Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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Online publication date: 06 August 2010

To cite this Article Binet, C. , Mitov, M. , Boudet, A. , Mauzac, M. and Sopena, P.(1999) 'PDLC-like patterns at the isotropic to cholesteric transition entrapped by in situ photopolymerization', Liquid Crystals, 26: 12, 1735 — 1741
To link to this Article: DOI: 10.1080/026782999203355
URL: http://dx.doi.org/10.1080/026782999203355

LIQUID CRYSTALS, 1999, VOL. 26, NO. 12, 1735–1741

PDLC-like patterns at the isotropic to cholesteric transition entrapped by *in situ* photopolymerization

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(*Received 30 April 1999; accepted 16 July 1999*)

When investigated by optical microscopy between crossed polarizers, the isotropic to cholesteric transition may appear like fingerprint-patterned droplets embedded in a black isotropic matrix. In the present work, such PDLC-like (polymer dispersed liquid crystal) patterns, only occurring over 0.7°C, have been entrapped and stored at ambient temperature in a polymer film. We used a UV polymerization process with different sequences in which illumination time and UV power progressively vary. From a conceptual viewpoint, these PDLC-like patterns come solely from liquid crystalline material, whereas all the conventional PDLCs are binary mixtures of a macromolecular compound or 'prepolymer' with a conventional low molecular mass liquid crystal. The fact that isotropic matrix and cholesteric droplets differ only from the viewpoint of molecular order and not in their chemical nature, permits comparisons with the usual case for which the choice of polymer-forming material is crucial and the polymer/liquid crystal interface is an important factor for controlling PDLC electro-optic properties. The present system gives an opportunity to investigate by scanning electron microscopy (SEM) the droplet microstructure (isotropic–cholesteric interface, fingerprint patterns or defects), whereas previous SEM studies were focused on the shape and size of empty cavities, since the fluid liquid crystal was inevitably removed from the PDLC system.

1. Introduction

Dispersion of liquid crystal (LC) droplets in the isotropic phase is a very old subject of interest in LC research since Lehmann [1] and Friedel [2] studied by optical polarization microscopy the behaviour of cholesteryl benzoate at the clearing point. In the 1980s, Fergason [3] and Doane *et al.* [4] proposed a new polymer–LC composite material made of nematic droplets embedded in an amorphous polymer film. By using an electric field, these polymer dispersed liquid crystal (PDLC) systems can be switched between scattering (OFF) and transparent (ON) optical states (for reviews see [5] and [6]). PDLCs have given rise to numerous applications such as switchable films in windows, direct view flexible displays (no polarizers are required) or spatial light modulators [7].

Beyond the applied research aspects of PDLCs, the confinement of LC to small cavities gives rise to very interesting fundamental problems. Dispersions of LC can be produced either from emulsions by encapsulation of LC with a hydrophilic polymer [3] or by phase separation [4]. Considerable research has been devoted to this last process in which a homogeneous blend of LC and 'prepolymer' is prepared and then polymerized by UV light or by heat; as the polymer forms, the LC is forced to phase separate by being less soluble in the polymer than in the 'prepolymer'. While the LC director distribution in the microdroplets depends on the LC properties and domain size, the chemical nature of the polymer-forming material is far more important and the polymer/LC interface is known to be an important factor for controlling electro-optic properties [5, 6].

Here we present a LC film with PDLC-like patterns coming solely from a chiral LC, whereas all the conventional PDLCs are binary mixtures. Cholesteric fingerprint-patterned droplets embedded in the isotropic phase are stored in a polymeric film by choosing a UV-curable material and establishing the relevant polymerization process. Isotropic matrix and cholesteric droplets are both solid and differ only from the viewpoint of molecular order and not in their chemical nature.

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Journal of Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 1999 Taylor & Francis Ltd
http://www.tandf.co.uk/JNLS/lct.htm
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The purpose of this paper is twofold. (i) To decide the polymerization process enabling us to store permanently at room temperature PDLC-like patterns intrinsic to the isotropic to cholesteric transition; these patterns existed at higher temperature than ambient temperature over a very short temperature range equal to a few tenths of a degree. It is shown that the success of pattern entrapping depends on the polymerization path followed. (ii) To investigate the cholesteric droplet microstructure by scanning electron microscopy (SEM), taking advantage of a fully polymerized biphasic film when previous SEM studies were devoted to investigating the shape and the size of empty cavities, since the fluid LC component was inevitably removed from the PDLC system.

2. Experimental

2.1. *Materials*

In order to achieve thermally stable polymerized films, LC monomers that have no mesophase in their polymeric state were chosen. The UV-curable LC material is an equimolar blend of two acrylate monomers without a spacer between the acryloyloxy group and the mesogenic core (mixture 'C' from Dainippon Ink & Chemicals, Inc.). The blend exhibits a nematic phase at room temperature and the nematic to isotropic transition is about 46.3°C [8]. Such a blend has been used for different retardation films with various types of molecular orientation [8]. For polymerization, 0.5 wt % of a photoinitiator ('Irgacure 907' from Ciba-Geigy) is added. The nematic LC is doped at 3 wt % with a chiral cyanobiphenyl ('CE1' from Merck (UK) Ltd) in order to obtain a large pitch chiral nematic phase (pitch in the micrometer range): the droplet size and the pitch are much larger than the wavelength of light, so that the texture can be first observed with an optical microscope. The polymorphism of the blend, determined by differential scanning calorimetry (DSC) during a temperature increase, is as follows: crystal–17.5°C–cholesteric–55.5°C–isotropic. The cholesteric LC is sandwiched between glass plates with any particular surface treatment. The sandwich-cell is put in a heating stage and optical textures are observed using crossed polarizers. We used a UV light curing system (ELC-403 from Electro-Lite Corp.) emitting at 365 nm with a maximum power of 50 mW cm^{-2}, measured with a UV intensity meter (ELC-365).

2.2. *Film preparation for SEM*

After polymerization, the sandwich-cell is plunged into liquid nitrogen in order to separate the two plates while minimizing plastic distortions of the polymeric material. The film is kept on one plate; observations of surface relief are thus made in the neighbourhood of the surface previously in contact with the cover glass plate. Then, the film is sputtered with a thin layer of gold and SEM observations are carried out using a Cambridge 250 microscope operating at 20 kV in the secondary electron imaging mode.

3. Results and discussion

3.1. *Optical microscopy textures*

Observations associated with the isotropic to cholesteric transition phenomena start from the isotropic phase at 70°C, which appears black. (i) Chiral patterns begin to appear at 57.2°C such as cholesteric droplets, embedded in an isotropic matrix, with periodic lines—having a

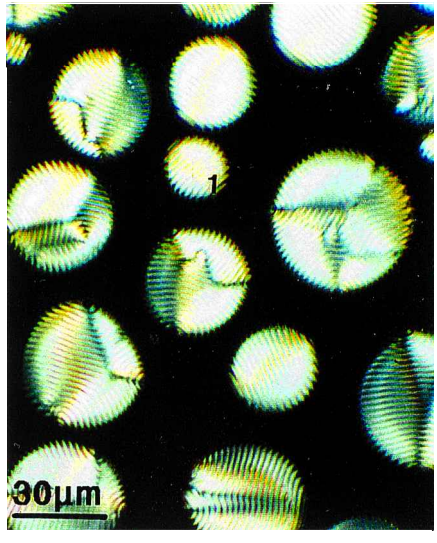

Figure 1. Cholesteric droplets embedded in a black isotropic matrix at the isotropic–cholesteric transition (57.2°C).

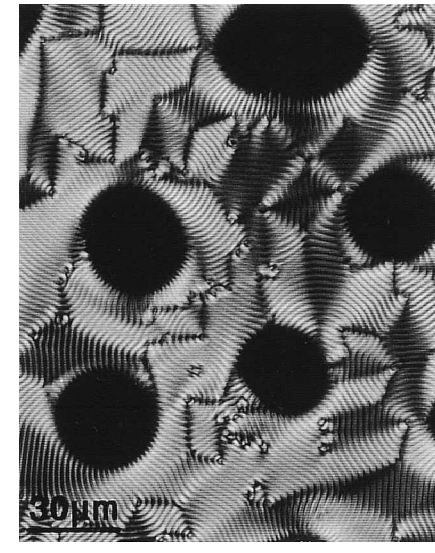

Figure 2. Inverse texture: isotropic droplets embedded in the cholesteric phase (56.5°C).

tendency to be perpendicular to the droplet surface—and typical defects (figure 1). These microdroplets are similar to those previously observed by light microscopy in chiral and biological materials [9–11]. Internal organizations of cholesteric droplets will be discussed in § 3.3. (ii) Droplets coalesce when the temperature continues to decrease, giving rise to the inverse texture at 56.5°C: black isotropic droplets embedded in a fingerprint-patterned matrix (figure 2). (iii) By about 56.2°C, the isotropic droplets have vanished: the sample now has a well known focal-conic cholesteric texture with fingerprint patterns which remains until room temperture (figure 3). Twice the value of the distance between two dark or bright lines gives an order of magnitude of the cholesteric pitch (the helix axis lying in the plane of observation), i.e. about 4.5 μm.

The isotropic to cholesteric transition, while exhibiting a biphasic state, occurs over only about 0.7°C. In the following section, we focus our investigations on the cholesteric droplets suspended in the isotropic phase.

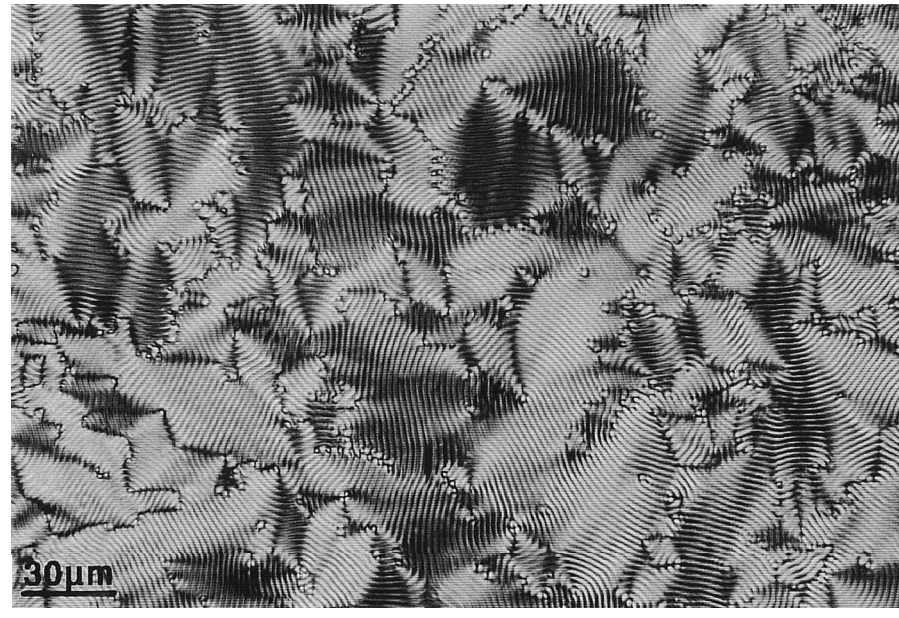

Figure 3. Focal-conic cholesteric texture with fingerprint patterns (25°C).

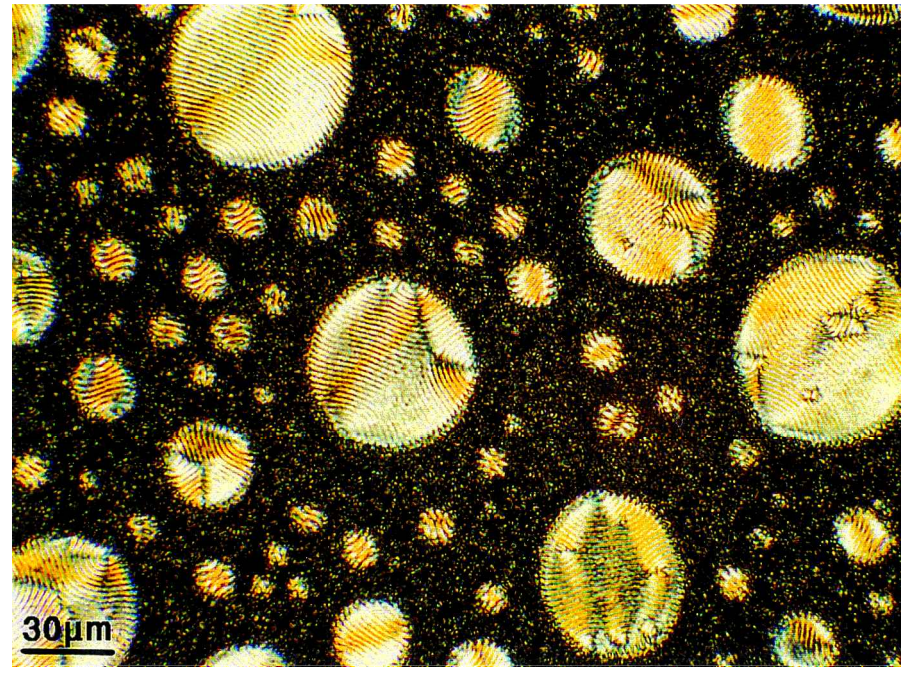

Figure 4. Cholesteric droplets embedded in the isotropic phase entrapped by UV polymerization (25°C).

3.2. *Photopolymerization process*

The objective was to entrap cholesteric droplets coexisting with the isotropic phase as soon as these patterns are thermally stabilized. The temperature was chosen equal to 56.8°C. Compared with polymerization by heat, the UV polymerization is vital here since there is a *sine qua non* requirement to keep thermostatted conditions. A first attempt consisted of irradiating the sample by a UV beam with an intensity equal to 30 mW cm^{-2} during one minute. Subsequent checking of the texture revealed that it was a homogeneous black texture which had been stored. The system was out of global equilibrium (but still near a properly defined local equilibrium) and the polymerization had occurred sharply inside the whole sample, leading it to an isotropic state. If the sample now experiences new temperature cycles, no texture transitions occur due to the fact that the polymer is not mesomorphic. Such a sudden process is therefore unsuitable for our purpose. Consequently, it was decided to polymerize gradually the sample exhibiting the desired biphasic texture by using UV illumination sequences as follows: (1) 10 mW cm^{-2} during 10 s; (2) 20 mW cm^{-2} during 20 s; (3) 30 mW cm^{-2} during 60 s; (4) 40 mW cm^{-2} during 60 s; (5) 50 mW cm^{-2} during 4 min (2 min on one side and 2 min on the other). The UV power per square centimeter of sample was progressively increased by decreasing the source–object distance. Sequence 5 was realized out of the heating stage at room temperature. The texture was monitored optically after every step. The patterns stayed identical at the end of the five sequences and at room temperature, as figure 4 shows it. By slowing the start of the polymerization process, the organization of the mesogenic cores inside the droplets can be fixed. The biphasic state, as well as fingerprint patterns are stored, even if the sample is heated or cooled again. The only microscopically visual consequence of the polymerization process lies in some granular aspects, especially visible in the black matrix; this might be due to some phenomena of anchoring and volume contraction arising during the polymerization. In contrast with the first route, a progressive polymerization was expected from this experimental method by involving a progressive structure entrapping.

Let us note that the photopolymerization process we describe borrows one characteristic from each of the two following classical methods of PDLC preparation [7]: (i) the film hardening is due to the UV polymerization as in PIPS (polymerization induced phase separation) but not the phase separation in itself; (ii) a temperature change leads the system to a biphasic state as in TIPS (thermally induced phase separation) but does not involve the film hardening.

The present process has a high reproducibility and gives the opportunity to store with high thermal stability the patterns intrinsic to the isotropic to cholesteric transition within a solid film. Besides, this would also be a convenient way to store a great variety of non-equilibrium patterns occurring in a reduced temperature range (instabilities, phase transition phenomena, ...) or induced by an electric or magnetic field [12].

3.3. *SEM investigations*

Figure 5 shows the SEM micrograph of cholesteric spherical inclusions in the non-patterned (isotropic) matrix. The same patterns as in light microscopy can be very clearly observed. They are also very similar to the droplet textures that we analysed by transmission electron microscopy (TEM) in a previous report [13] in which cholesteric droplets in a glassy solid state were embedded in a matrix made of photocrosslinked amorphous polymer—a classical PDLC system—and observed in three dimensions through a successive ultramicrotomed sectioning technique and 3D-image reconstruction. In these images, the cholesteric stratification was made evident by bright and dark lines due to the diffraction contrast. The cholesteric structure appeared as the result of competition between inherent elastic forces and anchoring surface forces. The result was a more or less curved cholesteric stratification accommodated with a small number of disclinations (0 to 4).

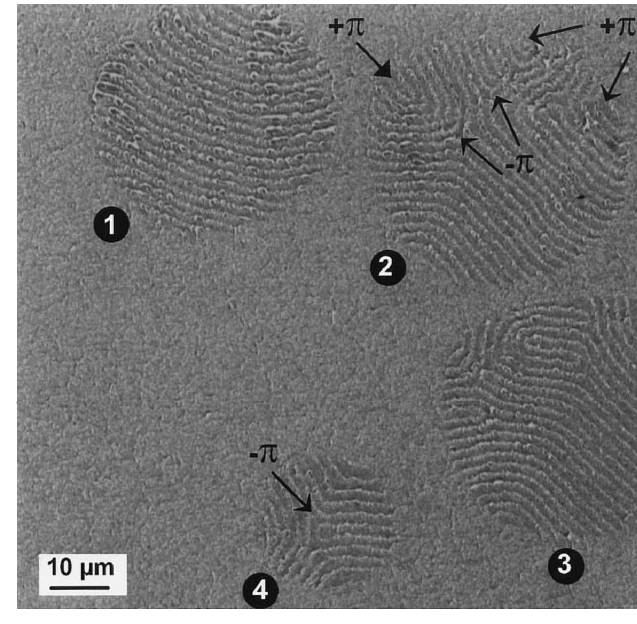

Figure 5. SEM micrograph of cholesteric droplets embedded in the isotropic phase.

In the present investigation of cholesteric droplets in a matrix of the same chemical nature as the droplets, most diameters lie statistically between 5 and 25 μm, although varying overall between 3 and 60 μm (between 0.4 and 6 μm in the TEM study [13]). The line periodicity is independent of the droplet diameter, but different droplet structures are observed depending on the value of the confinement ratio C. C is defined as equal to d/p where d is the droplet diameter and p the natural cholesteric pitch corresponding to a helicoidal structure developed in a free volume. For example, for $C < 1$, although a thermodynamically stable mesomorphic state might be reached, no fingerprint patterns would be observed as a consequence of frustration effects coming from competition between surface forces and elastic forces which attempt to limit the development of a helicoidal structure.

In the cases we describe, where $C > 1$, the textures are similar to those noticed in our previous work on a classical PDLC [13]. For the smallest diameters (between 5 and 20 μm), the striations are almost parallel over the whole droplet and could also be seen in light microscopy (as in droplet 1 in figure 1, but also in numerous small droplets in figure 4); as an experimental fact, the smallest droplets show parallel stripes with no defects in the bulk, which might be important from the viewpoint of the balance of surface and bulk energies.

Greater diameters give more freedom to the boundary forces to compel the striations to lie perpendicularly to the surface and to produce very typical cholesteric defects—the same disclinations already noticed in classical PDLCs. The cholesteric stratification is more or less curved as in conics, with a focus either inside (droplets 2, 3 and 4 in figure 5) or outside (droplet 1 in figure 5) the droplet. In the former case, a focus involves a defect. A droplet can exhibit several foci. Droplet 2 has four foci (three foci inside and one focus outside) and several $+\pi$ and $-\pi$ defects [14] as the intersection of disclination lines with the image plane; droplet 4 has three foci and a $-\pi$ defect. Generally, the number of foci, as well as the geometric complexity of the lines (concentric rings, spirals, ...) increases with the droplet diameter. For the largest diameters, the boundary forces lose their strong influence: the texture is then mainly governed by the elastic forces and assumes configurations similar to that of the free cholesteric structure. The same conclusion as that from our previous TEM results on a two-component PDLC [13] is again found here from SEM micrographs in a one-component system. The balance between the intrinsic anisotropic elastic forces and the boundary forces is strongly related to the confinement ratio and because of the similar results, the different natures of the boundary forces between the usual PDLC and our material will be underlined.

Figure 6 shows an isotropic droplet (diameter about 58 μm) in a surrounding cholesteric, whose morphology was discussed above in the section devoted to optical microscopy. Twice the periodicity (i.e. the apparent cholesteric pitch) is about 3.5 μm; the periodicity measurements are about 20% lower than the measurements realized from the optical textures. The isotropic/cholesteric interface as exhibited in the two regions marked with frames on figure 6 deserves special attention. The differences in these regions seem to find their origin in their history during cell opening. On the left part, a rupture section is exhibited as though a lack of cohesion arose between the isotropic droplet and its cholesteric environment (figure 7). Such a decohesion phenonemon may often be observed during electron microscopy investigations of heterogeneous polymer blends, but we will

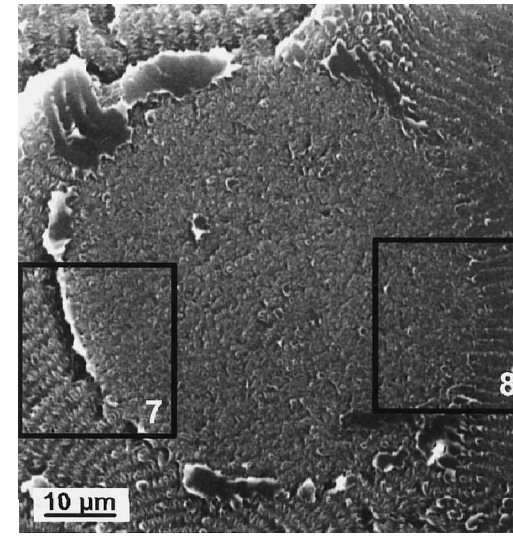

Figure 6. SEM magnified view of an isotropic droplet embedded in the cholesteric phase.

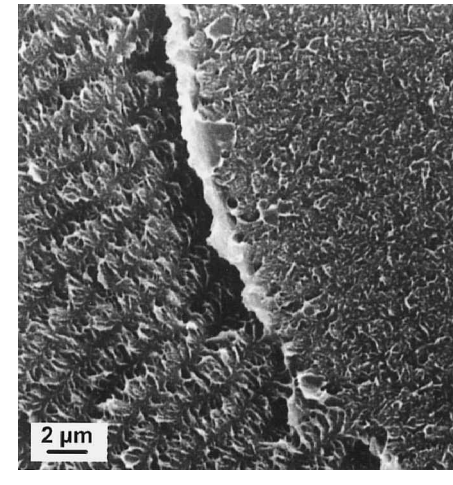

Figure 7. SEM magnified view of the left region of figure 6 (see frame).

stress here that the present material is a one-component system. The transition between the two domains appears to be more continuous on the right side (figure 8), which might be explained by a smoothing effect due to the earlier presence of the upper glass substrate (before the plates were split apart). In this region the matching of the two domains can be examined with far better resolution than in light microscopy. In light microscopy, it is impossible to describe the configuration below a 0.5 µm scale. In TEM, the resolution of the microscope itself is very good, but the images in [13] were obtained by a diffraction contrast that vanishes close to the boundary and does not allow collection of information from the interface. We find that the present micrographs in SEM deliver a good representation of the texture at the interface itself, at a resolution never shown before to our knowledge. Within the limit of this resolution, it can be observed that the striations (dark and bright lines) are visible up to the very interface.

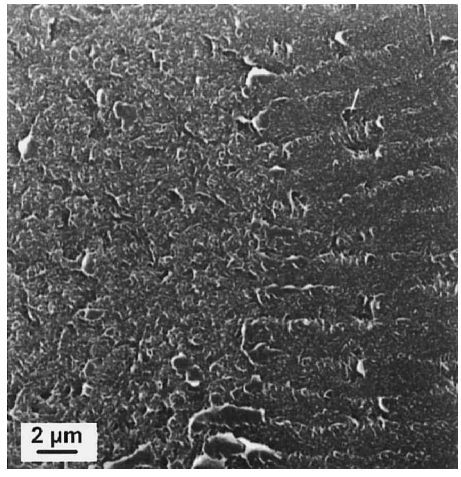

Figure 8. SEM magnified view of the right region of figure 6 (see frame).

Let us investigate magnified views of the fingerprint texture. Figure 9 (*a*) shows dark and bright lines regularly spaced. Figure 9 (*b*) shows at greater magnification a view of the region marked with a frame on figure 9 (*a*). It has been noted above that the textures in SEM and in TEM were very similar, with striations made of alternately bright and dark lines. At first glance, the similarity is very normal since it gives evidence for the cholesteric texture, present in both cases. But, by going deeper into the question, it is remarkable that this texture gives rise to the same contrast in TEM and in SEM since the mechanisms are very different. In an earlier study [15], we analysed three contributions to the contrast in TEM. We demonstrated that the images were the result of diffraction contrast, with a stronger diffraction in the dark lines. Therefore, we could infer that the orientation of the mesogenic part of the molecules was parallel to the lines in the dark lines, and perpendicular to the lines and to the observation plane in the bright ones. Now, the SEM contrast is due to the topology: in the bright lines, the matter is raised and tilted towards the detector, while in the dark lines it is low and tilted in the other direction. Therefore, there is no assurance that a dark line in TEM will also be a dark line in SEM.

In figure 9 (*b*), bright and dark lines present two types of substructure. Bright lines (A-regions) are made of fibril-like units preferentially disposed perpendicularly to the line direction, whereas dark lines (B-regions) have a granular aspect. These two types of line correspond to two deeply different regions from the viewpoint of the director distribution—parallel or perpendicular to the observation plane, although it is not possible to assign here the correspondence. However, it may be expected that these fundamental differences in the molecular orientation have found different signatures; (i) during splitting the plates apart, due to the anisotropic nature

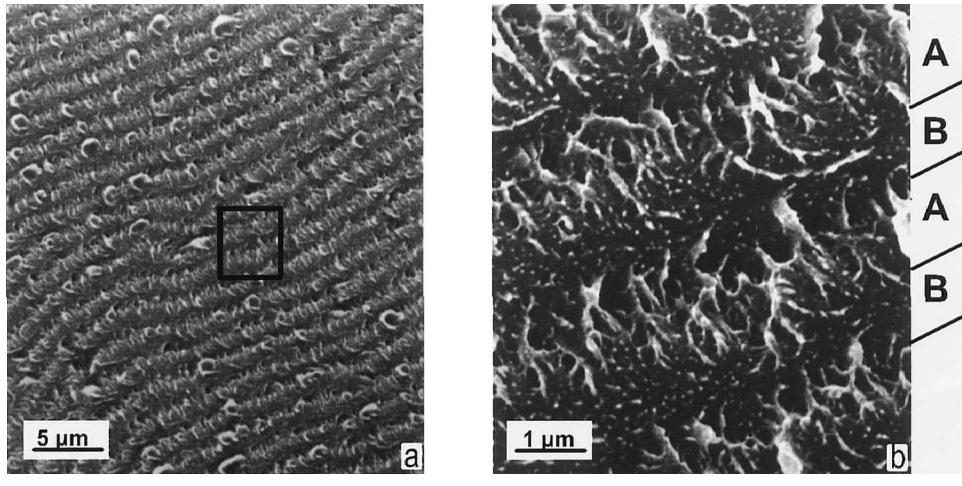

Figure 9. (*a*) SEM micrograph of fingerprint cholesteric texture. (*b*) SEM magnified view of fingerprint patterns, see frame in (*a*).

of extrinsic mechanical effects arising from regions with different anisotropies; and (ii) during the SEM observations, from intrinsic contrast effects due to interactions between the electron beam and the material surface. Granular patterns associated with the dark lines might be fibril-like structures disposed perpendicularly to the observation plane. Based on such a hypothesis, the fibril pattern would be the signature on this scale of the polymer molecular orientation, regularly twisting according to a direction perpendicular to the direction of the periodic lines [16].

4. Conclusion

PDLC-like patterns made up of cholesteric droplets with fingerprint patterns in suspension in the isotropic phase have been entrapped by *in situ* progressive photopolymerization. These phase transition phenomena only occur over 0.7°C. A UV polymerization process with different sequences has been established in order to store completely and durably the LC structures at ambient temperature. The process described is relevant for use with a great variety of non-equilibrium patterns. The conceptual fact that the isotropic matrix and the cholesteric droplets differ only in their molecular order and not in their chemical nature permits comparisons with common PDLCs for which the choice of polymer-forming material and the polymer/liquid crystal interface greatly influence the droplet morphology and the subsequent electro-optic properties. Contrarily to normal SEM studies dealing with the shape and size of empty droplets, the present SEM investigations revealed cholesteric defects, fingerprint patterns and interfaces, and have allowed us to recognize some of the droplet characteristics previously determined by optical microscopy, when periodic lines are perpendicular to the droplet surface.

The authors are grateful to Dr H. Hasebe (Dainippon Ink & Chemicals, Inc.) for providing the UV-curable liquid crystalline material.

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