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Transformation of banded structures on annealing thin films of thermotropic liquid crystalline polymers

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The structures of a range of thermotropic copolyesters based on hydroxybenzoic and hydroxynaphthalic acids are studied using transmission electron microscopy. Starting from the banded structure characteristic of as-sheared specimens, annealing of thin films either upon a rocksalt substrate or between two rocksalt crystals leads to a rapid microstructural reorganization. The bands, initially transverse to the shear direction, are replaced by domains of uniform molecular orientation elongated along the shear direction. Simultaneously, a substantial our-of-plane tilt of the molecules occurs, which for any domain is coupled with the degree of in-plane misorientation about the shear axis. Such orientation coupling may be associated with the need for splay–splay compensation to minimize energy. For longer anneals on specimens of lower molecular weight, distinctive boundaries separate the domains of alternating tilt "up" and "down" (relative to the specimen plane). The boundaries which appear as dark "veins" in bright-field images, are narrow regions of highly developed molecular tilt in which homeotropy is approached. The tendency towards overall homeotropy can be linked to the presence of constraining surfaces, and is absent for specimens annealed without a substrate.

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1. Introduction

Small molecule liquid crystals (SMLCs) exhibiting nematic phases have been extensively studied, and their characteristic textures are well documented (see, for example, reviews in [1–3]). It has long been recognized that the configurations adopted by such molecules are radically affected by the constraining surfaces. Depending on the nature of the interaction of the molecule with such a surface, two limiting cases of alignment can be identified, homeotropic and homogeneous (or planar). In the former, achieved for instance, by cleaning a glass surface with detergent, the molecules lie normal to the surface. The latter alignment corresponds to molecules lying parallel to the surface and may be achieved by rubbing the constraining surfaces. In this way the molecules are induced to lie along the rubbing direction, probably due to grooves being formed in the surface [4, 5]. Such surface-controlled alignment has played an important part in the development of liquid crystal devices. More generally, "conical anchoring" may occur, in which the molecules are inclined at some fixed angle to the surfaces, but all directions are equally probable. In this case the anchoring is degenerate.

The newly developed thermotropic liquid crystal polymers (LCPs) show many of the characteristics of their small molecule counterparts. However, they differ in the crucial respect that their long molecular length means a dramatic decrease in chain end density. A shortage of chain ends puts a severe restriction on the possible molecular arrangements; in particular splay deformations will become increasingly unfavourable as the molecular weight increases [6, 7]. The limiting case of LCPs of infinite molecular weight has been discussed by Meyer [8]: with no chain ends, and at constant density, splay is strictly impossible without the presence of hairpin defects or compensation in

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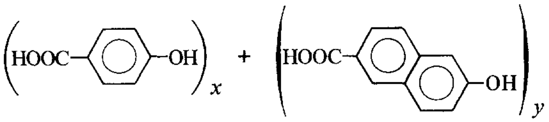
the third dimension. The absence of chain ends also necessitates homogeneous orientation at surfaces, since perpendicular alignment requires chain ends to condense at the surface. In practice, the finite length of polymer molecules will relax these constraints. but nevertheless substantial differences in low energy configurations are to be expected between LCPs and SMLCs.

For LCPs, one particular microstructure which has recently been identified and characterized by both polarized light and transmission electron microscopy (TEM) is the "banded structure". It is formed in sheared LCP melts [9–13] or lyotropic solutions [14, 15] as well as in spun fibres [16–19]. The structure, which clearly can form under a range of conditions, appears to be relatively insensitive to surfaces, forming both upon glass and freshly cleaved rocksalt as well as during fibre spinning where no substrate is involved [9]. The banding, which is perpendicular to the shear axis, is the result of the coordinated variation in the angle between the local optical extinction axes and the shear direction [9, 10]. Detailed analysis of the structure by TEM has shown that the molecules follow a serpentine path about the shear direction [22].

This paper describes the transformation of the banded structure when thin-film TEM specimens of thermotropic random copolyesters are annealed. Surface effects are examined by comparing specimens annealed on one or between two rocksalt surfaces with others annealed without a substrate. The importance of the chain length in influencing the structures obtained is also considered.

2. Experimental details

The random copolyesters used in this study were made from the following units:



Parameters for the polymers examined are given in Table I. The polymers are designated B–N ($x:y$), and T_m is the softening point at which the mesophase becomes mobile. The intrinsic viscosity (IV) is a measure of the molecular weight, but the polydispersity is not known. The material with an $x:y$ ratio of 70:30 was supplied by ICI (Plastics and Petrochemicals Division), the other three were made and characterized by Celanese Corporation, New Jersey, USA.

Specimens containing the banded structure were prepared as previously described [11] by shearing, with a glass slide, a small amount of the polymer on to a piece of rocksalt held at temperature T_s, (typically $> T_m$). Three different modes of annealing were used:

(a) the specimen and rocksalt substrate were held at T_s for up to 10 min to give a specimen annealed with one constraining surface. The specimen was then quenched on a metal block, the rocksalt dissolved in distilled water and the specimen picked up on a copper grid;

(b) immediately after shearing, a second piece of rocksalt was placed on top of the specimen, and the rocksalt–polymer–rocksalt sandwich held for times of up to 10 min at T_s to give a two-substrate annealed specimen. It was then quenched, and the rocksalt dissolved as in (a);

(c) the specimen and substrate were quenched on a metal block immediately after shearing. The rocksalt was then dissolved in a distilled water bath from which the specimen was picked up on a copper grid. This grid plus specimen was then annealed for times of up to 10 min at T_s. This method produces specimens annealed in contact with air at both surfaces, i.e. without a substrate.

All three types of specimens were carbon coated, and examined in a Philips 300 electron microscope operating at 100 keV and fitted with a single tilt holder with a range of ± 42°. It should be noted that no particular direction of shearing relative to the crystallographic axes of the rocksalt substrate was used. Although the significance of the anisotropy of rocksalt substrates has been recognized for SMLCs [19], there were no indications of any similar effect in these experiments on LCPs.

3. Results

The apparance of the specimens changes rapidly upon annealing. Two stages in the microstructural reorganization can be identified and these will be discussed separately. However, it must be recognized that, as implied by the names we shall use for the structures characteristic of the two stages of annealing, namely "domains" and "developed domains", the change is gradual with no abrupt transition between the stages. Most results refer to one-substrate specimens; differences due to the presence of no substrate or two substrates are discussed subsequently.

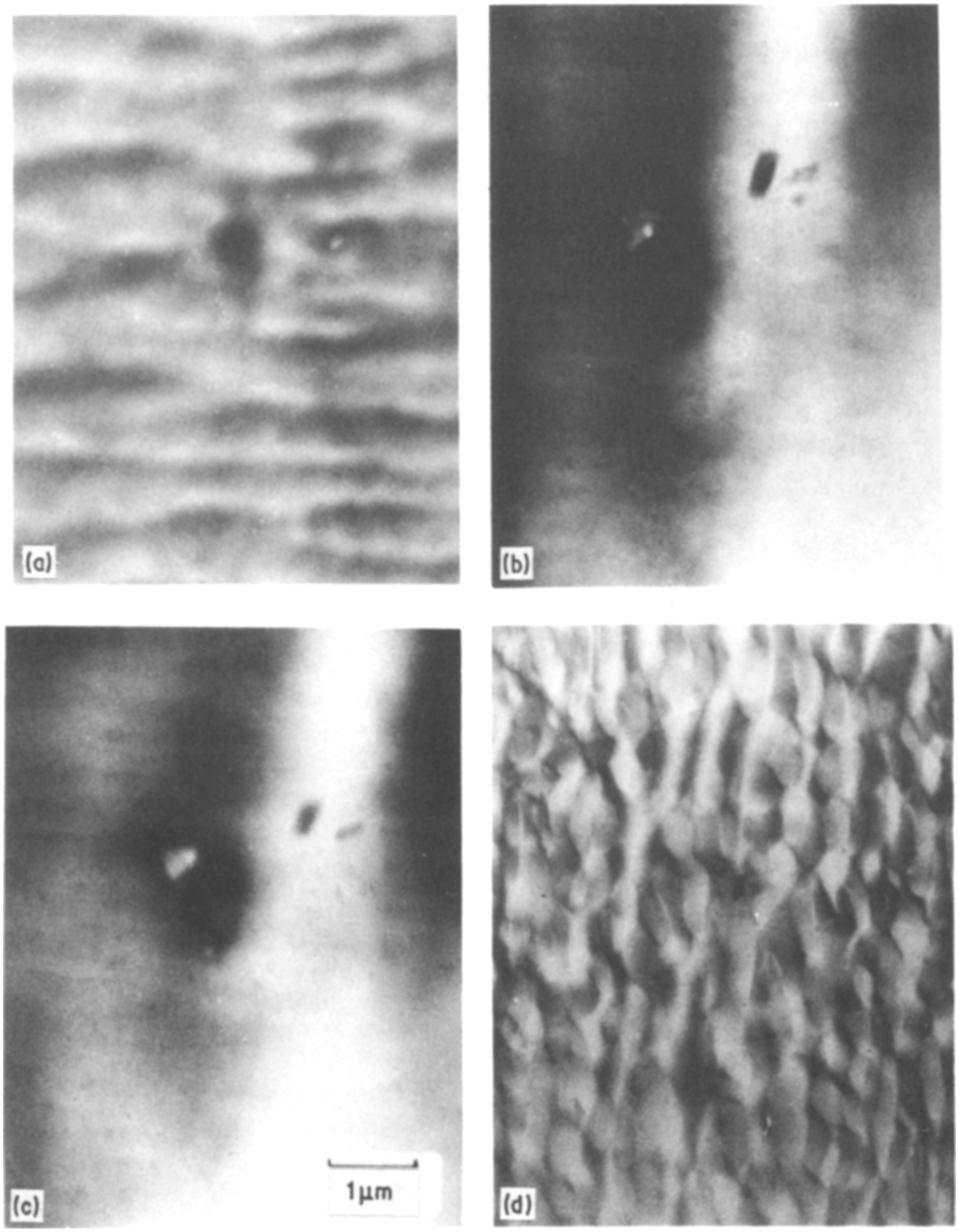


Figure 1 A series of micrographs of a given area of an unannealed sample (a, b, c) compared with a similar series (d, e, f) of a sample annealed for 5 sec at 300° C. (a), (b) Dark-field images formed in one wing of the equatorial reflection; (b), (e) bright-field images, and (c), (f) again bright-field but tilted 42° about the horizontal axis. The shear direction is vertical.

B–N (70:30), the polymer used in previous work [11, 20–22] has been most extensively studied. More restricted investigations on similar polymers of different composition, which have been characterized in terms of T_m and *IV* [23], indicate that the same basic trends occur, although at markedly different rates.

3.1. Domains

It is well documented that specimens which have been sheared and then cooled without delay, show bands lying perpendicular to the shear direction (e.g. [9–11]). The bands are apparent in dark-field TEM as in Fig. 1a (a dark-field image formed in one wing of the equatorial

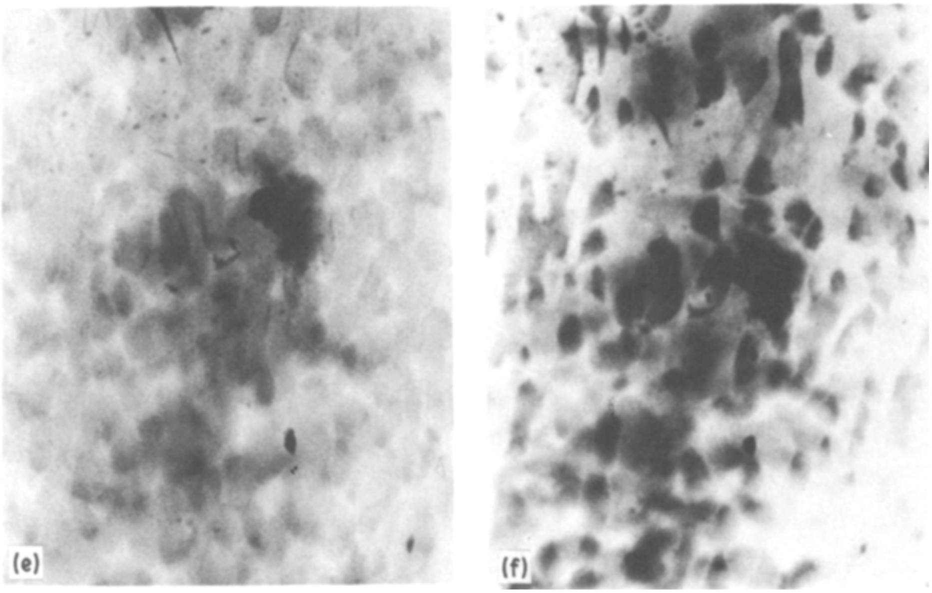


Figure 1 continued.

reflection), but they are not seen in the corresponding bright-field image (Fig. 1b) which shows contrast only where thickness variations occur. Analysis of the banding in the equatorial dark-field image has shown it to be the consequence of the serpentine path of the molecules about the shear direction [11]. Fig. 1d shows a dark-field micrograph, again imaged in one wing of the equatorial, for a specimen annealed for 5 sec on a single rocksalt substrate. After even this short anneal, the banded structure has disappeared and been replaced by a new microstructure also exhibiting strong contrast in the dark-field image. The contrast reveals well defined domains which are elongated along the shear direction (as "striations") and not perpendicular to it (as in "bands"). However, the overall level of molecular orientation is essentially unchanged by this microstructural rearrangement, as can be seen by comparing the electron diffraction patterns of unannealed and annealed specimens shown in Figs. 2a and b.

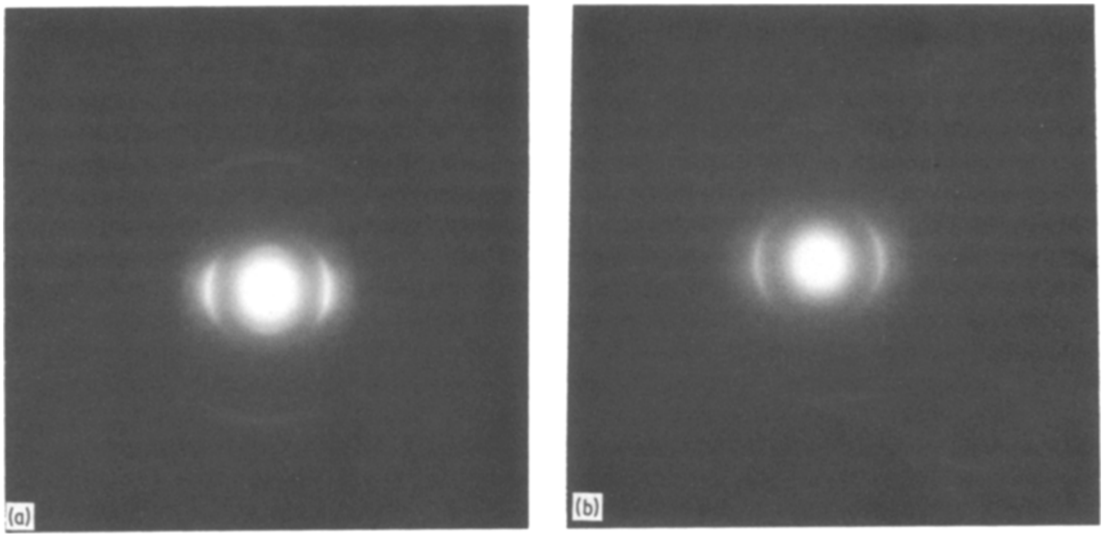


Figure 2 Electron diffraction pattern samples: (a) unannealed and (b) annealed for 5 sec at 300° C.

The domains are also apparent in the bright-field image of the annealed specimen where diffraction contrast can be recognized in addition to that due to mass thickness variations. However, whereas the domains are visible in equatorial dark field by virtue of a variation in contrast between them, they are only seen in the bright-field image because they are separated by boundary lines of different contrast (Fig. 1e).

Further information on the molecular arrangement within the domains can be obtained by tilting the specimen about an axis perpendicular to the shear direction. Fig. 1f shows the bright-field image at a tilt of 42°. Alternate domains now stand out in strong (dark) contrast, as they scatter strongly out of the straight-through beam. This micrograph should be compared with Fig. 1c which shows that the banded structure is only just made visible in bright field when a similar tilt is applied.

The origin of diffraction contrast in bright-field images of these thermotropic polymers has been previously discussed [20]. Where the variations in molecular orientation are predominantly in plane, as in the banded structure, virtually no contrast is to be expected (the plane referred to in this case is the one lying normal to the electron beam; for a tilted specimen this will not coincide with the specimen plane). However, a change in the out-of-plane component of molecular orientation will change the effective scattering cross-section. As the molecules tilt to lie more nearly parallel to the electron beam, a greater arc length of the equatorial ring will be excited, leading to a reduction of intensity in the unscattered beam and hence a region of darker contrast in the image. That alternate domains appear in dark contrast as in Fig. 1f, is indicative of an alternation in sense of tilt relative to the specimen plane.

Comparison of the tilted bright-field image of Fig. 1f with the domains visible in the equatorial dark-field image of Fig. 1d show notable correlations. Those domains that appear dark in tilted bright field, because they are scattering strongly, are those that are not scattering strongly into the (flat) dark-field image for the particular position of the objective aperture relevant to Fig. 1d. The converse is also true. The correlation between the tilted bright-field and the flat dark-field images therefore indicates a coupling between in-plane and out-of-plane orientation changes. This will be discussed further below.

3.2. Developed domains

After 10 min annealing with one rocksalt surface, strong contrast "veins" develop in the bright-field image of B–N (70:30), as can be seen in Fig. 3a. They outline the domains, which may therefore be considered to be developed. Corresponding images formed from one wing of the main equatorial reflection and from the interchain meridian (i.e. from a position on the meridian line at a spacing equivalent to the position of the equatorial ring), are shown in Figs. 3b and c, respectively.

The veins are again clearly apparent in Fig. 3c, but they are light instead of dark, which indicates that they scatter strongly into the interchain meridian. Thus, by the same arguments as above and discussed further in [20], the veins are narrow boundary regions with a large out-of-plane tilt of the molecules which is significantly greater than that within the domains themselves. The equatorial dark-field image shows some contrast changes, but the level of these changes is not as strong as in the specimens annealed for shorter times. The boundaries (i.e. veins) which separate the developed domains usually, but not invariably, appear as narrow black lines (as in Fig. 3b). Further discussion of the structure of the boundaries themselves will be deferred to a subsequent paper.

Figs. 3a to c were obtained for a specimen annealed on one rocksalt substrate, but similar results are obtained if both surfaces are constrained by rocksalt. Fig. 4a shows the bright-field image of such a specimen when viewed at normal incidence. It is comparable with Fig. 3a. Veins are clearly visible in both. Upon tilting the specimen through 24° about an axis perpendicular to the shear direction, alternate developed domains come into contrast (Fig. 4b) just as with the undeveloped domains in Fig. 1f. Thus, as for shorter anneals, half the domains in the tilted specimens are oriented correctly to scatter strongly and appear dark, demonstrating that the molecules in these domains are inclined at some small angle to the electron beam. Tilting through 24° in the opposite sense (Fig. 4c) brings the other set of domains into dark contrast; those that appeared dark in Fig. 4b are now oriented so as to be weak scatters and therefore appear bright. Again this indicates that the inclination of the molecules relative to the specimen plane is in opposite senses in the two sets of domains. For a specimen tilted through 42° about the axis

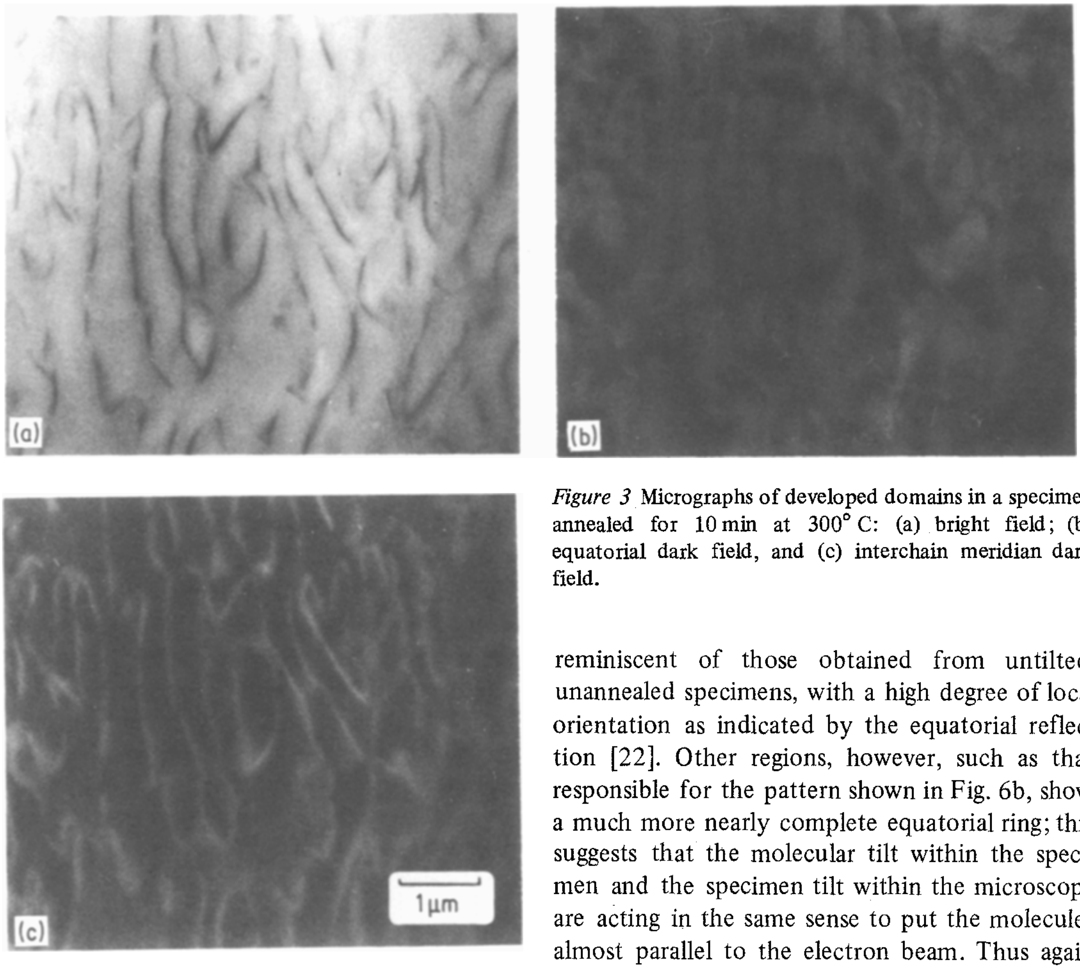


Figure 3 Micrographs of developed domains in a specimen annealed for 10 min at 300° C: (a) bright field; (b) equatorial dark field, and (c) interchain meridian dark field.

perpendicular to the shear direction, comparison of the dark-field image formed from the interchain meridian (Fig. 5b) and the bright-field image (Fig. 5a) shows very clearly that the domains that are scattering strongly out of the undeflected beam, are those that are bright in the interchain meridian. These micrographs confirm that the bright-field contrast originates from increased scattering into the equatorial ring as the local axis of orientation within a domain tilts away from the specimen plane. They also demonstrate that the molecular tilt within developed domains is greater than in the domains formed at earlier stages of annealing.

If a series of microdiffraction patterns, obtained as described by Donald [21], are taken from regions of 0.2 μm in diameter from a tilted specimen, the form of the diffraction pattern is found to vary substantially from place to place. Some regions, as in Fig. 6a, show a diffraction pattern reminiscent of those obtained from untilted, unannealed specimens, with a high degree of local orientation as indicated by the equatorial reflection [22]. Other regions, however, such as that responsible for the pattern shown in Fig. 6b, show a much more nearly complete equatorial ring; this suggests that the molecular tilt within the specimen and the specimen tilt within the microscope are acting in the same sense to put the molecules almost parallel to the electron beam. Thus again there is confirmation of the existence of two sets of domains within which the molecules are inclined in opposite senses to the specimen plane. The apparent alignment in Fig. 6a is seen to be much better than in the selected-area electron diffraction patterns obtained from areas ~ 2.5 μm across such as shown in Fig. 2a. This is because the latter encompasses all orientations present, as has been discussed by Donald and Windle [22] with respect to the banded structure, while a microdiffraction pattern effectively selects only a narrow window from the total range.

Whereas annealing on either one or two rocksalt surfaces leads to essentially identical results, the effect of annealing on a copper grid (i.e. effectively without any substrate) is radically different. After 10 min the bright-field image still exhibits only mass thickness constrast, as for the original banded structure. Few regions remain "electron-thin", because of the tendency for retraction due to surface tension, and thus dark-field microscopy is not readily performed;

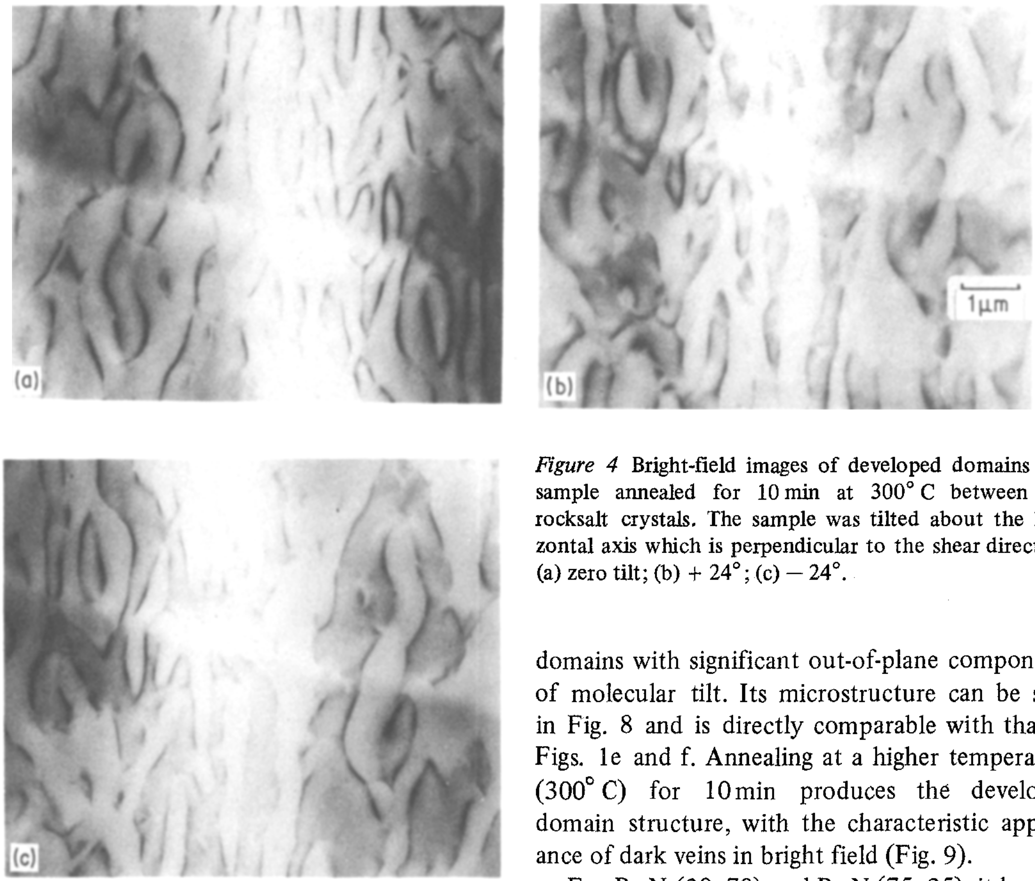


Figure 4 Bright-field images of developed domains in a sample annealed for 10 min at 300° C between two rocksalt crystals. The sample was tilted about the horizontal axis which is perpendicular to the shear direction: (a) zero tilt; (b) + 24°; (c) – 24°.

however, preliminary results indicate that some degeneration of the banded structure does occur, but without the appearance of clearly formed domains (Fig. 7).

3.3. Further samples from the B–N series

The annealing behaviour of sample B–N (58:42) most closely resembles that of B–N (70:30). Annealing for 10 min at 250° C (~ T_m) leads to domains with significant out-of-plane components of molecular tilt. Its microstructure can be seen in Fig. 8 and is directly comparable with that of Figs. 1e and f. Annealing at a higher temperature (300° C) for 10 min produces the developed domain structure, with the characteristic appearance of dark veins in bright field (Fig. 9).

For B–N (30:70) and B–N (75:25), it has not yet proved possible to reach the developed domain structure with dark veins. In fact, annealing at higher temperatures (~ 340° C) or for prolonged times appears to promote degradation before veins become established. However, the development of the basic domain structure with out-of-plane components of molecular orientation can be readily detected. Fig. 10 shows a bright-field micrograph of domains in B–N (30:70) annealed for 10 min at 300° C and Fig. 11 the appearance

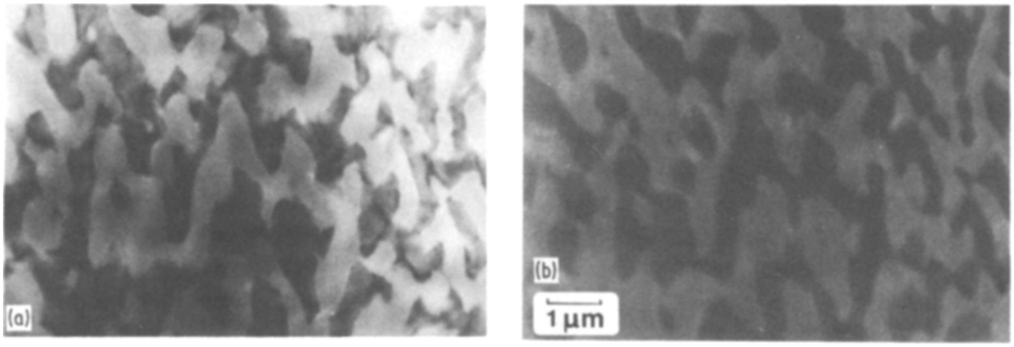


Figure 5 Developed domains (10 min at 300° C) in a sample tilted 42° about the horizontal axis imaged in: (a) bright field; (b) interchain meridian dark field.

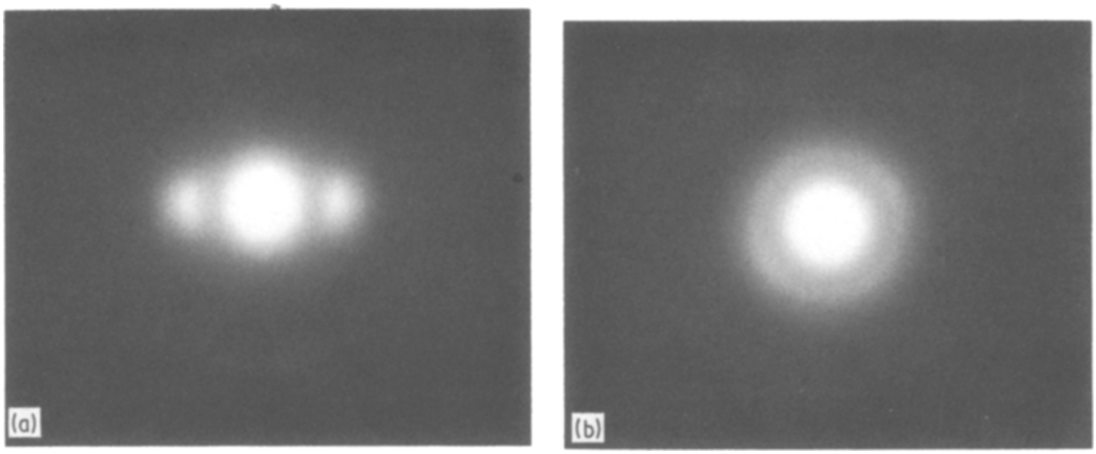


Figure 6 (a), (b) Microdiffraction patterns obtained from different areas of an annealed sample tilted through 42° about an axis perpendicular to the shear direction.

of the domains in a dark-field image of B–N (75:52) annealed for 10 min at 320° C. In this case the domains are particularly highly elongated, or "striated", along the prior shear direction. The gradual variations in contrast apparent in Fig. 11 arise from thickness variations normal to the shear direction.

4. Discussion

After an annealing time as short as 5 sec at 300° C, the bands of as-sheared B–N (70:30) have disappeared, to be replaced by a structure with domains of fairly uniform molecular orientation which tend to be elongated along the shear direction. For short anneals, the component of orientation in the specimen plane is not substantially different from that of the banded structure, as is clear from comparison of the selected-area diffraction patterns of Figs. 2a and b. The molecules thus tend to retain alignment along the original shear direction, despite the transformation of the banded structure; the memory of the prior shear is retained. Fig. 12 represents schematically a model for the variation of in-plane molecular alignment with position, consistent with the equatorial dark-field images such as that of Fig. 1d.

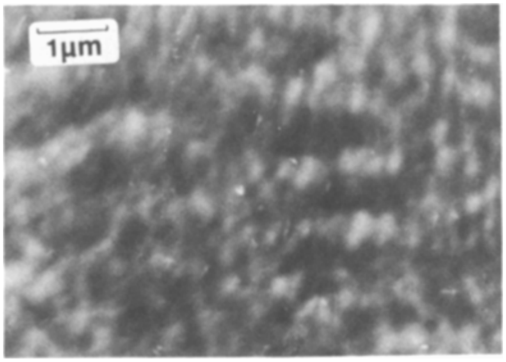


Figure 7 Dark-field image of a sample annealed for 10 min at 300° C with no substrate.

The path of the microstructural transformation from bands to domains is not as yet clear. Fig. 13a shows a dark-field (equatorial) image from a further specimen of B–N (70:30) annealed for 5 sec, for which the transformation to domains was less complete. It seems that small regions change orientation cooperatively, giving rise at the intermediate stage to bands with "scalloped" edges; the scallops are presumed to grow subsequently to give the striations elongated along the shear direction. It should be noted that the spacing of the incipient domain structure is approximately half the original band period. This intermediate stage of transformation is more easily intercepted for other members of the B–N family, where rates of transformation are far slower. Fig. 13b shows a dark-field image for B–N (58:42) annealed for 10 min at 250° C. The bands can still be seen but they are extensively scalloped, and domains, extended in the shear direction, are clearly recognizable.

Simultaneously with the formation of domains of relatively uniform molecular orientation, an out-of-plane component of molecular tilt develops. This is particularly clear from the appearance of diffraction contrast in the bright-field image of

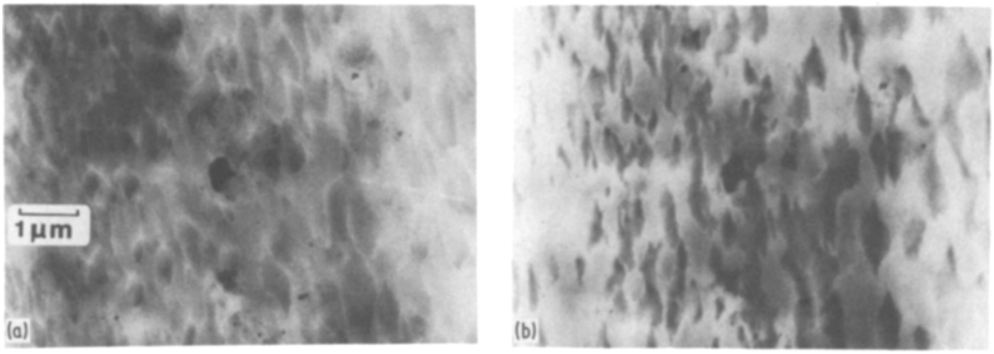


Figure 8 Domains in a sample of composition (58:42) annealed for 10 min at 250° C: (a) bright field; (b) bright field tilted 24° about the horizontal axis.

tilted specimens (Figs. 1f and 8b). The molecules in alternate domains are tilted either "up" or "down" relative to the plane of the specimen. Thus, if the specimen plane itself is tilted in the microscope, one set of domains can become oriented so as to give stronger scattering out of the zero order beam than the other set. The appearance of Fig. 1f is in contrast to that of Fig. 1c for a tilted specimen containing the banded structure. Preliminary calculations, to be published as a part of further work, indicate that changes in contrast may be detected for out-of-plane tilts of the order of 30 to 45°. Clearly, the observation that banded structures do not show marked diffraction contrast in bright field, even when the specimen is tilted through 42° (the maximum tilt possible for the Philips holder being used) indicates that the molecules are initially mainly confined to the specimen plane, although a faint banding is apparent in Fig. 1f.

For longer anneals the microstructure changes further in two respects, giving "developed domains". Firstly, the lighter boundaries of the bright-field images (Fig. 1e), which may merely represent a narrow region of zero molecular tilt separating the positive and negative tilts of adjacent domains, are replaced by dark veins. The fact that the veins, while appearing dark in bright field, are light in the interchain meridian dark field (compare Figs. 3a and c), shows that they are narrow regions of homeotropy or near-homeotropy, (i.e. where the molecular alignment is tending to be perpendicular to the substrate(s)). Secondly, the magnitude of the molecular tilt within the domain increases. This is evident, not only from the increase in bright-field contrast in tilted specimens, but also from a loss of contrast in equatorial dark field. As the molecules tilt away from the planar orientation, the diffraction pattern changes as a greater proportion of the equatorial ring is excited. The contrast in equatorial dark-field images decreases, since the increased equatorial arc length means a greater range of in-plane molecular orientations scatter

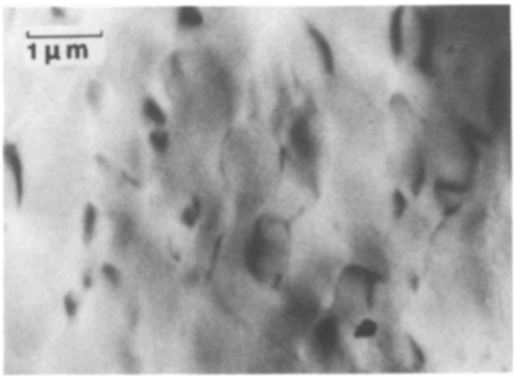


Figure 9 Developed domains and dark veins in a bright-field image of sample (58:42) annealed at 300° C for 10 min.

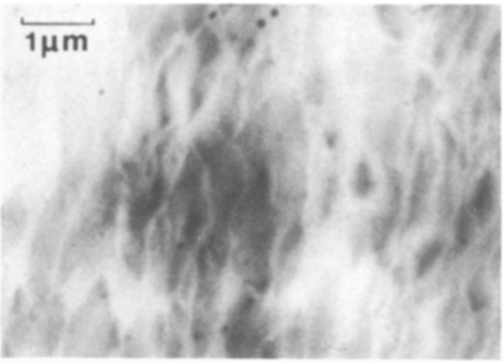


Figure 10 Domains in a sample of composition (30:70) annealed for 10 min at 300° C.

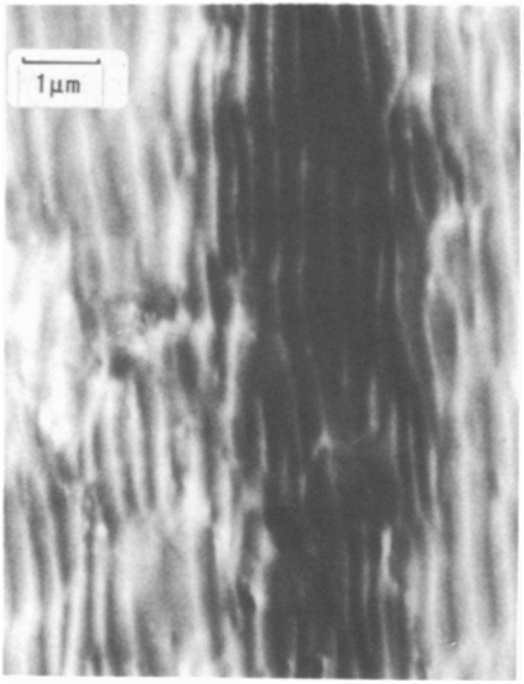


Figure 11 Dark-field image of elongated domains in a sample of composition (75:25) annealed for 10 min at 320° C.

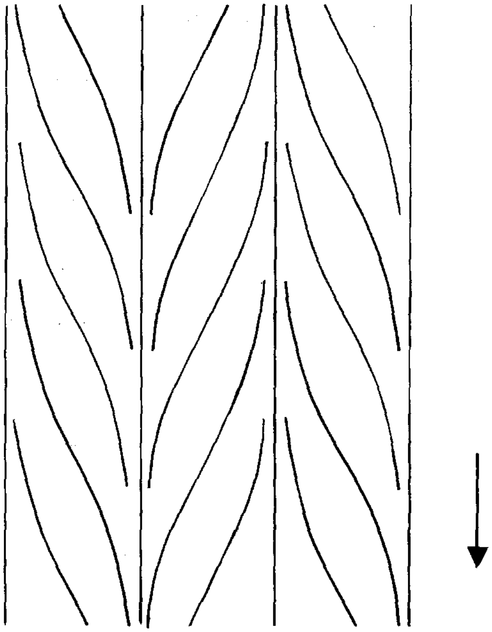


Figure 12 Schematic representation of molecular trajectories in the sample plane consistent with the dark-field contrast of the domains such as in Fig. 1d. Arrow indicates shear direction.

into a given objective aperture position. Thus it is believed that the low contrast of Fig. 3b is due to increased tilts up and down relative to the specimen plane, and not to a total loss of in plane molecular orientation. A similar tendency towards homeotropy upon annealing has been noted in a rather different LCP by Kleman *et al.* [24].

It should be emphasized that the rate at which the tendency towards homeotropy develops in the domains is not constant. Within the first few seconds of annealing a substantial tilt is generated, at least for B–N (70:30), but after times two orders of magnitude longer, the inclination of molecules within the developed domains is still far from perpendicular to the substrate(s), as is evident from the fact that the boundaries (where true homeotropy may be locally present) remain much darker than the domains. Why should the maximum molecular tilt be limited? Homeotropy itself requires chain end segregation at surfaces [8]. However, for a given molecular weight, the chain end density is determined, and this in itself will control the degree to which molecules can tilt towards homeotropy. In thin films such as used in these studies (~ 50 to 100 nm thick), where thickness is comparable with the molecular length, the problems for molecular packing due to the dearth of chain ends are likely to be particularly acute, in marked contrast to SMLCs. Thus, although initial rotation out of the plane of the specimen may be relatively easy, further tilting will become increasingly difficult as the possible segregation of chain ends to the surfaces approaches completion. Indeed, if molecules are longer than the specimen is thick, which is possible, then the degree of tilt will be limited by simple geometric consideration and we can write:

$$\sin \Omega = t/l$$

where Ω is the tilt angle (homeotropy = 90°), t is specimen thickness and l the molecular length. Evidence that the film thickness influences the extent of tilt possible is provided by Fig. 14a and b. In the thinner regions (at the left of Fig. 14) the veins are less dark and the overall level of contrast changes in the equatorial dark field (Fig. 14b) are greater than in thicker areas. Both facts support the proposal that the tendency towards homeotropy is more limited where the specimen thickness is less. If the length of the molecules effectively limits the tilts achievable within the developed domains, then one must

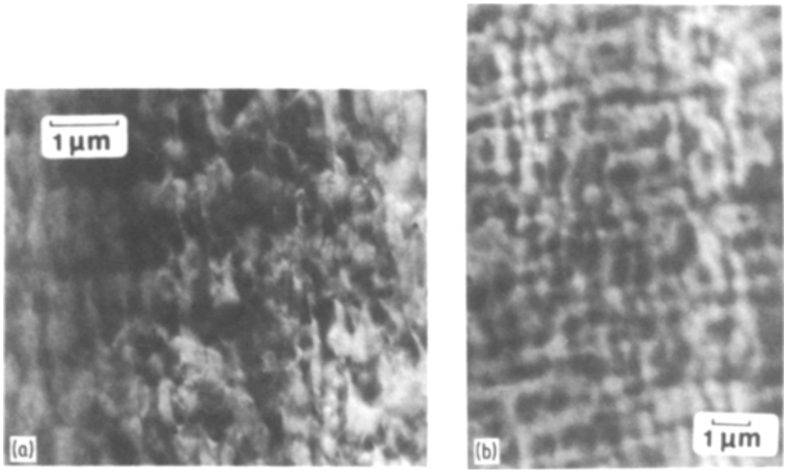


Figure 13. Equatorial dark-field images showing the degeneration of bands and the early stages of domain formation: (a) 70 : 30 sample annealed for 5 sec at 300° C; (b) 58 : 42 annealed for 10 min at 250° C.

question how it is possible to have larger molecular tilts within the narrow veins. It is possible that there is some tendency for shorter chains to segregate at the boundaries. (This could be envisaged as being analogous to the prospensity for grain boundaries in metals to act as sinks for impurities and defects in general.) The difficulty of GPC measurements on thermotropic LCPs has meant that very little information on molecular weights and polydispersity is available for these polymers. However, the *IV* measurements that have been obtained for three of the polymers under investigation (Table I) can serve as a guideline. Polymers B–N (70 : 30) and B–N (75 : 25) differ little in composition or T_m; however, they exhibit significant differences in response to annealing, with the former being the most rapid while the latter is the most sluggish of the four polymers investigated. Significantly, B–N (75 : 25) has the highest *IV* value of 9.2 whereas that of B–N (70 : 30) is of the order of 5. Furthermore B–N (58 : 42), the other polymer with a low value of $IV = 5.1$, also exhibits both incipient and developed domains, although the development appears to require annealing temperatures T_s somewhat further above T_m than for B–N (70 : 30).

It is clear from the absence of veins in bright-field images obtained from a specimen annealed without a substrate, and the slight extent of band degeneration of Fig. 7, that the presence of a substrate plays a crucial role in the development of homeotropy. Tilts "up" and "down" of equal angles will be degenerate in energy; thus domains of both orientations may be expected, and are indeed observed experimentally

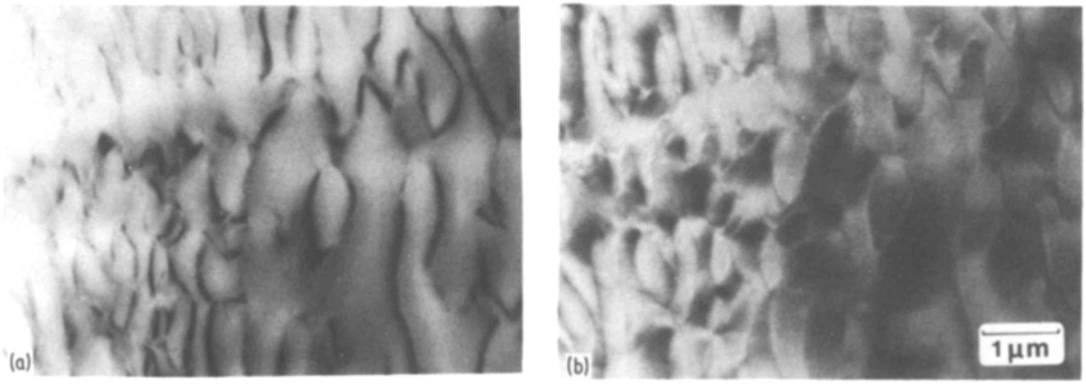


Figure 14 (a) Bright-field and (b) equatorial dark-field images of developed domains in 70 : 30 sample (10 min at 300° C) showing the influence of film thickness on microstructure. The thickness increases from left to right.

TABLE I Liquid crystal polymers examined of the type B–N (x:y)

x:y	T_{m}	IV
70:30	285	~ 5
75:25	290	9.2
58:42	246	5.1
30:70	313	7.8

in approximately equal numbers (Fig. 4). The tendency for complete homeotropic alignment at the surfaces will, however, be counteracted by the finite number of chain ends. Nevertheless, simple as this picture may be, we have no evidence that the tilt angle actually remains constant through the film thickness.

In the more general case, where a systematic through-thickness variation in tilt angle occurs, splay distortions will be involved. Consideration of splay can provide an explanation of the observed correlation between in-plane and out-of-plane components of the misorientation of the domains about the shear axis. The reasoning is exemplified by the arguments proposed by Meyer and Longberg and Meyer [25] for poly(γ-benzyl-L glutamate) (PBLG) solution between glass and air interfaces. He has shown that, for the case of homeotropic alignment of PBLG at one surface (glass) and planar alignment at the other (free) surface, the through-thickness splay deformation can be compensated by splay in the opposite sense within the specimen plane [8, 25]. The significance of this proposal is that it shows how splay is able to occur with a relatively low energy, whereas following de Gennes [6], it has been previously accepted that for LCPs of uniform density, splay deformations with $\nabla \cdot \boldsymbol{n} \neq 0$, where $\boldsymbol{n}$ is the molecular director, are energetically unfavourable because of an insufficiency of chain ends. Fig. 15 illustrates how splay–splay compensation may be associated with the in-plane orientation scheme sketched in Fig. 12, at least for the case of a single substrate. It can be seen that to obtain a minimum total splay deformation ($\nabla \cdot \boldsymbol{n} \sim 0$), where $\partial n_x / \partial x$ is negative ("up" domain), a positive $\partial n_z / \partial z$ is required, and *vice versa*. This is similar to Longberg and Meyer's model, and provides one possible rationale for the coupling observed between the in-plane orientation of the domains and the out-of-plane molecular tilts. It is also possible, however, that splay associated with the molecular trajectory in the banded structure is compensated by small (and thus not readily detectable) degrees of molecular tilt, which nevertheless are sufficient to determine the sense of tilt which develops in a domain nucleating from any one region of the banded structure.

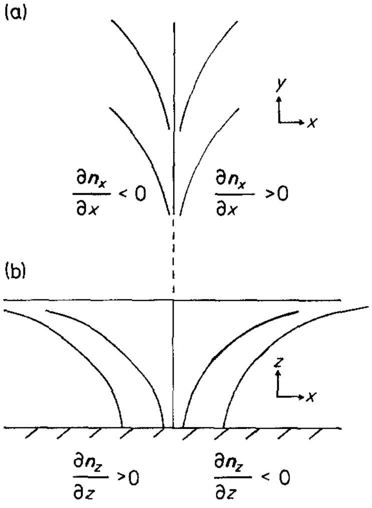


Figure 15 (a) Proposed in-plane orientation map for domains (as Fig. 12) and (b) possible splay compensation in the third dimension for the case of a single substrate.

5. Conclusions

1. The banded structure present in as-sheared thin films of LCPs has been shown to correspond to an approximately in-plane variation in molecular orientation.
2. Upon annealing thin films containing the banded structure, a rapid microstructural change occurs. The bands lying normal to the shear direction are replaced by domains elongated along the shear direction.
3. Simultaneously with the disappearance of bands, a tilt of the molecules out of the plane of the specimen occurs. Possibly because of the need for splay compensation, the sense of the molecular tilt in a domain is coupled with the in-plane misorientation of the domain from the shear direction.
4. After longer annealing times, the overall inclination of the molecules increass, and in the samples of lower average molecular weight well-defined boundaries or veins of near homeotropic orientation form. The rate at which the molecular inclination increases is a decreasing function of time.

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