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Large Scale Textures in Nematic Polyethers: 2. New Aspects of Orientational Order and Structure Hierarchy

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The flow-induced large-scale textures arising in thermotropic nematic polymers presented in Part I of this study have been further explored. Optical and scanning electron microscopy and light diffraction are employed to interpret the nature of these textures. It was found that on a large-scale, molecular arrangement similar to vector fields around disclinations in ordinary nematics, is created due to superposition of radial flow fields. On a fine scale, there are several stages of relaxation of the internal nematic substructure from the highly oriented state; first, a banding appears due to periodic variations of the local director along the long-range orientation, subsequently relaxing gradually to a polydomain texture. It is shown that interaction of these two processes on the long and fine scales is responsible for the range of complex textures. Once recognized for what they are, these textures can be interpreted without misconceptions, which may otherwise arise due to actual simplification of the polarizing optical analysis.

Keywords: nematic polyethers, optical textures, scanning electron microscopy, polarizing optical analysis

INTRODUCTION

Thin films of thermotropic nematic polyethers have been shown to form large-scale textures[1,2] induced by flow in the isotropic state and having dimensions as large as 1 mm or more. Between crossed polarisers, they show features typical of the disclinations in nematic *Schlieren* textures; the molecular director fields can be described in terms of their strength.[3] Formation of these textures appears to be a common feature for thermotropic nematic polymers.[2]

In our previous studies, coexistence of a long-range orientational order due to the sporadic multidirectional flow in the isotropic state and a finer substructure (short-range orientational order) due to self-ordering in the nematic region has

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been reported.[1,2] The latter was found to conform to the long-range orientation. The interaction between the large and fine scale structures will be the main subject of this study. As we shall see, such structures may be important, arising in typical processing conditions. Recognition of the cause of such textures should help to avoid possible misinterpretations of molecular behaviour of liquid crystal polymers on orientation, relaxation and their relation to phase transformations.

EXPERIMENTAL

The materials used were random copolymers of α-methylstilbene and methylene spacers, identical to those in the first part of this study.[2] Therein, chemical structure, molecular weights and transition temperatures of these polymers were summarized and so were sample preparation and experimental procedure leading to large scale texture formation.

Optical analysis of the textures was conducted on samples quenched to room temperature placed on the Zeiss Ultraphot II polarizing microscope. Light diffraction patterns were obtained by inserting a Bertrand lens into the optical path.

To prepare samples for scanning electron microscopy, the glass coverslips from melt-processed samples were first removed by repeated quick cooling of specimens in liquid nitrogen and their subsequent heating to room temperature. The polymer surface was then etched using the permanganic method pioneered by Olley and Basset[4]; the samples were immersed in the mixture $H_2SO_4/H_3PO_4/KMnO_4/H_2O$ (compounded in the ratio 13/5/15/40 mg) for 10 minutes, successively rinsed in diluted H_2SO_4, 30% H_2O_2 and H_2O and dried with acetone. Finally, they were coated with aluminium and studied in the scanning electron microscope JEOL 840.

RESULTS AND DISCUSSION

The results described in this section were mostly obtained on a polymer with M_w = 51,800 (PHMS 5, see Table I in Part I of this study[2]) with a few experiments done also on lower molecular weights.

Long-range Orientational Order

In Figure 1a, an image of the S_{+1} texture§ between crossed polars is shown with positive birefringence in terms of spherulite nomenclature (Figure 1b). Highest polarizability in the radial direction, coinciding in our case with the flow direction, implies also radial molecular orientation.

The same analysis of the S_{-1} textures (Figure 2) proved their characteristic symmetry; on rotation, the sign of birefringence changed every 45 deg (Figures

§To describe symmetry of the large-scale textures, we used the customary notation of disclination strength determined by a common test on rotation direction of the extinction brushes with respect to rotated polarisers, even though molecular origin of these textures is external preorientation rather than dislocation.

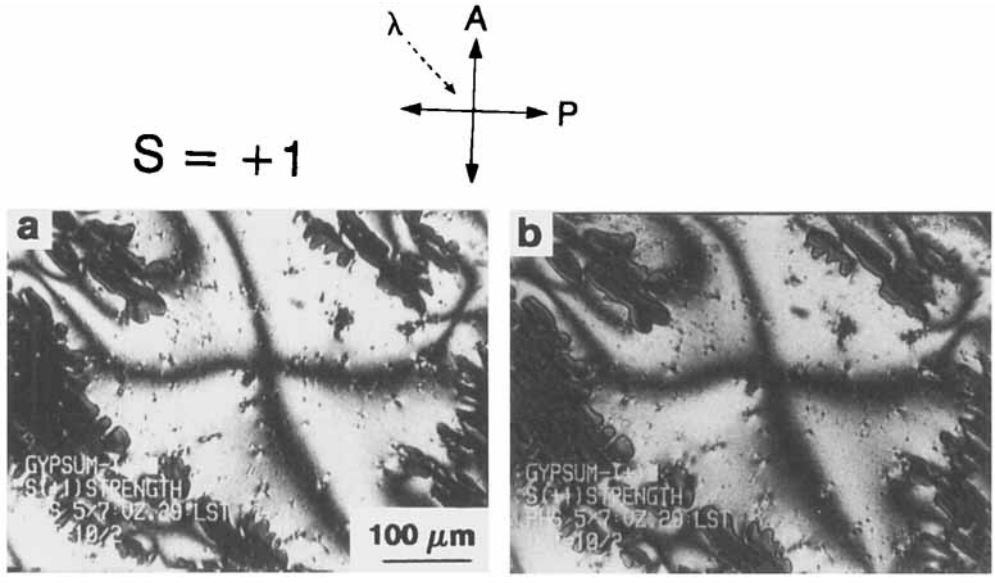

FIGURE 1 S_{+1} texture in the PHMS5 polymer (quenched) as seen between crossed polars without (a) and with a unit retardation plate (b). A, P, denote the directions of analyser, polariser and the retardation plate. See Color Plate XII.

2b–d). This reflects the corresponding alteration of tangential and radial orientations around an S_{-1} disclination as manifested by the colour changes with a first-order red plate inserted into the light path.

Analogous to nematic textures, large-scale textures of $+\frac{1}{2}$ and $-\frac{1}{2}$ strength were also observed (cf. Reference 1) and textures of opposite signs were found to combine sharing one extinction brush (Figure 3).

Short-range Orientational Order

The nature of short-range order in the underlying fine subtexture (arising in the nematic state) was found to depend on the molecular weight and on the time of holding the polymer in the nematic state before its solidification by further cooling.[2] Both dependences reflect the degree of relaxation from the initial oriented state (to be discussed further below).

Low orientation—"grainy" structure. As already stated[1] the basic elements of the fine substructure are intrinsic to the nematic structure. When no previous flow-induced long-range orientation has been locked in, or it has fully relaxed, only the usual grainy nematic texture is seen. When the long-range order has almost relaxed the grains appear superposed on the remnants of the long-range arrangement; large-scale extinction brushes become apparent in addition to the fine structure (Figure 4).

The latter case just corresponds to an advanced stage of relaxation when the fine structure takes on the seemingly random grain appearance. However, the extinction brushes demonstrate that there remains a certain anisotropy which, averaged over a local area, coincides with the long-range orientation. Obviously, the local director conforms to the overlying order.

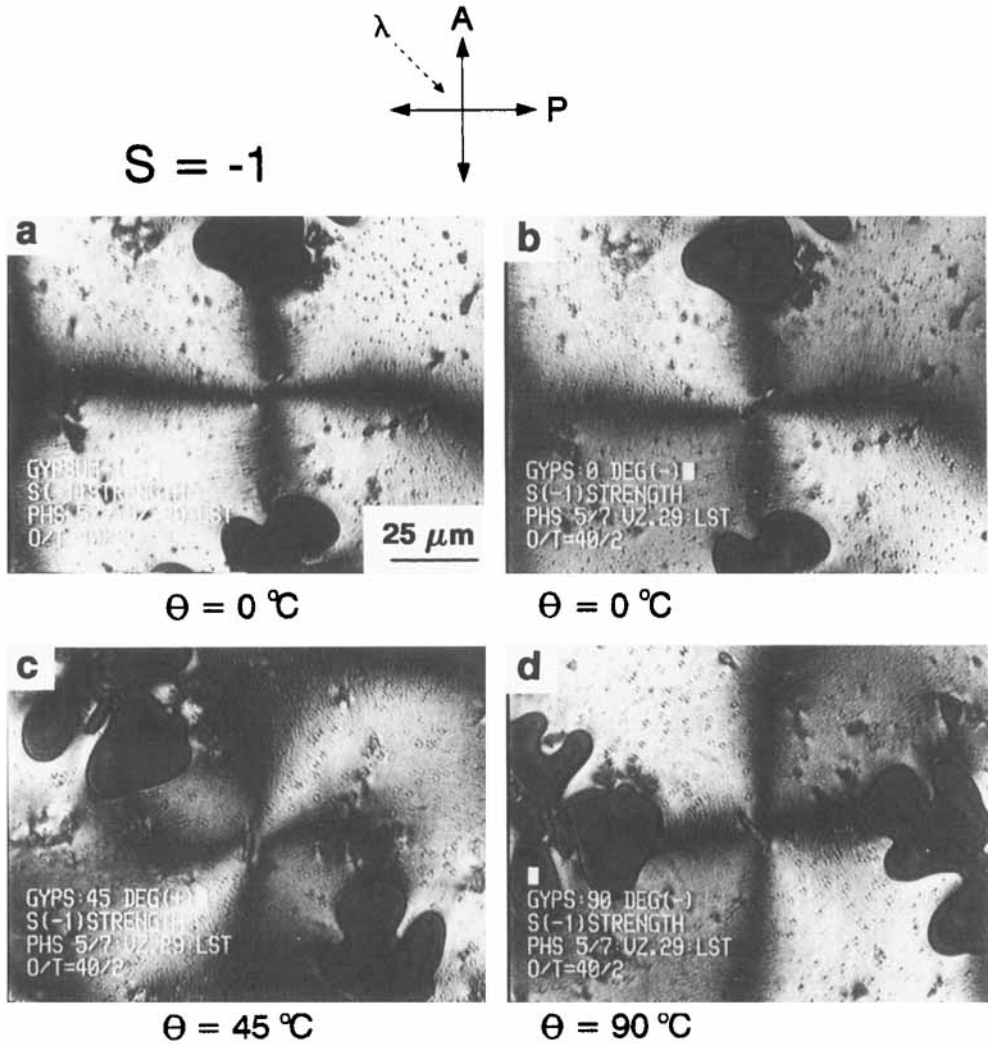

FIGURE 2 S_{-1} texture in the PHMS5 polymer (quenched) as seen between crossed polars without (a) and with a unit retardation plate at various angles of sample rotation (b, c, d). Symbols as in Figure 1. See Color Plate XIII.

High orientation. Anisotropy at the early stages of relaxation of the long-range order is much higher and even the short-range director largely coincides with the long-range orientation. Therefore, no fine structure is visible (Figure 2, bottom, in Reference 2) except perhaps within the extinction brushes themselves where even the minutest deviation of the local director from the long-range orientation becomes noticeable; any departure within a dark brush leads to localized light transmission which is sensitively detectable.

Intermediate orientation—banded structure. The most characteristic feature of the intermediate stage of relaxation in the nematic state, is a fine banded structure (Figure 5). Periodic banding is a familiar effect in uniaxially oriented sheared nematic systems, where it appears after cessation of the external orienting influence

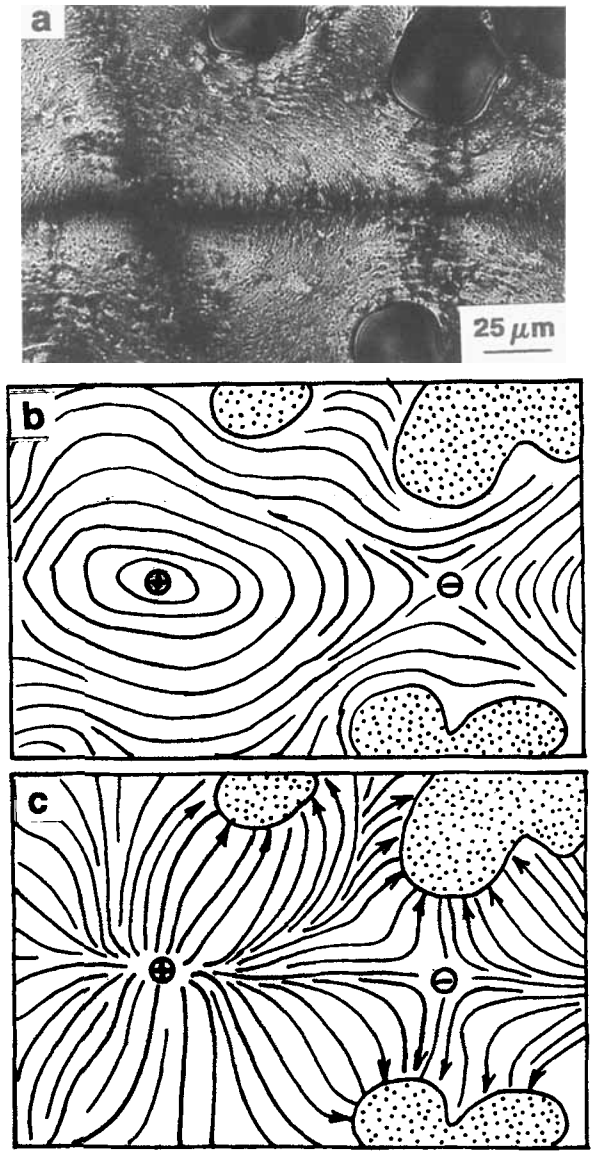

FIGURE 3 Combination of S_{+1} and S_{-1} textures in quenched polymer PHMS5 (a) and schematic drawings of corresponding band arrangement (b) and streamlines of the flow that had lead to their formation (c). Crossed polars orthogonal.

as a consequence of relaxation from the oriented state. It corresponds to a short-range periodic orientation variation (e.g., References 5 and 6) the origin of which is not fully understood and is currently the subject of intensive attention. Here we maintain that the presently observed banding is basically an identical effect where the banding has conformed to the local orientation produced by preceding flow in the isotropic state. It corresponds to a short-range periodic orientation variation with respect to the long-range orientation. The bands are more or less orthogonal

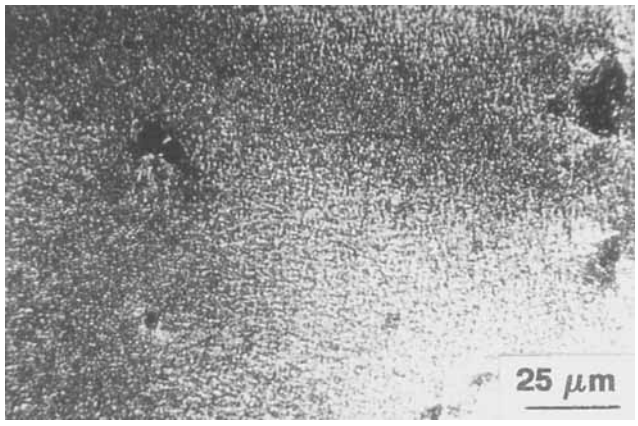

FIGURE 4 Optical micrograph showing fine structure underlying long-range orientation at an advanced stage of relaxation. Quenched PHMS2 (M_W = 16,000), crossed polarizers.

to the long-range director and help to define the vector field of the large-scale texture (see Figure 3).

To illustrate graphically the combined effect of banding and large scale texture, we select from the various large-scale patterns the S_{+1} director field with circular symmetry (the left side of Figure 3a and Figure 5a). Once understood this treatment can be readily extended to other symmetry patterns.

Figure 6 shows schematic patterns of the extinction lines in the case of spherical symmetry (such as S_{+1}) for hypothetical sinusoidal orientation variation of the short-range director with 3 successively increasing angles α (corresponding to the deviation of the short-range director from the long-range orientation). The explicit shape of these patterns depends on the geometry of the periodicity (zigzag, sinusoidal or any other director trajectory, to be dealt with in a separate study) but an overall feature is common to them all: the shape of the extinction lines reflects the underlying arrangement of the short-range director. Specifically, the radial distance between the extremities of the zigzag extinction line corresponds to the full period of the periodically varying orientation path of the short-range director, while the azimuthal spread of the extinction lines within an extinction brush (2α) corresponds to the maximum deviation (α) of the short-range director from the radius (long-range orientation). It is further apparent that at azimuths larger than α there is no extinction and the underlying periodicity remains between crossed polarisers invisible. In a real low resolution image, the extinction lines, where visible, will merge into a simple extinction cross.‖

Extension of the above to the S_{-1} disclination long-range field will now be evident and will not be separately examined here. An example of it showing the underlying

‖Zigzag extinction lines, in place of uniform Maltese extinction crosses, have been described previously by one of us in some polymer crystal spherulites[7] and interpreted in the same way as presented here. From the point of view of polarizing optics the two systems, namely the present liquid crystals and the crystalline spherulites are identical as both conform to the same geometry on the scale in question. However, the two systems are intrinsically different; the spherulites are the products of crystal growth, while the liquid crystalline system is a continuum under the constraints arising during various stages of relaxation.

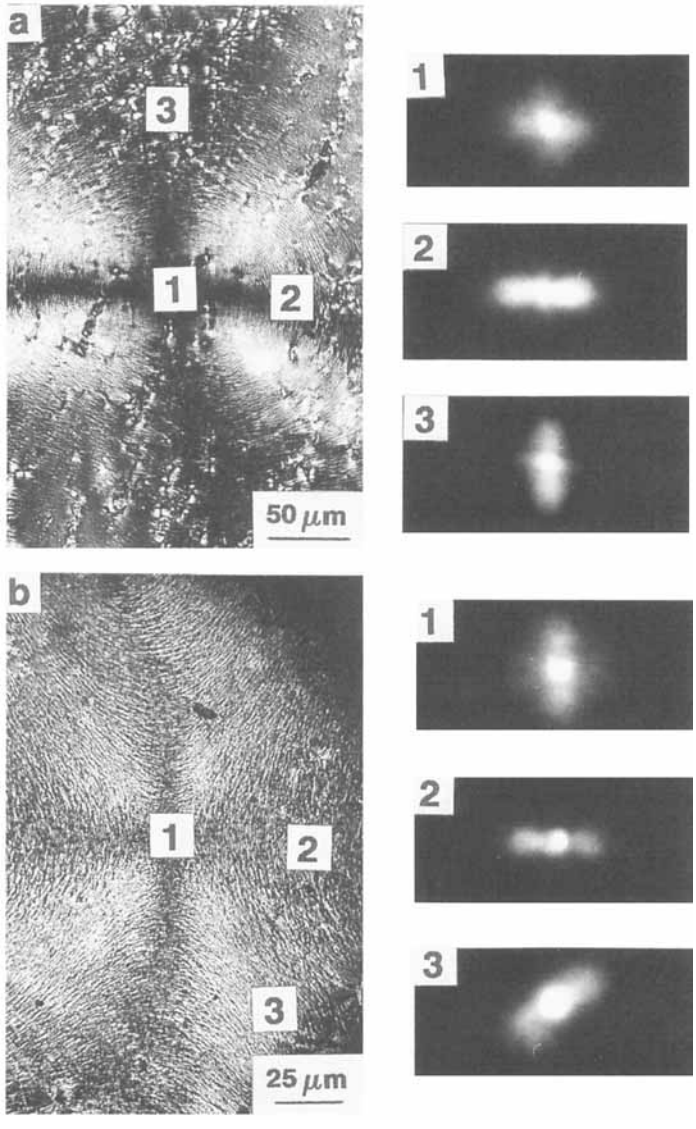

FIGURE 5 Optical micrographs of (a) S_{+1} and (b) S_{-1} textures and light diffraction patterns from particular areas. Polymer PHMS5 (quenched), diffraction in V_H position with respect to band orientation. Crossed polars orthogonal.

extinction lines at high resolution is given by Figure 7. The fine lines create a zigzag pattern just as for the $S = +1$, however, the curvature of the lines in S_{-1} field is convex (as opposed to concentric with S_{+1} symmetry) with respect to the centre.

The presence of periodic banding was further examined by optical diffraction in the microscope. Diffraction patterns provide a representative quantitative measure of the structure already recognized in real space, namely, banding gives rise to V_H diffraction maxima which are equatorially placed with respect to the appropriate

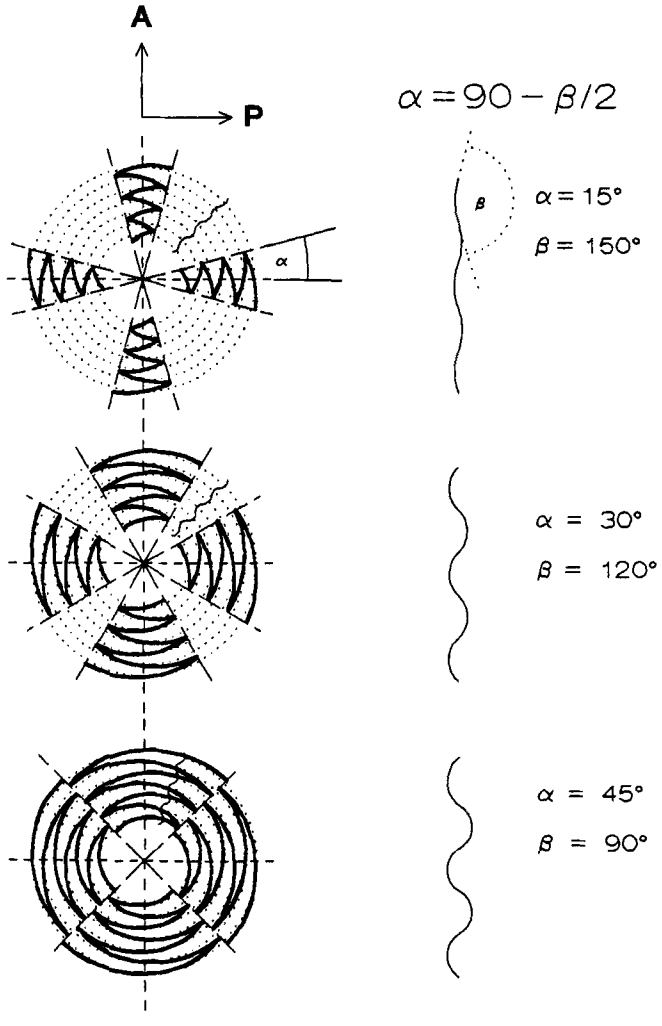

FIGURE 6 Diagram illustrating traces of minimum birefringence intensity (extinction lines, denoted by the heavy lines) in circularly symmetrical fine banding (S_{+1} texture) between crossed polars (A, P) for a sinusoidal periodicity of the director orientation. Symbols discussed in the text.

radial direction.[5,6] In our case, this is illustrated by Figure 5 where different areas in the S_{+1} and S_{-1} textures were selected for diffraction. As seen, the light diffraction maxima occur along azimuths perpendicular to the radii and change orientation accordingly when moving from one selected area to another. The spacing derived from the angular position of the maxima were between 0.5–1.3 μm, in good agreement with direct measurement on the image.

The above defined orientation in the diffraction pattern, however, is seen to deteriorate towards the centre of the large-scale texture and gradually change into the mottled structure at its centre. Here the diffraction pattern has four intensity maxima (not easily discernible due to closeness to the central beam) along both equator and meridian, typical of the usual unoriented nematic polydomain struc-

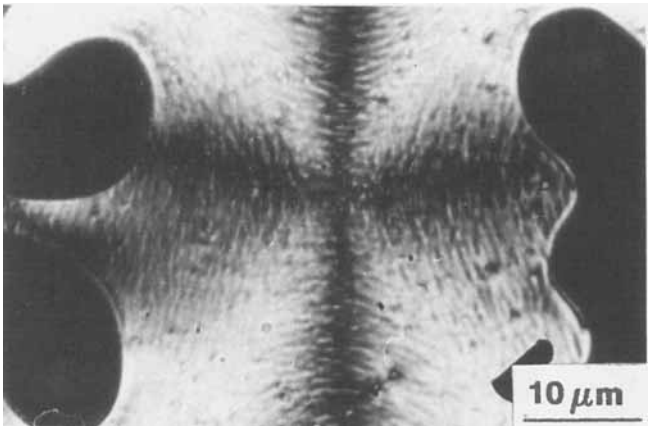

FIGURE 7 Zigzag type extinction lines within dark brushes of an S_{-1} texture. Optical micrograph, crossed polars, polymer PHMS5 (quenched).

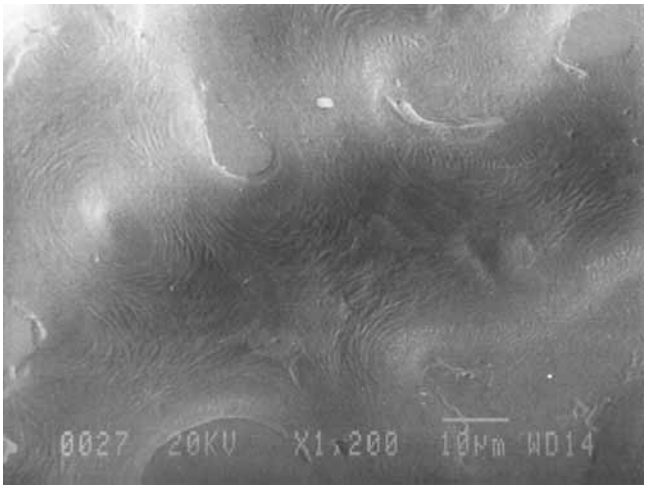

FIGURE 8 Scanning electron micrograph of bands in large scale textures. Polymer PHMS5 (quenched), textures with S_{+1} and S_{-1} symmetry apparent.

ture.[8,9] Detailed analysis of the light scattering patterns is beyond the scope of this study and will be given elsewhere.

Scanning electron micrographs of etched surfaces revealed features which correlate with the polarizing optical image. Figure 8 shows an area containing S_{+1} and S_{-1} large-scale disclinations containing corresponding concentric and convex banding with a spacing of approximately 1–2 μm. Thus, the quenched polymer must contain structure elements resistant to etching (probably crystallites), an inference which follows from similar observations reported elsewhere.[6,11,12]

Higher magnification revealed a fine structure within the bands (Figure 9). Even if there is considerable irregularity, the 1–2 μm vertical banding is recognizable,

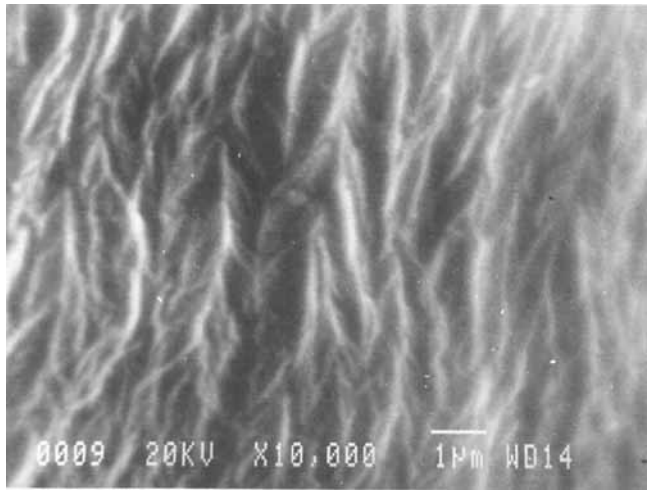

FIGURE 9 Zigzag fibrillar arrangement in bands as seen in scanning electron microscope. Polymer PHMS55 (quenched).

with a zigzag fibrous substructure of about 0.1 μm, perpendicular to the banding. It may appear tempting to associate these zigzag fibrils with the short range director trajectory. However, such correspondence has not proved satisfactory: the angle between the fine striations and the banding, itself perpendicular to the long-range orientation, is far too small and is closer to the complement of the angle to be expected if the fine striations represented the short-range director. It is suggested therefore that we are seeing crystal lamellae which, as known, can be perpendicular to the director.[10] The actual relation between the fine crystal structure and the liquid crystal banding will be further discussed elsewhere. At this stage, we shall not pursue this issue further, beyond stating that the morphological equivalents for the optically visible structure have been identified on both large and fine scale.

Hydrodynamic Origin of Large-Scale Texture Formation

In the light of the above analysis of structure hierarchy in the large-scale textures, we can now discuss their origin on a more general hydrodynamic basis.

We have already shown that the appearance of the overall texture reflects the multidirectionality of the flow before quenching; it is justifiable to assume that the long-range orientation follows the flow directions. More or less pronounced symmetry within the large-scale disclinations indicates that there also must have been some analogous symmetrical flow fields present in the isotropic state. Based on the optical orientation analysis (Figures 1 and 2) and banding arrangement (Figure 5) of the S_{+1} and S_{-1} textures, we can now show what is the hydrodynamic origin of such symmetries. In Figure 3b, the arrangement of banding in the textures from Figure 3a is schematically illustrated. The lines in Figure 3c perpendicular to the bands represent the long-range director field and, consequently, the streamlines of the frozen flow field. The radial and fourfold symmetry of the flow field in S_{+1} and S_{-1} texture, respectively, is seen.

The S_{+1} radially symmetrical field represents what is called, in terms of hydrodynamics, sink flow, in the centre of which the fluid velocity during a flow process remains zero.

The combination of two such flow sinks with radial symmetry can then produce a hyperbolic flow field in the centre of which there is also a singularity with zero fluid velocity. This kind of flow field analogous to that realizable in polymer melts and solutions in a four-roll mill or between two opposed sucking jets,[13,14] is in our case represented by the S_{-1} textures.

If the flow was dominated by the shear component (rather than the extensional component) the low fluid velocity around the flow singularities would be accompanied by little preferential long-range orientation. This would account for the presence of macroscopically random grain structure and associated non-anisotropic light diffraction (Figure 5) in the centres of the symmetrical textures as discussed above.

CONCLUSIONS

The origin of the large-scale director fields similar to those intrinsic to the nematic textures is due to combinations of flow fields of different kinds present in the isotropic state.

The underlying fine structure formed in the nematic state reflects consecutive stages of relaxation from the highly oriented to the random nematic state. At each stage the fine structure conforms with the overlying long-range order in a rational, analysable fashion. This recognition, beside leading to the more correct interpretation of complex effects, also simplifies the optical analysis of banded structures in liquid crystals: namely in a circular symmetrical arrangement of the large-scale director we have all orientations of the orienting field with respect to the polarizers simultaneously present. This obviates the need of step-by-step stage rotation as needed for the analysis of uniaxially oriented specimens, by providing an image of the overall extinction features.

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