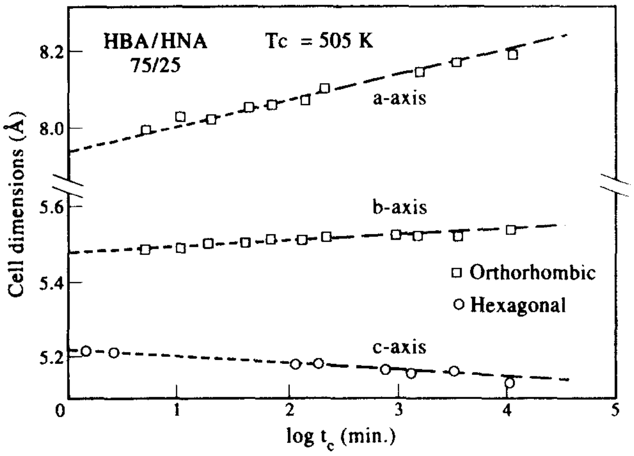

Figure 8 Size changes of the unit cells of HBA/HNA 75/25 as a function of annealing time at 232°C. The circular symbols represent the (pseudo-)hexagonal phase, and the square symbols the orthorhombic phase. (Reprinted with permission from Cheng *et al.*[39])

3.3 Å) are observed for all compositions. These maxima reveal the presence of some three-dimensional order and are arc-shaped due to the imperfect orientation. The non-Bragg scatter on the equator between $d = 3$ and 6 Å is the result of the irregular interchain packing of the chains.

- Diffuse scatter is observed above and below the equatorial maxima and on and near the meridian at $d = 2.3$ Å.

The fast crystallized form can be described with a (pseudo-)hexagonal orthorhombic unit cell. For HBA/HNA 75/25 the reflections can be indexed with the unit cell parameters $a = 9.2$ Å and $b = 5.2$ Å[26,57–59]. Cheng *et al.*[39] describe this structure with a hexagonal unit cell with $a = 5.22$ Å. For HBA/HNA 73/27 a (pseudo-hexagonal) unit cell is reported with $a = 8.94$ Å and $b = 5.16$ Å[60].

Solid state annealing of the samples at temperatures below $T_{m,f}$ leads to sharper diffraction peaks, apparently without affecting the aperiodicity along the chain direction. This is shown in *Figure 7*. The meridional maxima do not change much in position and remain aperiodic. The maximum at 2.1 Å shifts to a slightly higher d value, probably caused by a change in the conformation of the ester–aromatic linkage, leading to a more extended conformation of the chain[60]. The width of the layer lines, however, decreases, especially at the lower meridional values. This indicates that the bigger structural units such as phenylene units are involved[61]. Annealing affects mostly the diffraction pattern on and near the equator: some maxima shift to other angles and new maxima appear. Apparently the order perpendicular to the chain axis improves during annealing. The improvement of the intermolecular packing also leads to a change from a broad transition to a clear first-order transition in the d.s.c. thermograms.

Samples of HBA/HNA 75/25, crystallized from the nematic melt at 232°C, mainly consist of a (pseudo-) hexagonal phase with an a axis of 5.22 Å at short times[39]. With increasing crystallization time a mixture of two crystal packings is formed: a (pseudo-)hexagonal phase ($a = 5.15$ Å) and an orthorhombic phase ($a = 8.16$ Å and $b = 5.53$ Å). The existence of both packings is found to be independent of one another at this temperature. As can be seen in *Figure 8*, the a and b axes of the orthorhombic phase increase with increasing crystallization time, whereas the a axis of the hexagonal phase shrinks. The estimated amount of crystallinity at short times is about 8–10%; after 10 000 min the estimated value is 40%. The existence of both phases is also clear from the d.s.c. thermograms, in which two separate endotherms with independent crystallization kinetics are present.

Solid state annealing of HBA/HNA 73/27 at temperatures below 230°C does not lead to significant changes in the equatorial WAXD profile[60]. This is consistent with the observation in d.s.c. measurements that the melting endotherm at about 280°C remains unchanged on annealing at relatively low temperatures. Higher annealing temperatures induce a transition from the pseudo-hexagonal packing to an orthorhombic packing. The deviation from pseudo-hexagonal packing becomes larger with increasing annealing temperature, as is shown in *Figure 9* for samples annealed for 6 h. The orthorhombic unit cell parameters $a = 7.6$ Å and $b = 5.7$ Å are also reported by Cheng[57], Sun *et al.*[58] and Wilson *et al.*[59]. The annealed sample melts at 320°C, which also demonstrates the higher degree of order. The transition from (pseudo-)hexagonal to orthorhombic packing in HBA/HNA 75/25 is reported to occur at temperatures as low as 120°C[62]. Structural changes at this low temperature have not been observed elsewhere, but this might be caused by the slowness of the transformation process just above the glass transition temperature.

Higher-molecular-weight samples require a higher annealing temperature for the transformation from pseudo-hexagonal to orthorhombic packing[59]. The transformation is apparently controlled by some diffusive process which depends on the chain length. The structure formation is accompanied by significant internal strains, since nearby cells distort towards orthorhombic along different axes. It will, therefore, be more favourable for the new phase to grow by a

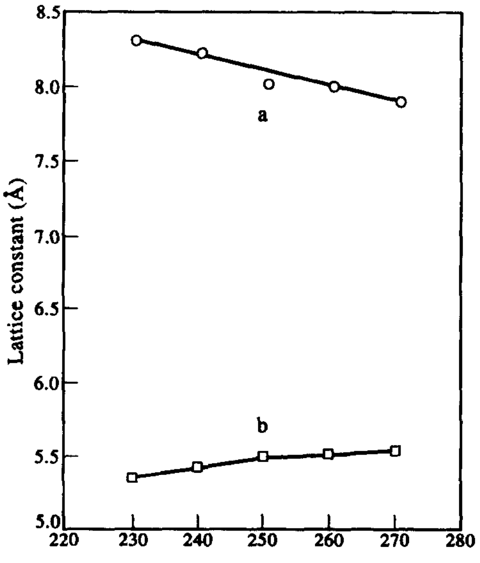

Figure 9 Effects of annealing temperature on the lattice constants of the HBA/HNA 73/27 copolymer. The annealing time was 6 h. (Reprinted with permission from Kaito *et al.*[5])

process of nucleation and growth. This leads to a similar orientation of the orthorhombic cells on the new lattice and, consequently, a reduction of the strains.

The reported values for the unit cell parameters of the annealed HBA/HNA samples agree very well with the low-temperature form of the HBA homopolymer. The reflections in the HBA/HNA copolymers, however, are much broader than the corresponding reflections in the HBA homopolymer, suggesting that the crystals in the copolyester have a lower degree of perfection and are smaller in crystallite dimensions than those of the HBA homopolymer. It also indicates that the orthorhombic crystals of annealed HBA/HNA do not consist of HBA blocks alone. The orthorhombic crystal structure developed by annealing can revert back to the (pseudo-) hexagonal structure on heating to temperatures above the melting point, followed by rapid crystallization.

Morphology of the crystallites

Morphological studies showed that the crystallites that are formed in HBA/HNA copolymers are slab-like lamellar structures, having larger lateral dimensions (normal to the chain axis) than longitudinal dimensions[63–72]. In the direction of the chains, henceforth called the thickness, the typical dimensions of the crystallites are 10–20 nm. In the direction perpendicular to the chains, henceforth called the length, the structures can be up to 300 nm.

A clear relationship between the composition of the copolymer and the crystallite dimensions was not found[71]: for all investigated compositions (75/25, 58/42 and 30/70) the crystallites had a thickness of 20 nm; the length of the crystallites for 75/25 and 58/42 was about 60 nm, and 40 nm for 30/70. The thickness of the crystallites of the 75/25 copolymer was found to depend little on the degree of polymerization, whereas the lateral dimension decreased with increasing molecular weight[68]. Shearing below the melting point leads to longer crystals. The radiation saturation dose (a measure for the perfectness of the crystallites) is higher for the copolymers with the higher melting point, which is attributed to the higher content of HNA. The radiation saturation dose decreases with increasing degree of polymerization, indicating a less perfect crystalline structure with increasing molecular weight.

The lamellar crystals that are formed in quenched samples of HBA/HNA 73/27 have a period of about 34 nm[73]. The thickness of the crystallites is about 10 nm, while the lateral size is approximately 100 nm. From the ratio of the lamellar period and the weight-average molecular length (which is about 200 nm[74]), it seems that the lamellar crystals are bridged by many tie chains, with the average chain having segments incorporated in several different lamellar crystals. The structure of the disclinations shows that the splay elastic constant in this material is greater than the bend elastic constant, indicating a degree of flexibility of the long extended molecules[74]. No evidence was found[74] in thermotropic LCPs for crystallization via a folded chain mechanism, as has been proposed by Kent and Geil[75,76] and Lin *et al.*[77].

Samples aligned in a magnetic field show a remarkable regular morphology, with the length and straightness of the crystallites being greater than for the non-aligned samples[29,78]. The periodicity of the aligned samples is 70 nm, which is about twice the value that is normally reported. This behaviour is possibly the result of chain segment segregation due to the presence of a field. The molecular weight was found not to influence the long period.

The influence of thermal history was investigated by Spontak and Windle[70] and Hanna *et al.*[63]. Crystallites were always observed in the samples, even after quenching. An increase of the number of crystallites was observed after annealing at 200 or 250°C for 30 min. Annealing for longer times resulted in a similar morphology, but with thicker crystallites. Higher annealing temperatures lead to an increase of the crystallite thickness and the spacing between the crystallites. A coarsening of the structure was observed after annealing at 290°C, with the formation of a small number of very big crystallites. The crystallinity calculated from the transmission electron micrographs is always about 20%, except for the samples annealed at 290°C or higher, for which the crystallinity is estimated at about 14%.

Similar results were obtained with small-angle X-ray scattering (SAXS) measurements of the crystalline structure of HBA/HNA copolymers[59]. No SAXS maxima were found in quenched samples, which indicates that the densities of the (pseudo-)hexagonal phase and the non-crystalline material are equal. Annealing of the samples led to the formation of maxima that correlated well with the development of the orthorhombic phase. The diffraction pattern that was observed after annealing is consistent with a structure of microfibrils within which crystalline and amorphous regions alternate along the fibre axis with a long period of about 30 nm. The lateral extent of the order was estimated to be at least 50 nm. The long period was found to increase with increasing annealing temperature, with hardly any influence of the molecular weight and the composition. The molecular weight and the composition were also found not to influence the degree of crystallinity, except for the 50/50 copolymer, for which significantly lower values were found. The crystallinity

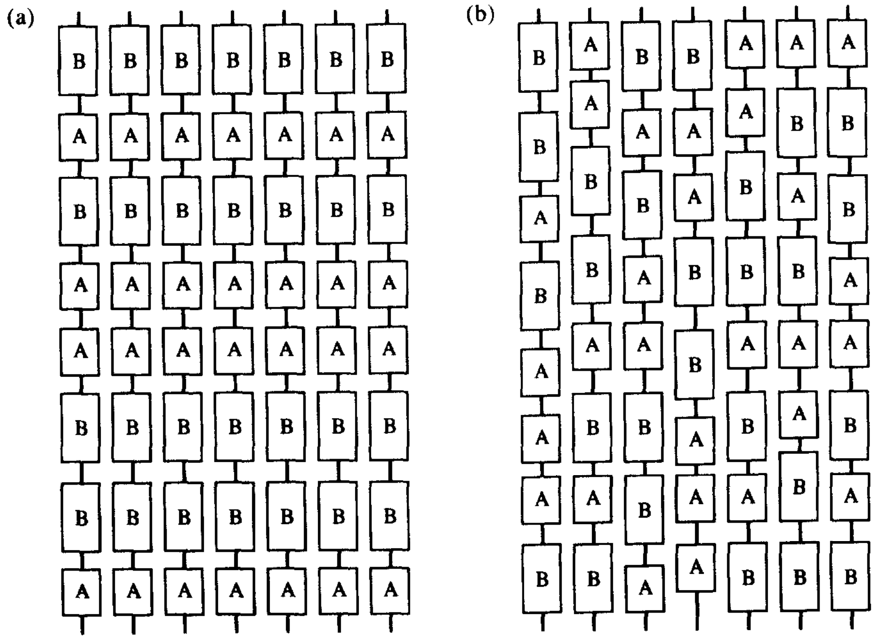

Figure 10 Schematic two-dimensional representation of the order in the solid state of HBA/HNA copolymers as described by (a) the PCL model and (b) the NPL model. A and B designate, respectively, the HBA and the HNA monomers. (Reprinted with permission from Biswas[53])

had a tendency to fall with increasing annealing temperature, which might, however, be the result of the quenching of the material after annealing.

Similar crystallites are observed in a thermotropic copolyesteramide which was annealed for 60 min at 250°C[79]. As for HBA/HNA, the crystallites are oriented with their thin axes parallel to the molecular axis and have a thickness of 15 nm and a length of 90 nm.

Models for the solid structure in HBA/HNA copolymers

Two models have been proposed to describe the experimental observations of the solid-state order in the HBA/HNA copolymers. Based on the non-periodicity of the meridional maxima and the morphological studies, Windle and co-workers have proposed a model in which ordered domains are formed by the lateral register of similar but non-periodic sequences of neighbouring chains. This is the non-periodic layer (NPL) model. A different model has been proposed by Biswas and Blackwell. In this paracrystalline lattice (PCL) model, ordered domains are formed by the presence of conformational correlations between adjacent monomers without explicit sequence matching. Schematic illustrations of both crystallites are shown in *Figure 10*.

The NPL model. To explain the results of the morphological studies, Windle and co-workers have proposed a model in which short identical sequences in random HBA/HNA chains match each other laterally, forming NPL crystals with a three-dimensional order[63,64,72]. From the presence of the non-periodic layer lines in the X-ray patterns it is clear that the random copolymer character is retained in the crystallites. The NPL model assumes that the crystallites consist of random sequences of both monomers, paired with identical sequences on neighbouring chains. The NPL model predicts the following[72]:

- The thickness of the crystallites (dimension parallel to the chain axis) is greater if the composition of the copolymer is closer to one of the homopolymers; the 50/50 composition gives the thinnest crystallites.
- The thickness of the crystallites is greater if the molecules can slide past one another to search for the best matching sequences. Hanna and Windle suggest that this mechanism of searching occurs during annealing.
- The amount of crystallinity increases with decreasing length of the molecules.

When compared to experimental data, the amount of crystallinity predicted by the NPL model is too low. Golombok *et al.*[80] found that the experimental results could be best described if the NPL packing occurs with a less strict correlation (allowing a variation of ±0.5 Å in the axial positions of the monomers). The NPL model has been further modified by taking into account the contribution to the intensity of the diffraction maxima of the polymer chains at the edge of the NPL crystallite, even though they are not strictly correlated to the neighbouring chains[63]. This transformation zone (the so-called 'fringe') increases the estimated amount of crystallinity.

The PCL model. In the PCL model of Biswas and Blackwell the development of three-dimensional crystallinity requires only that one monomer sequence on each chain lies about a register plane perpendicular to the chain axis; the lateral matching of identical copolymer sequences is not regarded as a necessary condition for forming aperiodic crystals.

In the first version of this model each monomer was replaced by a point[56,81,82]. The point model could accurately describe the position of the meridional WAXS maxima. The agreement in intensity between the model and the experiments was less, because the model did not account for the (differences in) scattering properties of the monomers itself. Modelling of the monomers on an atomic level gave a better agreement with the measured intensity[81,83]. In this atomic model the torsional angle between the carboxyl group and the aromatic planes was set to 30°, and the axis of the monomers was chosen parallel to the axis of the whole polymer.

The length over which linearity persists in the chain was calculated from the width of the maximum at 2.1 Å. This correlation length increased from nine to 13 monomers with increasing HBA content, indicating that the HNA monomers disturb the linear structure to some degree. The second assumption in the atomic model is, therefore, not completely realistic. The deviation from linearity is taken into account by Biswas and Blackwell[84].

For the description of the off-meridional maxima the correlation between the monomers perpendicular to the chain axis has to be taken into account. Blackwell *et al.*[81] and Chivers and Blackwell[85] have done so by describing two extremes in the conformation:

- completely random distribution of the torsional angles between the aromatic planes, leading to a completely extended chain with a cylindrical cross-section;
- completely fixed torsional angles between the aromatic planes.

Both these conformations could not describe the weak reflection that was observed on the layer line of 12–15 Å. To describe this reflection, a pseudo-dimer repeat unit was introduced, in which the aromatic planes have a fixed position with respect to each other, and the carbonyl groups point in opposite directions from the chain[86]. Both dimer models described the observed reflections very well; the observed intensities of the off-meridional maxima were described best with the model with the random torsional angles.

The influence of the three-dimensional packing of the chains is accounted for by the introduction of the 'plane start model'[87,88]. In this model there has to be a plane within a crystallite in which all polymers have a carbonyl group. This condition, however, was shown not to be a strict one: the best agreement with the experimental intensities was observed when 68% of the carbonyl groups were located within a distance of 2 Å of this common plane.

In the final, most likely structure, the aromatic planes within one dimer are rotated by 60°. There is rotational correlation perpendicular to the chain axis between the different aromatic planes of the neighbouring chains, but not between the subsequent dimers in the chains. This results in planes perpendicular to the chains, with which the rotation angles of the phenylene groups are correlated, but without correlation between the subsequent planes in the chain. This situation, however, is difficult to imagine, since there will be no complete conformational freedom for successive dimers if they are also required to form layers with their axes on the same lattice. In a recent publication, using molecular mechanics energy minimalization, Hofmann *et al.*[89] confirmed that segregation of identical sequences is not necessary to achieve three-dimensional ordering in HBA/HNA copolymers.

Predictions of the two models. A comparison of both models with respect to the experimental results has been made by Biswas[53]. The NPL model considered by Biswas, however, is the first version, without the previously described modifications regarding less strict correlations and the fringe zone.

When compared to experimental data, the amount of crystallinity predicted by the NPL model is too low, even when the transition zone (fringe) is taken into account. The PCL model gives better agreement. Experimental determination of the amount of crystallinity in HBA/HNA copolymers, however, is not straightforward since the persistence of the nematic order in thermotropic LCPs complicates the collection of background scattering profiles from truly amorphous samples. Also, Yoon *et al.*[13] indicate that the values for the crystallinity calculated from scattering data are in general too high because the order in random copolyesters must not be considered truly crystalline.

The improvement of the perfection and size of the ordered domains with heat treatment below the melting transition is difficult to describe using the NPL model. For a change of structure the NPL model requires the chains to slide past one another ('searching'), but molecular motions are restricted in the solid state. In the PCL model the growth of ordered domains is achieved by better positional and orientational correlations over larger volumes without significant chain displacements.

In spectroscopic studies of HBA/HNA copolymers, a negligible influence of annealing on the low-temperature relaxations is found, despite the changes which occur in the diffraction and calorimetric data (e.g. see Wissbrun and Yoon[90]). A detailed dielectric study on the crystallization of HBA/HNA 73/27[91] showed that the dipole mobility does not essentially change upon crystallization or melting. This may be caused by the relatively low amount of crystallinity in the material, but the change in dipole mobility may also be masked by the thermally induced dipole movements at these high temperatures. The interfacial polarization, however, was found to increase during crystallization. This indicates that during the crystallization a phase is formed with different dielectric properties than the melt. At the interface between the two phases accumulation of charges takes place, which gives rise to the increasing interfacial polarization. The dielectric studies thus show that the crystalline phase that is formed in HBA/HNA copolymers is different from the melt phase, but melting of this crystalline phase is not accompanied by an observable increase of the dipole mobility. It is, therefore, not possible to draw conclusions from these measurements that favour one of the two models.

The experimentally observed crystallites are slab-like lamellar structures, having larger lateral dimensions (normal to the chain axis) than longitudinal dimensions. This crystallite shape is predicted by both models since order is expected to develop faster in the lateral direction than along the chain axis. Both models also assume the occurrence of cocrystallization between HBA and HNA residues in the random copolymer, which is in agreement with the experimental observations and the close resemblance between the high-temperature structures of PHBA and PHNA. The meridional data suggest that cocrystallization is compatible with the placement of dissimilar units both axially and laterally, as in the PCL model, and not limited only to the axial direction, as in the NPL model.

So far, it has not been possible to fully describe the

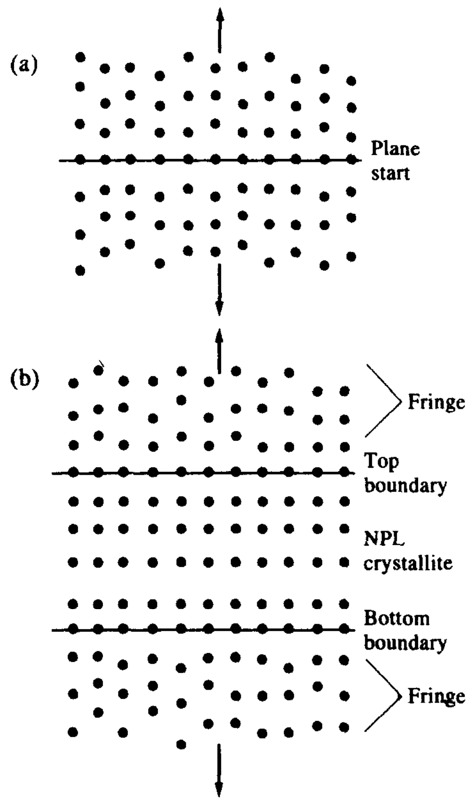

Figure 11 (a) Schematic representation of the PCL model of copolymer crystallinity. The ester groups on the HBA and HNA units are represented as dots. (b) Schematic representation of an NPL crystallite showing the fully ordered core and partially ordered fringe regions. (Reprinted with permission from Hanna *et al.*[63])

experimental X-ray patterns with the NPL model, but the morphology of the crystallites that is predicted is in good agreement with the experimental results. Calculations using the PCL model gave a good agreement with the observed scattering data, but with a physical picture that is not very plausible. Probably the best of both models has to be taken. In fact, the introduction of a fringe zone on the NPL crystallites can be considered as a first step. In this model a short segment of matched sequences provides a core for the PCL crystal. Dependent on the number of matched sequences the plane start (one row) or an NPL crystallite (more than one row) is the core. This is shown in *Figure 11*.

SOME CONCLUSIONS ON THE CRYSTALLIZATION BEHAVIOUR OF HBA/HNA COPOLYMERS

Being copolymers and having relatively rigid chains, the HBA/HNA copolymers show complicated crystallization behaviour and crystalline structures. Despite the several contradictory and unexplained observations that were mentioned in the previous sections, a number of features in the crystallization behaviour of these materials can be identified. In this section we try to summarize and discuss these features.

Perhaps the most important characteristic of the crystallization of the copolyesters is that it may occur through two distinct processes: fast and slow. These processes result in different crystalline structures and different transition (melting) temperatures.

The fast crystallization process occurs when the nematic melt is cooled down rapidly. Fast crystallization of the HBA-rich HBA/HNA copolymers leads to the formation of a pseudo-hexagonal orthorhombic unit cell. The dimensions of this cell are similar to the ones of the HBA homopolymer at temperatures above 340°C. This high-temperature form is stable at lower temperatures as a consequence of the disorder caused by the presence of the comonomer HNA units. The cross-sectional area of the unit cells clearly indicates that a certain degree of cocrystallization is present in the crystals of the HBA/HNA copolymer formed by rapid cooling[59]. Cocrystallization is expected from the agreement of the high temperature forms of the unit cell of the HBA and HNA homopolymers. The cocrystallization, however, is not perfect as is demonstrated by the eutectic-like phase diagram (see *Figure 2*). Dielectric measurements[14] confirmed that the local conformation and rotations of the HBA units in the HBA/HNA copolymers are the same as in the high-temperature form of the HBA homopolymer. The melting point of the pseudo-hexagonal phase is about 280°C for the HBA/HNA 73/27 copolymer. It is independent of the crystallization conditions. The low heat of transition and entropy reveal that the chain packing is far from perfect, and chain conformations do not change much during the fast transition from nematic melt to crystal. This is also clear from the absence of SAXS maxima in the quenched material.

The slow crystallization process of HBA/HNA copolymers occurs when the nematic melt is cooled down slowly or in isothermal crystallization experiments. The crystalline phase that results from the slow crystallization process can be described with an orthorhombic unit cell. The value of the *a* axis of the unit cell decreases with increasing annealing temperature, while the value of the *b* axis increases. The orthorhombic unit cell that is found after annealing of the copolymers resembles the low-temperature form of the HBA homopolymer. The melting point of the slowly crystallized material is highly dependent on the crystallization conditions. It shifts to higher temperatures with increasing crystallization temperature and time.

When samples are first quenched and subsequently annealed at higher temperatures, a mixture of the (quenched) pseudo-hexagonal and the (annealed) orthorhombic phase is observed. The existence of both packings is independent of one another. The kinetics of the fast and the slow transition process are also independent, although the existence of the quenched form hampers the growth of the annealed form. Because they are less ordered, the fast-grown crystallites cannot act as nuclei for the more ordered orthorhombic form that originates from the slow crystallization process. This explains the independence of the two crystallization processes. The higher melting point of the less ordered crystallites at short times is the result of the lower entropy of transition. Since the heat of transition of the annealed form increases with increasing annealing time, the melting temperature of this form increases and, eventually, becomes equal to that of the quenched form. At this point the quenched form is transformed too, which leads to a combined shift of both melting peaks to higher temperatures.

The slow crystallization process is also responsible for the recrystallization of the nematic melt at high temperatures. When the HBA/HNA copolymers are heated to temperatures above the melting point of the fast-formed crystallites, residual crystallites with a higher melting point can grow further in the nematic melt and cause the melt to eventually solidify again. From the nature of the WAXS reflections it is clear that the crystallites in HBA/HNA copolymers do not consist of segregated HBA blocks alone. The high-melting nuclei are most likely the small matched sequences expected in the assembly of chains with random sequences.

The presence of two crystallization processes is not restricted to the liquid crystalline polymers. Similar crystallization phenomena have been reported for the (flexible) random copolymers of polyethylene terephthalate-*co*-adipate[30]. Eutectic-like melting diagrams as in *Figure 2* have also been observed for several other random copolymers, indicating that highly defective metastable crystals can be formed. On rapid cooling the major constituent crystallizes, but this crystallization is frustrated by the presence of the non-crystallizable units. The low melting temperature of these highly imperfect crystals can be shifted to higher values by annealing in the vicinity of the melting point or by slow crystallization. Slow crystallization leads to an increase in the amount of crystallized material since the imperfections can be built in into the crystals. This phenomenon might be explained in terms of the existence of two distinct crystallization processes. The structural heterogeneity may also be the origin of the very broad glass transition of the random HBA/HNA copolymers. The anisotropic nature of the glass and the presence of crystallinity cannot be the only reason for the broadness of the glass transition.

A possible mechanism for the structure formation in the HBA/HNA copolymers is the following[60]. In the nematic melt the aromatic planes are randomly distributed along the chain axis. When the polymer is quenched the conformational disorder of the molecular chains is frozen. Although a lateral interchain correlation of aromatic planes exists, the aromatic planes of one molecular chain are less correlated along the chain axis. This leads to a more or less circular cross section of the chains, which pack on a (pseudo-)hexagonal lattice. This packing is facilitated by a certain degree of cocrystallization resulting from the similarity of the high-temperature forms of the HBA and HNA homopolymers. On annealing, the disordered conformation tends to be transformed into an energetically stable form having twofold symmetry, similar to what has been found in the molecular chains of the HBA homopolymer. In this form, the HNA units are built in as imperfections. The increased conformational order and the connected changes in packing result in an orthorhombic unit cell. In principle this structure improvement may start to take place at temperatures just above the glass transition. This might explain the observation of Flores *et al.*[62] that the transition from (pseudo-)hexagonal to orthorhombic already starts at 120°C.

The crystallites of HBA/HNA copolymers do not consist of segregated HBA blocks alone. Two models have been proposed to describe the solid state structure of these copolymers. The NPL model agrees very well with the morphological studies, but cannot describe the WAXS diffractograms. The PCL model shows good agreement with the experimental diffractograms, but the molecular picture behind the model is not very plausible. A modification of the PCL model using ideas from the NPL model seems to give a more realistic physical image of the crystalline structures of the random liquid crystal copolyesters.

REFERENCES

1 McArdle, C. B. 'Side Chain Liquid Crystal Polymers', Blackie, Glasgow, 1989
2 Huynh-Ba, G. and Cluff, E. F. *Polym. Sci. Technol.* 1985, **28,** 217
3 Keller, A. and Ungar, G. *J. Appl. Polym. Sci.* 1991, **42,** 1683
4 Mandelkern, L. 'Crystallization of Polymers', McGraw-Hill, New York, 1964
5 Butzbach, G. D., Wendorff, J. H. and Zimmermann, H. J. *Makromol. Chem., Rapid Commun.* 1985, **6,** 821
6 Ambrosino, S. and Navard, P. *Ann. Chim. Fr.* 1990, **15,** 275
7 Wunderlich, B. 'Macromolecular Physics', Vol. 1, Academic Press, San Diego, 1973
8 Lieser, G. *J. Polym. Sci., Polym. Phys. Ed.* 1983, **21,** 1611
9 Blackwell, J., Lieser, G. and Gutierrez, G. A. *Macromolecules* 1983, **16,** 1418
10 Rutledge, G. C. and Ward, I. M. *J. Polym. Sci., Polym. Phys. Ed.* 1993, **31,** 513
11 Hanna, S. and Windle, A. H. *Polym. Commun.* 1988, **29,** 236
12 Lyerla, J. R., Economy, J., Maresch, G. G., Mühlebach, A., Yannoni, C. S. and Fyfe, C. A. in 'Liquid Crystalline Polymers' (Eds. R. A. Weiss and C. K. Ober), ACS Symposium Series 435, American Chemical Society, Washington, DC, 1990, p. 359
13 Yoon, D. Y., Machiocchi, N., Depero, L. E., Viney, C. and Parrish, W. *Macromolecules* 1990, **23,** 1793
14 Kalika, D. S. and Yoon, D. Y. *Macromolecules* 1991, **24,** 3404
15 Coulter, P. D., Hanna, S. and Windle, A. H. *Liq. Cryst.* 1989, **5,** 1603
16 Economy, J., Storm, R. S., Matkovich, V. I., Cottis, S. G. and Nowak, B. E. *J. Polym. Sci., Polym. Chem. Ed.* 1976, **14,** 2207
17 Cao, M. Y. and Wunderlich, B. *J. Polym. Sci., Polym. Phys. Ed.* 1985, **23,** 521
18 Economy, J., Volksen, W., Viney, C., Geiss, R., Siemens, R. and Karis, T. *Macromolecules* 1988, **21,** 2777
19 Mühlebach, A., Lyerla, J. and Economy, J. *Macromolecules* 1989, **22,** 3741
20 Liu, J. and Geil, P. H. *J. Macromol. Sci.-Phys.* 1992, **B31,** 163
21 Liu, J. and Geil, P. H. *Polymer* 1993, **34,** 1366
22 Hanna, S. and Windle, A. H. *Polymer* 1992, **33,** 2825
23 Iannelli, P., Yoon, D. Y. and Parrish, W. *Macromolecules* 1994, **27,** 3295
24 Schwarz, G. and Kricheldorf, H. R. *Macromolecules* 1991, **24,** 2829
25 Mühlebach, A., Johnson, R. D., Lyerla, J. and Economy, J. *Macromolecules* 1988, **21,** 3115
26 Economy, J., Johnson, R. D., Lyerla, J. R. and Mühlebach, A. in 'Liquid Crystalline Polymers' (Eds. R. A. Weiss and C. K. Ober), ACS Symposium Series 435, American Chemical Society, Washington, DC, 1990, p. 129
27 Yoon, H. N. *Colloid Polym. Sci.* 1990, **268,** 230
28 Yoon, H. N., Charbonneau, L. F. and Calundann, G. W. *Adv. Mater.* 1992, **4,** 206
29 Anwer, A. and Windle, A. H. *Polymer* 1993, **34,** 3347
30 Wunderlich, B. 'Macromolecular Physics', Vol. 3, Academic Press, San Diego, 1980
31 Wunderlich, B. 'Macromolecular Physics', Vol. 2, Academic Press, San Diego, 1976
32 Goldbeck-Wood, G. *Polymer* 1992, **33,** 778
33 Sauer, B. B., Beckerbauer, R. and Wang, L. *J. Polym. Sci., Polym. Phys. Ed.* **31,** 1861, 1993
34 Sauer, T. H., Zimmermann, H. J. and Wendorff, J. H. *Colloid Polym. Sci.* 1987, **265,** 210
35 Yonetake, K., Sagiya, T., Koyama, K. and Masuko, T. *Macromolecules* 1992, **25,** 1009
36 Butzbach, G. D., Wendorff, J. H. and Zimmermann, H. J. *Polymer* 1986, **27,** 1337
37 Cheng, S. Z. D. *Macromolecules* 1988, **21,** 2475

38 Kamal, M. R., Khennache, O. and Goyal, S. K. *Polym. Eng. Sci.* 1989, **29,** 1089

39 Cheng, S. Z. D., Janimak, J. J., Zhang, A. and Zhou, Z. *Macromolecules* 1989, **22,** 4240

40 Johnson, R. L. and Cheng, S. Z. D. *Macromolecules* 1993, **26,** 94

41 Kim, S. S. and Han, C. D. *Macromolecules* 1993, **26,** 3176

42 Blundell, D. J. *Polymer* 1982, **23,** 359

43 Blundell, D. J. *et al. High Perf. Polym.* 1989 **1,** 97

44 Lin, Y. G., Winter, H. H. and Lieser, G. *Liq. Cryst.* 1988, **3,** 519

45 Lin, Y. G. and Winter, H. H. *Liq. Cryst.* 1988, **3,** 593

46 Lin, Y. G. and Winter, H. H. *Macromolecules* 1988, **21,** 2439

47 Lin, Y. G. and Winter, H. H. *Macromolecules* 1991, **24,** 2877

48 Winter, H. H. and Lin, Y. G. *Polym. Prepr.* 1989, **30,** 524

49 Langelaan, H. C. PhD thesis, Delft University of Technology, 1995

50 Nicholson, T. M., Mackley, M. R. and Windle, A. H. *Polymer* 1992, **33,** 434

51 Langelaan, H. C. and Gotsis, A. D. *J. Rheol.* 1996, **40,** 107

52 Huang, K., Lin, Y. G. and Winter, H. H. *Polymer* 1992, **33,** 4533

53 Biswas, A. *J. Polym. Sci., Polym. Phys. Ed.* 1992, **30,** 1375

54 Schmack, G. and Vogel, R. *Kunststoffe* 1992, **82,** 1011

55 Kachidza, J., Serpe, G. and Economy, J. *Makromol. Chem., Macromol. Symp.* 1992, **53,** 65

56 Gutierrez, G. A., Chivers, R. A., Blackwell, J., Stamatoff, J. B. and Yoon, H. *Polymer* 1983, **24,** 937

57 Cheng, H. M. *Dissertation*, Case Western Reserve University, 1990

58 Sun, Z., Cheng, H. M. and Blackwell, J. *Macromolecules* 1991, **24,** 4162

59 Wilson, D. J., Vonk, C. G. and Windle, A. H. *Polymer* 1993, **34,** 227

60 Kaito, A., Kyotani, M. and Nakayama, K. *Macromolecules* 1990, **23,** 1035

61 Stamatoff, J. B. *Mol. Cryst. Liq. Cryst.* 1984, **110,** 75

62 Flores, A., Ania, F., Baltá Calleja, F. J. and Ward, I. M. *Polymer* 1993, **34,** 2915

63 Hanna, S., Lemmon, T., Spontak, R. J. and Windle, A. H. *Polymer* 1992, **33,** 3

64 Windle, A. H., Viney, C., Golombok, R., Donald, A. M. and Mitchell, G. R. *Faraday Discuss. Chem. Soc.* 1985, **79,** 55

65 Donald, A. M. and Windle, A. H. *J. Mater. Sci. Lett.* 1985, **4,** 58

66 Viney, C., Donald, A. M. and Windle, A. H. *Polymer* 1985, **26,** 870

67 Lemmon, T. J., Hanna, S. and Windle, A. H. *Polym. Commun.* 1989, **30,** 2

68 Spontak, R. J. *J. Polym. Sci., Polym. Lett.* 1990, **28,** 271

69 Anwer, A., Spontak, R. J. and Windle, A. H. *J. Mater. Sci. Lett.* 1990, **9,** 935

70 Spontak, R. J. and Windle, A. H. *J. Mater. Sci.* 1990, **25,** 2727

71 Spontak, R. J. and Windle, A. H. *J. Polym. Sci., Polym. Phys. Ed.* 1992, **30,** 61

72 Hanna, S. and Windle, A. H. *Polymer* 1988, **29,** 207

73 Hudson, S. D. and Lovinger, A. J. *Polymer* 1993, **34,** 1123

74 Krömer, H., Kuhn, R., Pielartzik, H., Siebke, W., Eckhardt, V. and Schmidt, M. *Macromolecules* 1991, **24,** 1950

75 Kent, S. L. and Geil, P. H. *J. Polym. Sci., Polym. Phys. Ed.* 1992, **30,** 1489

76 Kent, S. L. and Geil, P. H. *J. Macromol. Sci.-Phys.* 1992, **B31,** 413

77 Lin, D., Dean, D. and Geil, P. H. *J. Polym. Sci., Polym. Phys. Ed.* 1992, **30,** 1483

78 Anwer, A. and Windle, A. H. *Polymer* 1991, **32,** 103

79 Spontak, R. J. and Windle, A. H. *Polymer* 1990, **31,** 1395

80 Golombok, R., Hanna, S. and Windle, A. H. *Mol. Cryst. Liq. Cryst.* 1988, **155,** 281

81 Blackwell, J., Biswas, A., Gutierrez, G. A. and Chivers, R. A. *Faraday Discuss. Chem. Soc.* 1985, **79,** 73

82 Mitchell, G. R. and Windle, A. H. *Colloid Polym. Sci.* 1985, **263,** 230

83 Chviers, R. A., Blackwell, J. and Gutierrez, G. Z. *Polymer* 1984, **25,** 435

84 Biswas, A. and Blackwell, J. *Macromolecules* 1987, **20,** 2997

85 Chivers, R. A. and Blackwell, J. *Polymer* 1985, **26,** 997

86 Biswas, A. and Blackwell, J. *Macromolecules* 1988, **21,** 3146

87 Biswas, A. and Blackwell, J. *Macromolecules* 1988, **21,** 3152

88 Biswas, A. and Blackwell, J. *Macromolecules* 1988, **21,** 3158

89 Hofmann, D., Schneider, A. I. and Blackwell, J. *Polymer* 1994, **35,** 5603

90 Wissbrun, K. F. and Yoon, H. N. *Polymer* 1989, **30,** 2193

91 Willems, C. R. J. PhD thesis, Delft University of Technology, 1995