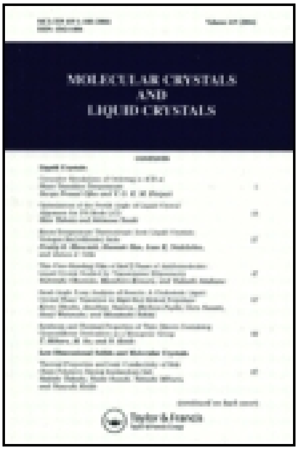

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Large Scale Textures in Nematic Polyethers: 1. New Aspects of Formation

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Large Scale Textures in Nematic Polyethers: 1. New Aspects of Formation

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It has been shown previously[1] that nematic polyethers can form large-scale textures, similar to low molecular weight nematic *schlieren* textures but on a scale up to hundreds of microns. Here we demonstrate that their origin is sporadic flow-induced orientation arising due to external strain fields in the isotropic state. Such circumstances may arise during usual sample handling giving rise to effects which are similar to those characteristic of nematic orientation textures but on a larger scale, overlaying the effects intrinsic to the liquid crystal nature. Accordingly, we have a two-tier structure hierarchy, a large-scale one due to external orientation and one within on a finer scale, due to the intrinsic nematicity where the latter conforms geometrically to the former. The recognition of this situation is essential for interpretation of the polarizing optical images in samples which display these features. The effect of molecular weight is also described in terms of chain mobility during relaxation from flow orientation.

Keywords: nematic polyethers, optical textures

INTRODUCTION

In a previous study[1] formation of unusually large birefringent textures in nematogenic polymers has been reported. These textures were found to originate from sporadic flow orientation in the isotropic state. The present study, in two parts, is a resumption of the previous work clarifying and partially amending it. We believe that the presented results are of general interest for liquid crystalline polymers, particularly in revealing textures which may arise as a result of melt processing.

Experimental observations are reviewed in a manner to show the following:

In a liquid crystalline polymer, optical textures are formed to exist on two scales:

1. Large-scale textures (hundreds of microns) induced by multiaxial flow fields in the isotropic state, imposing overlying orientational order over the nematic order on subsequent cooling.

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2. Fine-scale texture (a few microns) intrinsic to nematic molecular order, this must conform to the above overlying flow-induced order creating interesting textures.

In the present paper (Part I) we distinguish between the two separate effects within their overall combination and describe the finding of the conditions which lead to formation of either one. In Part II we shall pursue the structural analysis of the compounded large and fine-scale texture in their various combinations, in the light of the recognitions reported in this part.

Characterization of the two-level hierarchy is an instructive exercise in analyzing polarizing optical effects, deserving a record, particularly as it is applicable to other situations and systems where similar effects may arise.

EXPERIMENTAL

The materials used were random copolymers of mesogenic α-methylstilbene and flexible alkyl spacers linked through an ether oxygen with 5 or 7 methylene units in the 1:1 ratio[3] (Figure 1, further referred to as PHMS). The experiments were performed on grades with various molecular weights having different phase transition temperatures. The respective data are summarized in Table I; T_{NI} and T_{NC} are the nematic-isotropic and nematic-crystalline transitions, respectively, and were taken as onset peak temperatures from DSC traces recorded at heating and cooling rates of 10°C/min. The molecular weights were measured by GPC.

Toluene-cast films with thickness in the range of 5–100 μm were sandwiched between two glass coverslips. Further preparative procedures were carried out either on the Kofler hot bench or in the Mettler FP82 hot stage. All observations were made in a Zeiss Ultraphot II polarizing microscope between crossed polars. Experimental observations in situ were made in a Mettler hot stage. Quenched specimens were prepared on the hot bench.

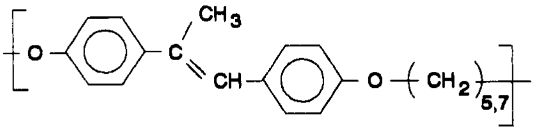

FIGURE 1 Chemical formula of PHMS 5/7.

TABLE I

Molecular parameters and phase transition temperatures of the polymer PHMS 5/7

Grade	M_w	M_w/M_n	T_{NI}[°C]	T_{NC}[°C]
PHMS1	1980	1.1	62.8	16.2
PHMS2	16000	2.1	134.5	57.6
PHMS3	24400	2.3	158.1	76.2
PHMS4	31600	2.6	158.8	72.2
PHMS5	51800	2.9	159.8	68.0

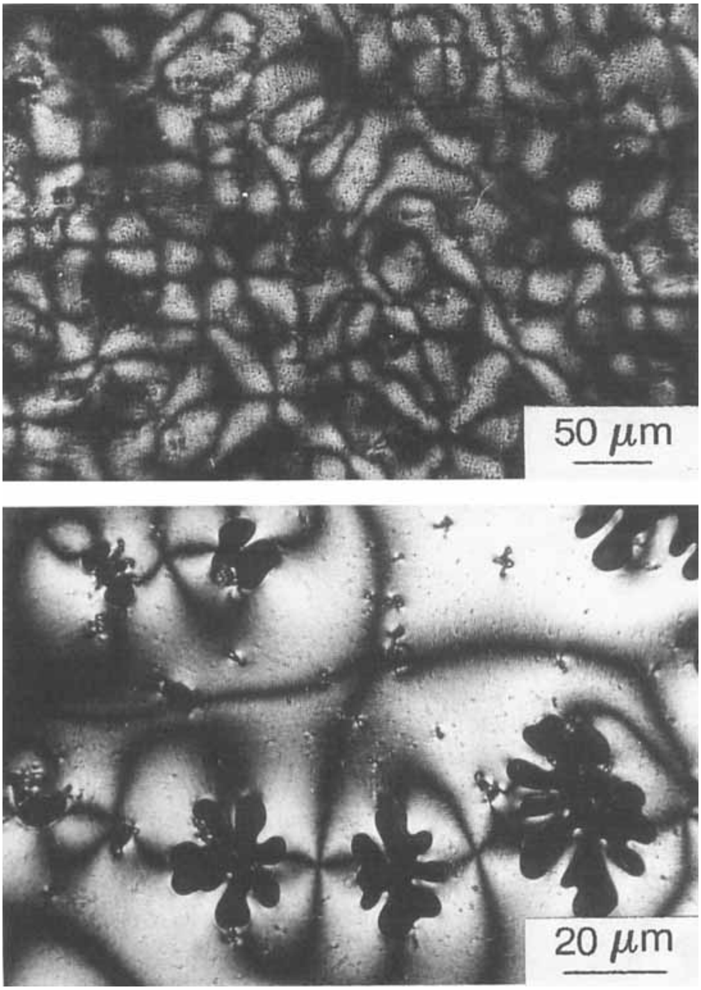

FIGURE 2 Typical examples of large scale textures showing a variety of disclinations in PHMS5 as seen in the polarizing microscope between crossed polars.

RESULTS AND DISCUSSION

Formation of Large-Scale Textures

Large-scale textures (Figure 2) first appeared accidentally and were further obtained purposefully.[1] They were found to arise along a variety of experimental routes. The essentials are as follows.

Liquid crystalline polymers are highly orientable even while in the isotropic state. Any accidental flow, as created by, e.g., combined sliding and pressing of a coverslip onto a sandwiched liquid layer (common in microscopy) can produce complex orientation resulting in correspondingly complex birefringent patterns (the "large-scale texture"). When pressure and/or shear ceases the orientation will decay in

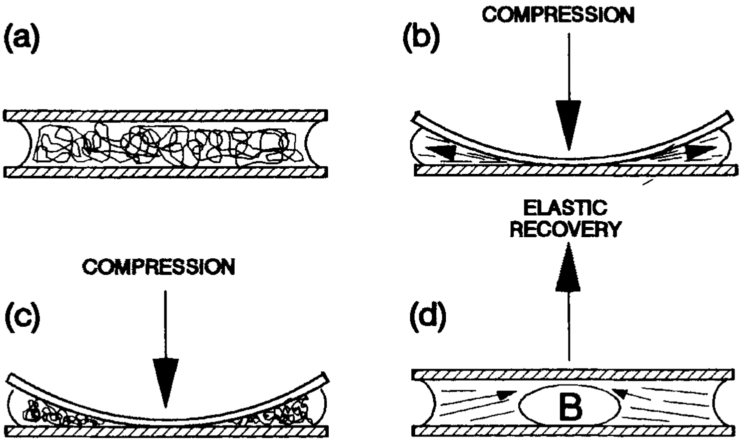

FIGURE 3 Scheme of single stages of the experimental procedure; (a) before compression in the isotropic state, (b) after compression (polymer oriented by flow directed radially out of the pressure centre), (c) under compression (stretched chains relax) and (d) after pressure removal (polymer reoriented by flow directed radially back to the centre). Arrows inside the film show the direction of flow, B denotes possible formation of vacuum bubbles.

time. If at the same time the sample is being cooled, the strained and relaxing polymer will pass through the isotropic-nematic transition. The flow-induced order may persist in the nematic region if a sufficiently fast cooling rate (quenching) has been applied, or fully relax before the transition has been reached at slow cooling.

In the first case the isotropic-nematic transition will develop a new fine scale texture. This, however, does not affect the overall appearance of the overlying large-scale pattern as seen between crossed polarisers at low magnification. Orientational order on both levels can be preserved on further cooling into the crystalline (or, alternatively, glassy) state which will freeze in the preexisting birefringent pattern without creating new features of its own at least on the scale of the polarizing microscope.

In the second case, i.e., when the flow-induced orientation has been allowed to relax before reaching the nematic region, the characteristic randomized polydomain texture appears without any trace of the previous large-scale order. This is contrary to Reference 1, where a reappearance of large scale textures was erroneously interpreted as if the isotropic-nematic transition itself "developed" a latent image of the preexisting large scale texture. This inference was based on failing to recognize another factor to which we shall now turn.

Stresses arising in the sample after cessation of compression applied to the coverslip will give rise to a radial shrinkage of the still fluid polymer film, initially thinned down by the compression (Figure 3). The shrinkage then creates its own strain field and the corresponding large-scale birefringent pattern. The decompression effect (Figure 3d) can take place either after the orientation due to the primary compression (Figure 3b) has relaxed§ (Figure 3c) or before; in the latter case, the compression and decompression effects will compound and give rise to large-scale

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§This case must have pertained in Reference 1.

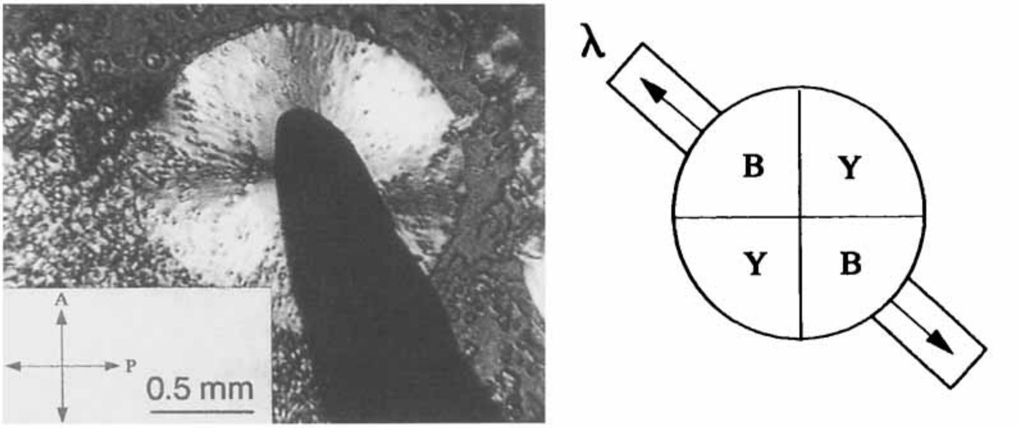

FIGURE 4 Circular Maltese cross pattern in PHMS 5 under compression by a sharp tip in the isotropic state. Optical micrograph between crossed polars (left) and a scheme showing colours (B—blue, Y—yellow) in separate quadrants with a unit wavelength retardation plate inserted (right). Flow direction radial from the centre of the cross.

texture as well. Unrecognized this effect could give rise to serious misinterpretations, hence our justification for looking into the matter in some length.

To illustrate this Figure 4 shows a circularly symmetrical strain pattern which arises under compression by a sharp tip while in the isotropic state. The pattern with Maltese cross brushes coinciding with the directions of the polarisers. Obviously, squeezing of the coverslips causes the melt to flow out from the pressure centre as demonstrated in Figure 3b. This gives rise to local orientation (compression-induced flow). The largest polarizability was radial, i.e., birefringence of the pattern was positive in terms of spherulite nomenclature.||

Figure 4 represents the simplest strain pattern in a real situation. However, in most cases the compression is not centred on a single point and also the coverslips can slip past each other causing the polymer to shear. Such a complex procedure then will bring about a multiaxial, multicentered diverging (or converging) flow field, generating the typical large-scale textures which originally attracted our attention in Reference 1. If these patterns are allowed to decay, still under compression, they may reappear, as stated in the foregoing, on subsequent decompression. This is often accompanied by bubble formation (Figure 3d) and leads to textures such as in Figure 5. The bubbles may act as local centres of the reverse flow during uneven shrinkage.

The large scale textures are a striking manifestation of high orientability of liquid crystalline polymers even in the isotropic state. Moreover, the orientation patterns correspond to vector flow fields which, just like the director fields intrinsic to liquid crystallinity, display their own disclinations on the correspondingly larger scale. In

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||(*) In terms of molecules, positive birefringence normally indicates radial molecular orientation. Although large polarizability across the chain can produce positive spherulites even with tangential chain arrangement (e.g. Nylons), with radial flow the presumption of radial chain orientation seems justified.

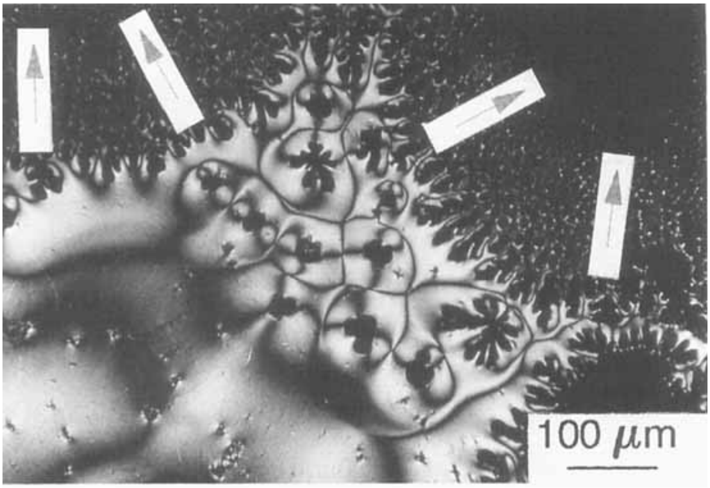

FIGURE 5 Low magnification optical micrograph of a quenched sample showing centre points of compression. Arrows denote average directions of flow after pressure removal. PHMS5, starting film thickness ca 15 μm.

Reference 1 some of these patterns were already classified in accordance with the Frank notation.[4] Further analysis will be provided in Part II.

Fine-Scale Texture and Its Relation to the Large-Scale Texture

As already indicated, as soon as a sample has passed into the nematic region, the true fine nematic texture develops within the large-scale orientation, creating a two-tier structure with corresponding long and short-range order. The two are not independent; the nematic arrangement must conform to the preexisting flow-induced order and the appearance of the large-scale effects (e.g., the dark brushes) is influenced by their substructure, this will be discussed in Part II.

Figures 6 and 7 provide examples of the two-tier hierarchy, large dark brushes and fine nematic striations and mottles are apparent.

Figures 6a and 6b show the effect of relaxation on the large scale when a sample is held in the nematic region. The existing flow-induced orientation gradually decays (the dark brushes fade) while the fine nematic texture becomes more apparent. We can now explain retrospectively the "grainy" background described in Reference 1: namely, it corresponds to a texture of genuine nematic nature formed at an advanced stage of relaxation of the strain field created previously in the isotropic state.

Figure 7 shows an example of textures within a bubble interior. The accidental presence of bubbles was found useful for studying the effect of film thickness on relaxation of the long-range order; it is immediately apparent that decay of the large-scale orientation is much slower in the thinner film within the bubble (the brushes in surrounding regions decay much faster). This may be due to higher chain mobility in the thicker film compared to the thin parts.[5]

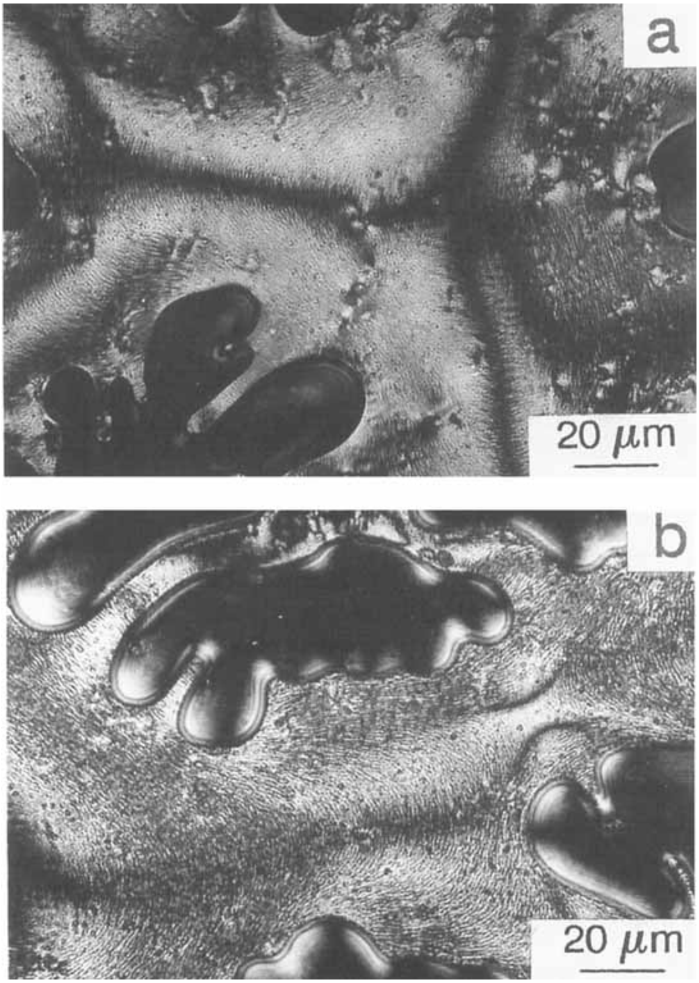

FIGURE 6 Decay of extinction brushes due to relaxation in the nematic state. Holding time is (a) immediately quenched, (b) 20 sec.

The Effect of Molecular Weight

The phenomenon of large scale texture formation was observed with each of the grades summarized in Table I, irrespective of their molecular weight. Even the lowest molecular-weight grade employed (PHMS1) having only a few repeating units per chain, was found to form large scale textures using the above procedure. However, the long-range order could not be successfully preserved at room temperature because of the low T_{NC} of this oligomer. As relaxation is generally faster with lower molecular-weight polymers preservation of textures in these materials requires higher quenching rates.

It follows from the above that the ability of polymers to form large scale textures is not confined to the highest molecular weights as reported (Reference 1, Figure

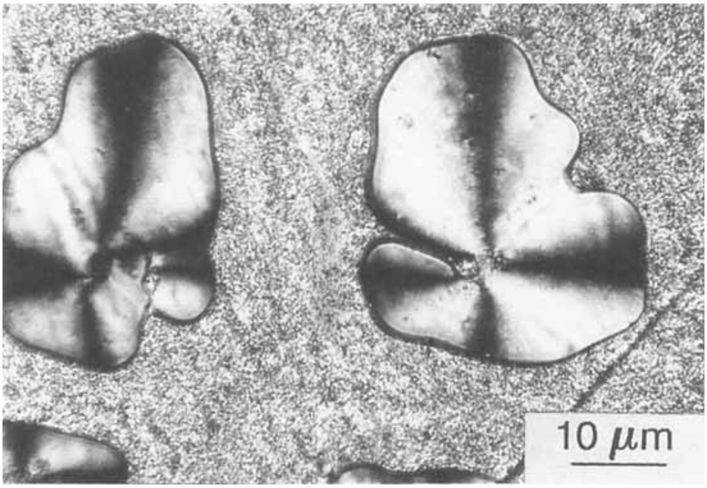

FIGURE 7 Examples of bubbles showing slower relaxation in thinner film within bubble interior.

11). All molecular weights can give it but the time scale of the treatment sequence, such as in Figure 3, must be shorter for the lower molecular weights. This of course means that the effects in question will be more readily observable for high molecular weight material in accord with Reference 1.

CONCLUSIONS

In summary, the large-scale textures result from multiaxial strain fields in the isotropic state, frozen in by crystallization or vitrification. The strain fields may arise through both compression and subsequent decompression during the usual sample preparation. These considerations are generally applicable to all orientable materials and apply particularly to liquid crystalline polymers because of their ready orientability even in the isotropic state. These effects may be the source of serious misinterpretations and are of relevance to structures arising during processing.

The fine substructure arises due to nematic self-ordering within the large-scale texture to which it conforms geometrically. The precise nature of this two-tier texture is determined by the interplay between the relaxation of the long-range orientation and the formation of the fine nematic texture.

The formation of the large scale textures was not found to be molecular weight limited.

Acknowledgment

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