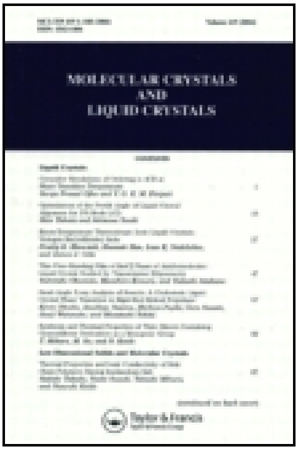

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Evidence for the Appearance of Disclinations under Shear in the Isotropic State of Liquid Crystal Forming Polymers

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Evidence for the Appearance of Disclinations under Shear in the Isotropic State of Liquid Crystal Forming Polymers

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The unexpected title phenomenon, here described, has arisen in the course of the investigation of the light microscopic texture of the liquid crystal (LC) forming family of polymers, poly-4,4′-dihydroxy-α-methylstilbene with aliphatic spacers.

In common with most liquid crystal polymers (LCPs) the above polymers normally display only a grainy LC texture, becoming increasingly fine with increasing molecular weight. However, after having been sheared and allowed to relax while in the isotropic state (realizable with these thermotropic polymers), and subsequently cooled below the isotropization temperature, rather strikingly, a large scale birefringent texture developed, such as is normally observed for the nematic state of small molecular LCs, displaying disclinations with extinction brushes extending to over distances of hundreds of μm. Within this large scale texture, a finer scale graininess was apparent which indicates that the orientation producing the effect is not directly due to a "liquid crystalline" arrangement of the molecular directors, but to the alignment of the same fine grain units as those normally present in the nematic state without a preceding shear in the isotropic state.

As yet we do not understand the role of shearing; it is obvious nevertheless that a skeleton of the disclination-containing structure must have existed within the isotropic state itself and has developed to full visibility when cooled into the nematic state. Implications for the whole LCP field include the molecular arrangement in isotropic melts, memory effects and flow behaviour, and this also calls for retrospective reviewing of some past reports on LCP textures.

Keywords: disclinations, vortices, shear flow, polymer melt rheology, optical textures, liquid crystal polymers

INTRODUCTION

The polarising optical image has been the principal hall-mark of the liquid crystalline state by which it has been discovered and identified historically, and which ever

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since has been the basis for its classification, providing the starting point for its more intimate, molecular characterization. While this has been unconditionally so for traditional low molecular weight LCs, the same light optical criteria were in general not equally effectively transferable to LCPs, at least to their thermotropic variety which are particularly topical at present as potential structural materials. The reason lies in the ever decreasing scale of the optically discernible structure features with increasing molecular weight (MW). For thermotropic main chain LCPs of representative polymeric MW, usually only a fine scale mottling is apparent (of say 1–3 μm) (see e.g. Figure 1) which, particularly as superposed on each other in film thicknesses normally used for polarising light optical (POL) examinations, precludes detailed study or even conclusive detection. In the present state of knowledge, the fine grains seen are believed to correspond to regions of uniform orientation correlation within nematic structures, bounded by disclinations. Even, as for example our own work has shown,[1] if this texture can be developed (coarsened) by heat annealing in the nematic state (Figure 2), the resulting increased size range still remains within only several microns and does not even approach the scale of texture observed for small molecular LCs.

We encountered this effect in the study of thermotropic polyethers. Inexplicably (at the time) the largest POL textures (on the scale of hundreds of micrometers)

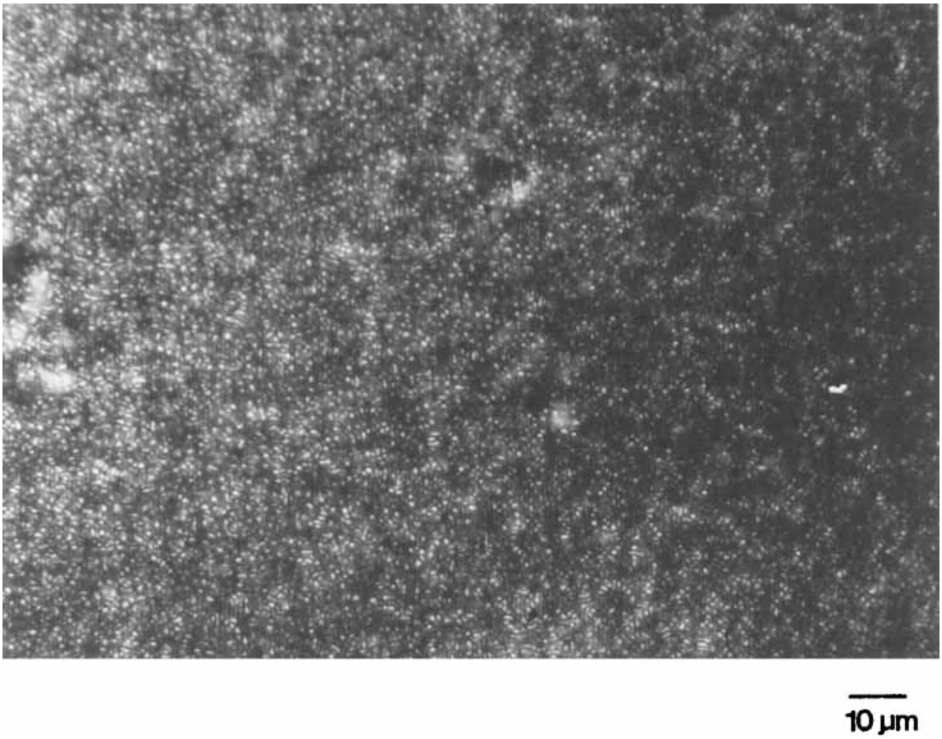


FIGURE 1 Dense disclination texture in copolymer PHMS-517 (1:1), M_n = 32,700, as seen under the polarizing microscope.

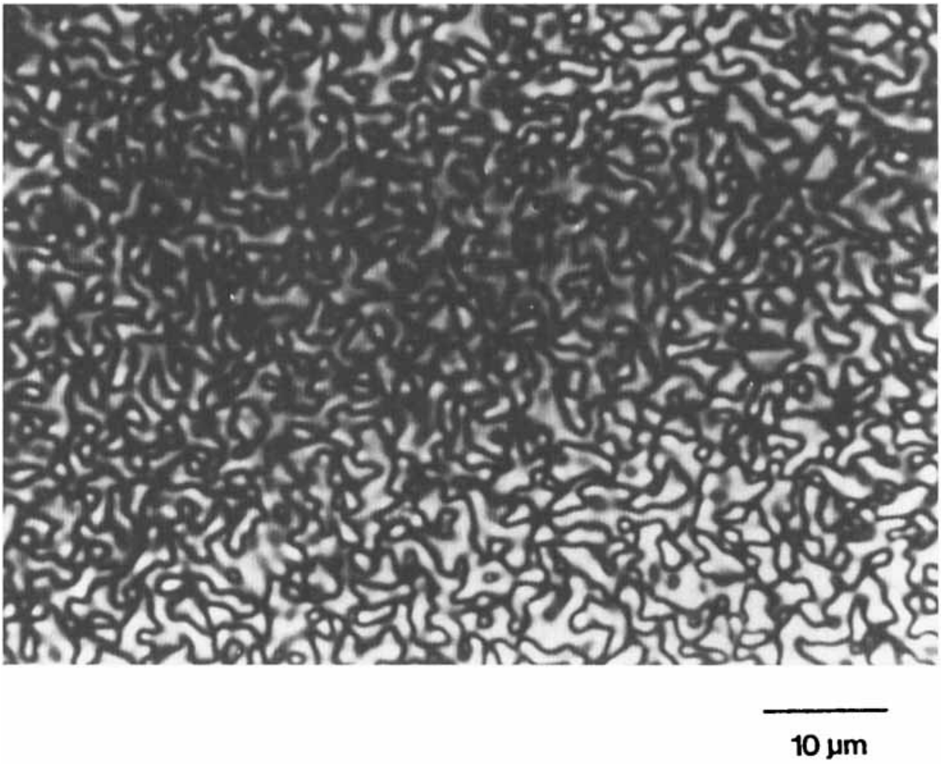


FIGURE 2 The same as in Figure 1, but after annealing in the nematic state.

appeared in materials of the highest MWs used, contradicting the general trend, otherwise observed also by ourselves, that the scale of the textures decreases with increasing MW. Figure 3 (compare with Figure 1) shows one example. However, at first, we could not reproduce these features, until the important part played by a new factor had been recognized. The purpose of this note is to announce the recognition just indicated, in particular the observation of disclinations in sheared isotropic melts and their frozen in versions in the nematic and crystalline states. We believe this could be significant even merely as an observational record, as it could influence preparative procedures and circumscribe the scope of what may be deduced from POL observations in this whole field. Additionally, however, we hope that the observations here reported point to new, so far unrecognized features of LCPs which, when adequately interpreted, will contribute to their understanding and utilization.

MATERIALS

The materials were polyethers constituted by a mesogenic α-methylstilbene and flexible alkyl spacers linked through the ether oxygens of the formula below.[2]

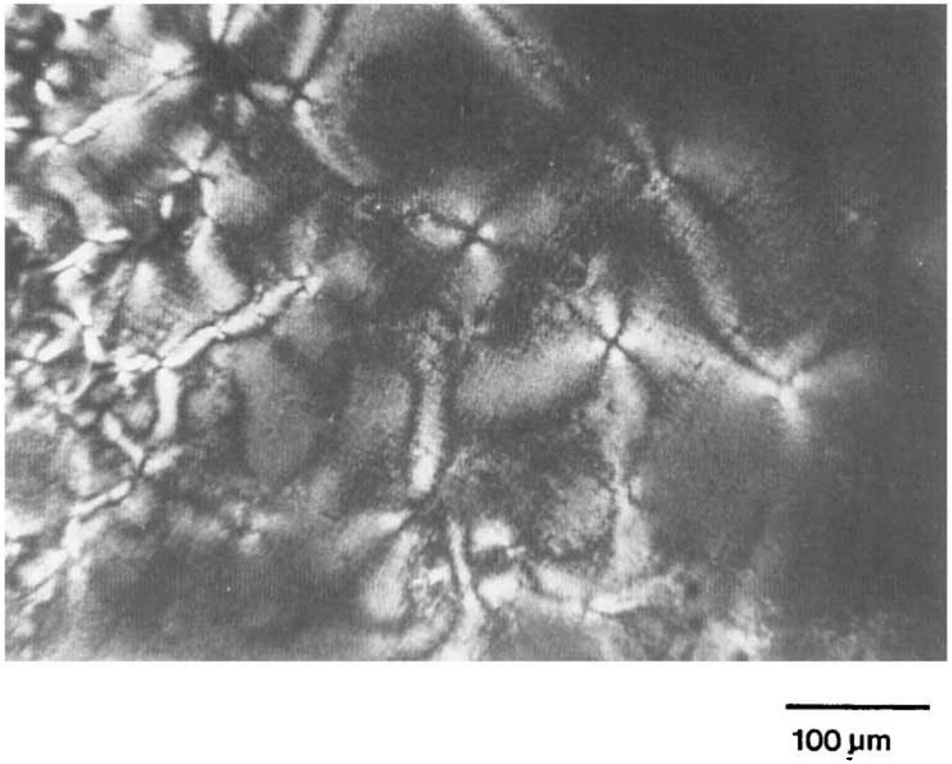
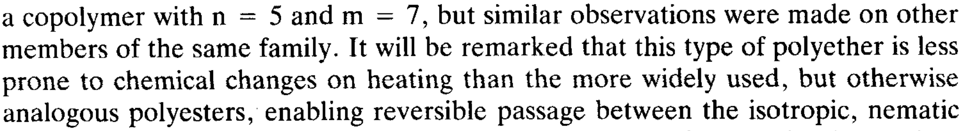


FIGURE 3 Large scale texture in copolymer PHMS-517, as seen under the polarizing microscope.



Here n and m are variables determined by the synthesis. The case of n = m corresponds to a homopolymer, and that of n ≠ m to a random copolymer of two different flexible spacer lengths. The experimental results reported here relate to a copolymer with n = 5 and m = 7, but similar observations were made on other members of the same family. It will be remarked that this type of polyether is less prone to chemical changes on heating than the more widely used, but otherwise analogous polyesters, enabling reversible passage between the isotropic, nematic and crystalline states. Also, due to the particular route of synthesis, the random copolymeric nature of the product is guaranteed, again in contrast to the usual polyesters.[3] In brief, we have here both a stable and well-defined chemistry. While a range of MWs was used throughout the work, in the illustrations quoted $\overline{M}_n$ was 32,700 with $\overline{M}_w/\overline{M}_n = 2$.

EXPERIMENTAL PROCEDURE

The samples studied were in the form of films cast from solvent on a microscope slide. This method was adopted originally to ensure uniform film thickness which was *ca.* 10μm in the different preparations. The observations were made using a hot stage mounted on a polarising microscope. The relevant transition temperatures were known from previous calorimetric work. These are in ascending order, glass transition T_g = 35°C; crystal melting point (highest achievable) T_m^o = 110°C; isotropization temperature (highest achievable, i.e., equilibrium—see Reference 1) T_i^0 = 190°C.

In the standard procedure, the sample was heated above T_i^0, i.e. to the isotropic state, then cooled into the nematic range (i.e. to between T_i^0 and T_m^0 or into the crystalline range (below T_m^o). POL observations were made *in situ* in all these ranges. The effects seen in the nematic or crystalline ranges were indistinguishable, corresponding to the textures displayed in the nematic range. This is a reflection of the fact that the overall nematic texture is retained on crystallization, or conversely, that the crystalline texture remains indistinguishable from the nematic one on the scale of the POL observations, which in turn means, that the occurrence of crystallization cannot be detected by POL observations alone. It needs stressing that this is a characteristic of the present comparatively high MW material; in low MW LCPs of the same family (e.g., MW = 1800), just as in small molecular LCs, below T_m^o, the crystals are seen as distinct entities growing within a nematic background. The difference of behaviour with MW is clearly due to the decrease in chain mobility with increasing MW through which the memory of the preceding nematic texture is retained even in the crystalline state. While this is an important finding in itself (possibly already noted in previous LCP work), it affects this note in as far that in what follows we need not distinguish between photographs taken in the nematic and crystalline states, as on the POL scale the images are the same for a given sample.

The actual observations to be reported have been selected from wide ranging experimental observations (best seen or recorded on video) in service of the point made in the Introduction.

EXPERIMENTAL OBSERVATIONS

As implied by the foregoing, the new recognition arose from the confluence of three lines of initially separate work involving the polyethers: the effects on the POL image of MW, of prehistory (i.e., non equilibrium states[1]) and of shear. Combined, they led to the recognition that the large scale POL structure such as that in Figure 3 can be systematically obtained in the nematic state, provided the MW is sufficiently high, and the sample has been subjected to shear while in the preceding isotropic state (Figure 4). In the first stages, the shear applied was unidirectional (cover glasses were slid in relation to each other), but through subsequent findings, uniaxial compression (squeezing of the slides) against each other alone sufficed. Clearly in the latter case the *shear* produced by the compression must have been operative in bringing about the effect in question.

The procedure leading to a texture like that in Fig. 4 was as follows: 1) heating the cast film into the isotropic region to a temperature T where $T > T_i^0$ (T = 220°C); 2) shearing at T (slide or squeeze cover glasses) at this stage an overall birefringence appears at T; 3) holding at T, when the birefringence is seen to decay

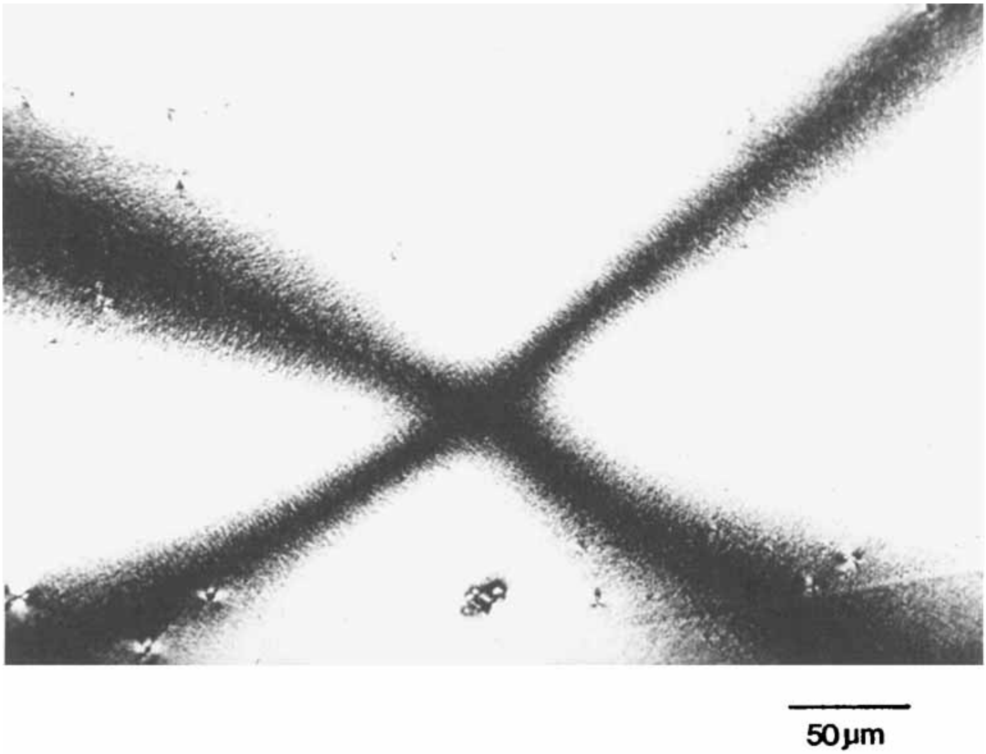


FIGURE 4 Typical optical image, viewed between crossed polarisers, of a PHMS-5,7 sample heated to the isotropic state (220°C), pressed while in the isotropic state and cooled to room temperature.

in a few seconds, but not before displaying large scale extinction brushes prior to its final disappearance; 4) cooling below T_i^0 (as said before it makes no difference to the POL image whether cooling stops in the nematic or crystalline ranges), when large scale extinction brushes, such as those seen transiently in the preceding isotropic state, reappear, but this time are there to stay.

Images as in Figure 4 clearly indicate nematic structures, with brushes as markers of disclinations. This was tested by rotation of the sample in relation to the polariser/analyser direction. In this way disclinations of $s = 1$ and of $s = \frac{1}{2}$ (Figure 5) were readily identified. Thus, by observing the POL images such as those in Figures 3–5, there would be no reason to suppose that we are not viewing conventional nematic textures on the scale usual in small MW materials, but in this case in (comparatively) high MW thermotropic polymeric materials.

Unlike the texture observed in the isotropic state soon after shearing, the large scale patterns in Figures 3–5, i.e., those which reappear on cooling below T_i, do not seem to represent the elementary textural units any more, but rather a super-texture. Thus the higher magnification images of these re-emerged patterns reveal a grainy domain texture underlying the large scale POL texture (Figure 6). This graininess, best visible within the dark brushes themselves, is on the scale of 1–3µm, and hence on that of the usual dense disinclination texture[5] in LCP samples

FIGURE 5 Large scale structures (brushes) showing disclinations of strength $s = 1$ (full arrow) and $s = \frac{1}{2}$ (half arrow).

which have not been pretreated in the isotropic state (see Figure 1). Its prominence can vary from sample to sample. Figure 7 shows an example where the combination of large brush and fine grain is particularly evident. In particular, the prominence of the grains is a function of holding time in the isotropic state (step 3 above), where this holding time itself is a function of MW. For the highest MW sample (32,700) the holding time (within the limits permitted by thermal stability) had hardly any noticeable effect, while for the lower MW of 11000, the graininess became increasingly prominent on longer holding in the preceding isotropic state. This was increasingly at the expense of the large scale brushes, until on protracted holding (e.g., over tens of seconds), the dense disclination texture alone remained. Thus, for the low MWs, the large scale textures, resulting from the pretreatment in the isotropic state, may easily be missed, emphasizing the MW dependence of the whole effect as already indicated.

The existence of grains clearly indicates that the large scale brush structure is not *directly* the consequence of the parallelisation of the molecular directors over the corresponding areas. Rather, these directors are in the first place organized over smaller scale domains, possibly defined by a correspondingly fine scale disclination network. These grains themselves have then common orientations on a larger dimensional level, giving rise to the large scale brush texture, the subject of

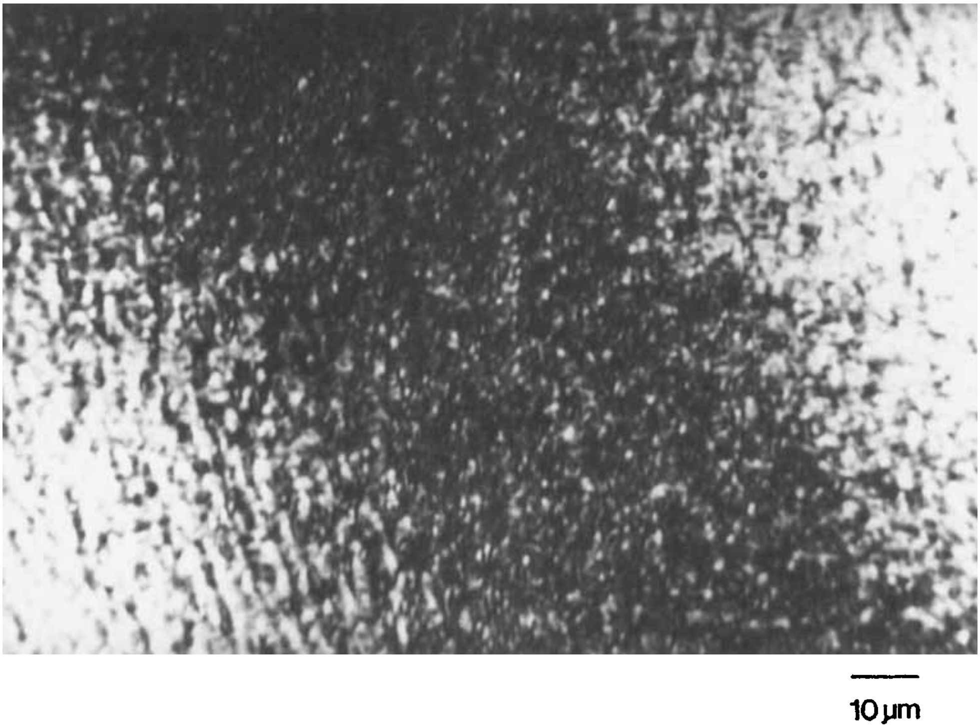


FIGURE 6 Dense disclination texture underlying the large POL texture in Fig. 5, revealed at increasing magnification.

our investigation. Thus, so it seems, we have uncovered a two-stage structure hierarchy in LCPs: the primary grain texture, and a larger scale organization of these grains—a kind of supertexture. The former seems to correspond to the previously described and commonly observed dense disclination texture, while the hitherto elusive supertexture, seen only occasionally in the past, seems to arise through a further, longer range organization of the dense disclination texture as an overlay on the primary structure.

A further feature to note is the effect of the bubbles present in profusion (e.g., Figure 5). Bubbles are usually the centre points of extinction brushes, and hence clearly can initiate such extinction patterns. Yet it is important to note that they are not a necessary condition for the existence of the latter. There are many clearly defined brushes without any visible bubbles at their centres, and they represent disclinations in the usual sense.

DISCUSSION

Observational consequences

Irrespective of the significance of such textures and their basic source of origin, we hope that the purely observational results as they stand should be helpful for

FIGURE 7 Combination of large POL texture and dense disclination texture in PHMS-5/7.

LCP research. In the first place, when and as required, we are now in a position to provide a recipe for producing these textures. The scheme outlined here may well be general, except that for different compounds some of the parameters would need to be adjusted, e.g., the ratio of MW and holding time. Secondly, our findings may well invite rescrutiny of past reports and observations on such large scale textures, as to how far they may have been dependent on pretreatment in the isotropic state, and further, how far they correspond to secondary structures resulting from organization of primary 'grains.' The latter point, i.e., the recognition of an (at least) two-tier hierarchy, is likely to have many further forward-looking, and possibly retrospective consequences on which we refrain to speculate further at this stage.

Origin of large scale texture

The most surprising aspect of the present findings is that the structures in question originate from the treatment the samples have received *in the isotropic state.* This necessarily implies that the corresponding structures must have been created while in the isotropic melt. Indeed the birefringent pattern fleetingly observed after compression does, before its disappearance, possess features of images such as those eventually displayed in a lasting manner by the nematic state after cooling. The question clearly arises as to what these textures are, and secondly why do they reappear on cooling and then only under certain circumstances?

The molecules in question are semi-rigid. This means in the first place that they always possess some localized orientational correlation, and secondly, and chiefly, that such short range orientational correlation can be readily extended over macroscopic volumes under externally imposed orienting influences. This is evidenced by the ready development of uniform birefringence on even slight shear or pressure, such as would hardly cause any visible effect in the case of the usual fully flexible polymers. This birefringence rapidly disappears after cessation of the flow, through stages which display large scale brush/disinclination textures. It is the vestiges of this latter, partially relaxed structure which must have remained in the isotropic state in order for them to reappear on cooling below T_i.

At present we can only speculate on the mechanism by which the memory of the large-scale texture is preserved in the isotropic state after the birefringence has disappeared. One possibility is that the memory is carried predominantly by the highest molecular weight fraction. Namely, the orientational relaxation of the longest molecules is expected to be the slowest which, in general terms, is responsible for the increasingly pronounced memory effects in high molecular weight materials.[5] In the present instance, we may assume that the longest species in the molecular weight distribution retain the long-range orientational correlation created by the shear, while the rest of the molecules disorient. The former, being small in number, will not produce a registerable effect in themselves. However, they may serve to provide preferential orientation to the nematic domains growing below T_i. In support of this suggestion, we recall the well established fact that T_i of a high MW polymer is higher than that of a low MW polymer.[6] In addition, nematic self-ordering is expected to be nucleated by the highest MW molecules upon cooling through the T_i range. This fact is illustrated, e.g., by the biphasic nature of a polydisperse polymer in equilibrium in the T_i range.[7] Hence the average domain orientation in a given area could be predetermined by the remaining preferential orientation of the high MW component. Accordingly the role of the nematic state would be to 'develop' a latent 'texture,' present to begin with, to full visibility. The scheme just outlined would account for the sequence of events observed, including the requirement of high molecular weight (which would thus serve to retain the memory in the isotropic state).

It is evident that shear-induced orientation is the factor responsible for the long-range order under discussion. It seems to matter little as to whether this shear is unidirectional or multidirectional as would arise by compression. The overall final textures seem to bear no obvious relation to the orientation caused by the shear initially. It seems that it reflects, not the initial, but a relaxed texture as indeed seen transiently within the isotropic melt while the shear induced birefringence decays. Beyond stating the above, we are not in a position to be more specific at this stage.

An important outcome of this work, we believe, is the realization that the changes in orientation in any continuous phase made up of reasonably rigid anisotropic objects imply the existence of disclinations. This must be true irrespective of whether we have a nematic liquid crystal, i.e., a self-ordered system, or an intrinsically isotropic melt which has attained preferential molecular orientation through the action of an external field such as a flow field. The combined effects of such a field and slow overall relaxation due to high molecular length may lead to unusual transient non-equilibrium states of which the present coarse texture 'isotropic' state appears to be an example. While the current observations raise a number of unanswered questions, they seem to illustrate a wider generality of the curvature elasticity theory[8,9]; the principle of the latter, i.e., the minimization of the splay, bend and twist elastic energies through disclinations, as usually seen in the self-ordered nematics, ought also to apply to systems which have been oriented through external action. The necessity of disclinations will arise as long as some directionality is associated with a given position in sample space in an orientationally non-uniform but otherwise continuous structure.[10] In this sense, the features identified, e.g., in Figures 4 and 5 are true disclinations. We consider the extension of the disclination concept to, what is thermodynamically an isotropic phase, as one of the notable outcomes of this work. The disclinations could be present on any scale. In this respect the large scale of the features in Figs. 3 and 4 merely serves to make the effects in question conspicuously apparent.

To end with, we remark that the shear or pressing treatment when applied in the nematic state did not produce the above effects. Unidirectional shear of course produces strong unidirectional orientation which relaxes via the conspicuous, but familiar regular banding effect, into the initial fine grained texture. Neither did compression have any lasting effect on the final relaxed nematic texture. It appears that the long range orientation effect in question can only be attained from the initially isotropic true melt.

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References

1. J. L. Feijoo, G. Ungar, A. J. Owen, A. Keller and V. Percec, *Mol. Cryst. Liq. Cryst.*, **155**, 487 (1988).
2. T. Shaffer and V. Percec, *Makromol. Chem. Rapid Commun.*, **6**, 97 (1985).
3. G. Chen and R. W. Lenz, *Polymer*, **26**, 1307 (1985).
4. N. J. Alderman and M. R. Mackley, *Faraday Discuss. Chem. Soc.*, **79**, 149 (1985).
5. M. Doi and S. F. Edwards, "*The Theory of Polymer Dynamics.*" Oxford Science Publication, Clarendon Press, Oxford (1986).
6. A. Blumstein, S. Vilasagar, S. Ponrathnam, S. B. Clough and R. B. Blumstein. *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 877 (1982).
7. J. F. d'Allest, P. Sixou, A. Blumstein and R. B. Blumstein, *Mol. Cryst. Liq. Cryst.*, **157**, 229 (1988).
8. C. W. Oseen, *Trans. Faraday Soc.*, **29**, 883 (1933).
9. F. C. Frank, *Discuss. Faraday Soc.*, **25**, 19 (1958).
10. W. Pechold and S. Blasenbrey, *Angew. Makromol. Chem.*, **22**, 3, (1972).