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Trapping of field-induced liquid crystalline structures by a polymeric network

Michel MITOV and Pierre SIXOU

Laboratoire de Physique de la Matière Condensée, CNRS-URA 190,

Université de Nice – Sophia Antipolis, Parc Valrose, F-06108 Nice Cedex 2, France

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It can be useful to fix a liquid crystal phase. On the one hand, a microstructural study can be carried out by electron microscopy, and on the other, fixing is useful for obtaining optical and electro-optical devices with specific properties for applications. This aim is achieved with polymeric liquid crystals, which can be quenched to the glassy or partially crystalline states without any apparent disturbance of the local orientation characteristics of the liquid mesophase [1]. Freeze-fracture methods are also possible [2, 3]. However, many cases exist where these methods are unsatisfactory or even inadequate, such as when the experimental apparatus is a constraint (film orientated under an electrical field or within the gap of an electromagnet), when the phase equilibrium is only obtained on a few tenths of degrees or, more generally, when this equilibrium is very delicate (instabilities). We show that the use of a photo-crosslinkable polymer, by ultraviolet (UV) irradiation,

can solve these kinds of problems. The example given makes use of the new structures that we have observed during the field-induced cholesteric to nematic transition: spiral patterns linked to the cholesteric phase.

It is well known that an electrical or magnetic field can lead to untwisting of the helicoidal structure of the cholesteric liquid crystal phase. The mechanism was first described theoretically by de Gennes for a thick film [4]. This phase transition was the object of numerous studies during the 1970s on account of potential applications for display devices [5]. Recently, we have observed a new phenomenon, superimposed on this classical transition [6-8]. The electro-optical effects give rise to spiral patterns (Fig. 1). A large pitch cholesteric liquid crystal is submitted to an electric field. The sample, with an important dielectric anisotropy value (+7), is the result of mixing a cholesteric liquid crystal side-chain

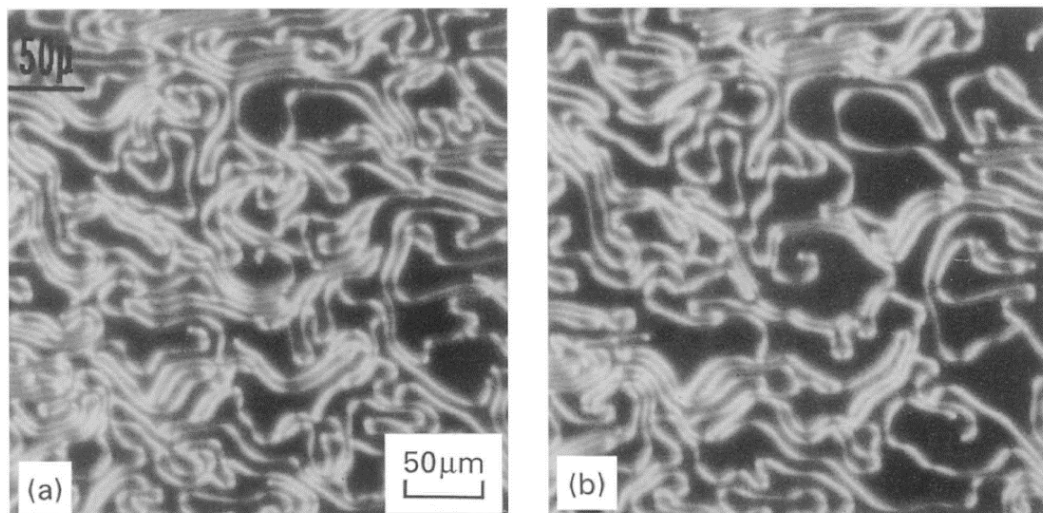


Figure 1 Nucleation and growth of a spiral pattern from a large-pitch cholesteric liquid crystal in a confined geometry (cell thickness/natural pitch ratio is about 1) and submitted to an alternative electric field (50 Hz). Observations were made by polarized light microscopy between crossed polarizers. Molecules are progressively aligned according to the field direction (perpendicular to the glass plates) when voltage increases, which corresponds to an untwisting of the helicoidal structure. The increase is stopped at a value (4.2 V) near the threshold value for which the untwisted state (the pseudo-nematic state) is obtained. The photographs were taken at different times. (a) $t = 0$ s. Texture exhibits disordered filaments (linked to the cholesteric phase) embedded in a dark matrix (pseudo-nematic matrix: molecules are aligned according to the field direction and, thus, the optical axis). (b) $t = 3$ s. Nucleation begins from an extremity of a filament, which is a fixed point. (c) $t = 6$ s. The filament curves in on itself and forms a whorl. (d) $t = 9$ s. Growth progresses. (e) $t = 12$ s. (f) $t = 18$ s. After a sufficiently long time (frequency-dependent), the space will be totally filled by spiral patterns embedded in a pseudo-nematic matrix.

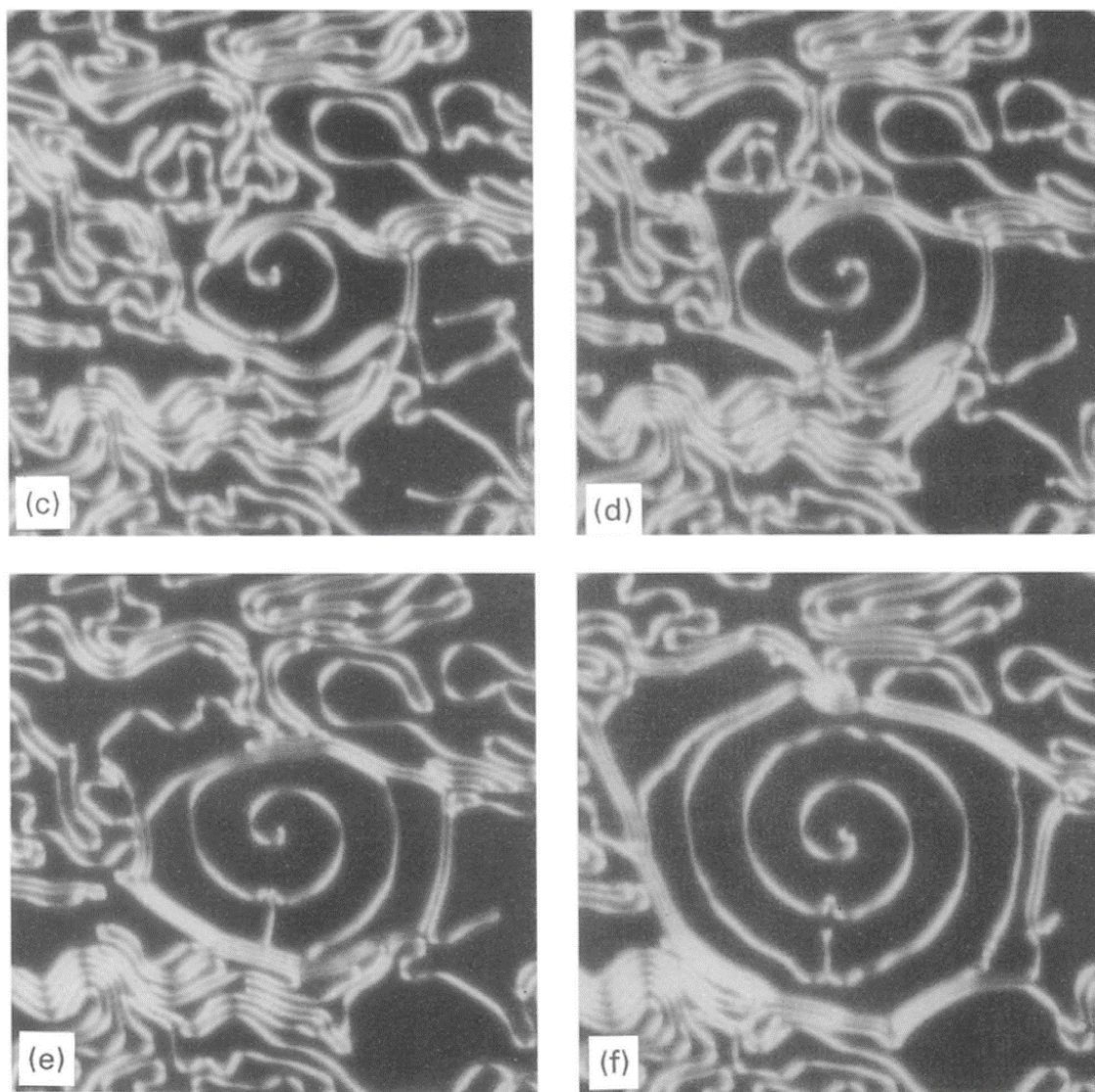


Figure 1 (c)-(f).

polymer (cyclic polysiloxane [9]) with a nematic cyanobiphenyl liquid crystal (5CB) in a 9:91 ratio (wt%). The spiral phenomenon is a threshold phenomenon (near the pseudo-nematic state). The frequency of the electrical field is important for both the nucleation and the growth of rotative spirals: the nucleation time is greater and the growth speed is slower at high frequencies than at low frequencies. The characteristics of this phenomenon have been described previously [6-8].

Freezing these dynamic structures presented a challenge. Using a quenching or freeze-fracture technique was unrealistic to maintain the structures: the polymer part is only a small percentage and these structures are obtained out of equilibrium (drastic disturbances may be predicted). Therefore, the cholesteric polymer is substituted in the blend by a photo-crosslinkable cholesteric polymer with active groups. Consequently, the polymer is at the same time the chiral doping and the crosslinking agent:

crosslinking molecules that are not mesogenic by themselves could disturb the liquid crystal order. The same mixture as in the previous case was made with 5CB nematic and a catalyst (Irgacure 907, Ciba-Geigy, for 2 wt% polymer). When field-induced spirals are obtained, the cell is irradiated by UV light for some tens of seconds. The first consequence is that the spirals stop rotating. Strikingly, when the field is switched off, the structures (pseudo-nematic matrix and spirals) are trapped in their entirety by the creation of the polymeric network, although experimental conditions were *a priori* unfavourable. Indeed, the structures are out of equilibrium and the polymer component (from which the network will be created) is in the minority.

Several recent studies have shown that the polymerization of liquid crystalline compounds can lead to the formation of anisotropic networks with a very interesting range of anisotropic properties and applications, such as optical and thermo-mechanical

properties [10], temperature-independent properties [11] and fast switching networks [12]. In the present case, the orientational properties of the liquid crystal matrix in the presence of an electrical field (obtained in low viscosity conditions) have been associated with the solid properties of the network, created after orientation.

Because one of the investigation methods is to obtain a film for electron microscopy, the following stages are essential: (i) separation of the glass substrates, (ii) evacuation of the free molecules of liquid crystal (a liquid phase cannot be handled easily within a vacuum column) and (iii) reinforcement of the macromolecular network (in the expectation of microtomy). All of these operations must, of course, be achieved without altering the polymeric architecture. If we try to separate the substrates without caution, the structures are lost. A solution is to plunge the sample into liquid nitrogen and to separate the two glass plates quickly: when the ambient temperature is reached, it can be verified easily, by using polarized light microscopy, that the structures are retained. However, the next stage, involving a flow of resin on the substrate, will damage the film. We can prevent this by proceeding with several successive baths of the sample (still reduced to a "sandwich" state) in pure ethanol. Alcohol diffuses by capillarity and voids free molecules from the sample while permitting separation of the plates without breaking the structures in the last stage. An optical microscopy control shows that colours are lost after this process: optically active molecules have been drained off. It is now necessary to separate the film formed by the polymeric network from the glass plate. We lay on the film an orthophthalic polyester

resin which polymerizes at ambient temperature in a few minutes by adding 2% of a catalyst (methyl-ethylacetone peroxide). When the resin is dried, the lump can be torn from the glass plate: the film is pulled away in its entirety. It is then possible to run another layer of resin on the free surface. In this way, the film will be totally coated. Fig. 2 shows the textures obtained before and after these steps.

The qualities required of the resin are that it should not adhere to the glass, it should not be birefringent (to permit a control in polarizing microscopy of the capsule containing the film, for marking it), it should polymerize without a great change of volume (or else the network will be dramatically deformed) and it should be sufficiently supple for microtomy.

A subtler process is as follows. A sandwich-cell cleared of free molecules after several baths in alcohol and dried under vacuum (or, more cautiously, at ambient temperature for several days) is taken. This cell is plunged into a rather fluid UV cross-linkable resin (NOA-65, Norland-Epotechny, for example). While the cell is sheltered from light, the resin will slowly diffuse into it (completely after several days); on account of the slowness of this mechanism, it is not convenient to use resin that polymerizes quickly at ambient temperature. After diffusion, the cell is irradiated with UV light. This permits consolidation of the network in much more detail. This procedure is similar to the procedure employed by biologists for electron microscopy, with the following successive steps [13]: fixation, rinsing (to avoid any reaction between fixatives), dehydration (because commonly used embedding resins are immiscible with water) and embedding (when the material is extremely small, fragile, porous or brittle).

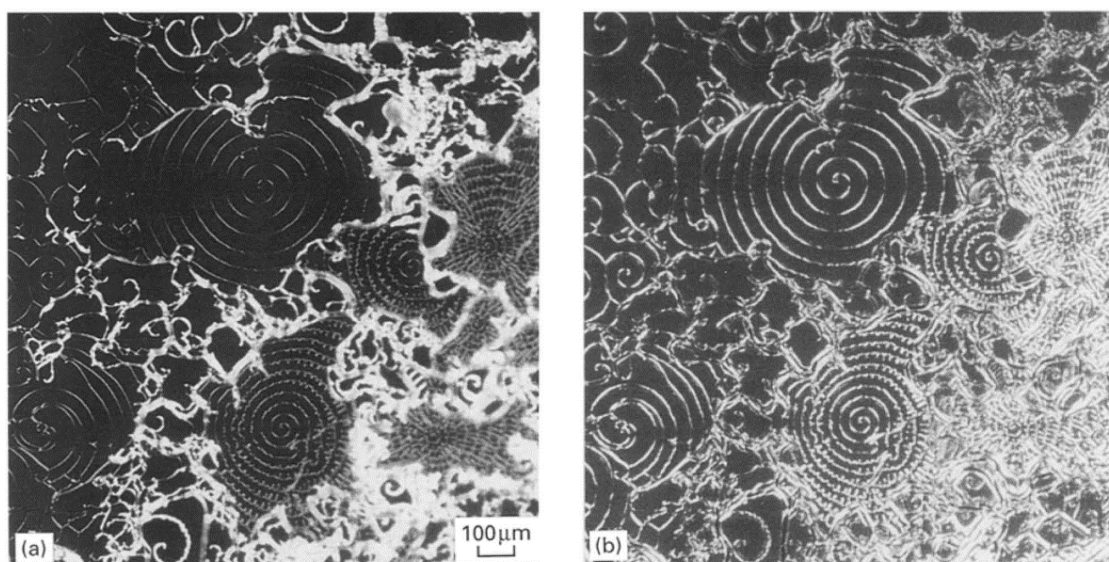


Figure 2 (a) Spiral pattern embedded in a pseudo-nematic matrix after photo-crosslinking and after the electric field is switched off. The cell (thickness = $3.5 \mu\text{m}$) was irradiated by UV light (wavelength = 365 nm , power = 400 W) for 1 min (duration depends on source-object distance, here 30 cm). When the field is switched off, the structures are trapped as a consequence of the creation of the polymeric network. (b) Same view after having dipped the sandwich-cell in alcohol (to evacuate free molecules), separation of the glass substrates and inclusion of the film in a resin. Birefringence has been lost (optically active molecules have been drained off). The structures are retained.

With respect to our system, the voiding of free molecules of liquid crystal is the analogue of dehydration; embedding is likewise useful for strengthening the structures.

Spirals are the dominant type of pattern in a remarkable variety of systems, such as electrohydrodynamic convection [14, 15], oscillatory chemical reactions [16–21] and biological systems [21, 22], and are now one of the main themes of non-linear science. Recent research has revealed that spiral patterns are encountered in thermal convection in a liquid [23], and they are currently believed to be responsible for the sudden transition from ventricular tachycardia to fibrillation [24], inhibiting the heart muscle from pumping coherently and leading to sudden death. The mechanisms at the origin of these similar patterns found in very different experimental conditions are not fully understood. A microstructural study can contribute to understanding, by permitting study of each step of the nucleation and growth of spiral patterns by freezing them. However, it is important to note that in the quoted examples, the experimental conditions – fluid phase in the former case, *in vivo* experimentation in the latter – do not offer the possibility of an electron microscopy study. To our knowledge, we have described the first example of the fixation of an out-of-equilibrium system constituted by spirals induced by an external field. The realization of cuts in planes that were impossible in structures that were not frozen, notably cross-sections, has been achieved.

In conclusion, field-induced structures in liquid crystal materials can be trapped via the creation of a polymeric network. The method has been demonstrated with the example of a new spiral texture induced by an electric field, close to the cholesteric to nematic untwisting transition. Since this makes possible a microstructural study of the structures (notably by electron microscopy), the experimental process to obtain an undamaged film embedded in a resin has been presented. The technique is of general value for the fixation of liquid crystalline structures obtained under conditions where the usual techniques (quenching, freezing) are not possible. Indeed, the method of *in situ* gelation that we describe oversteps the framework of field-induced structures and is powerful in many other systems where classical methods are breaking down or are approximates. This is the case when the system describes a more or less large number of successive thermodynamic states between the moment when you have chosen to freeze a definite configuration and the moment when you have effectively frozen a certain state, such as a biphasic state in mixtures between polymers, an ordered phase only existing on a few tenths of degrees or a thermal gradient in polymeric films (a

typical example unrealizable with methods based on the fall in temperature). Several applications can be derived from the decoupling of molecular orientation and initiation of crosslinking. For example, it is possible to freeze several cells at different field-induced configurations involving different optical properties with a solid film at the end of the process. Potential applications are passive optical components as reflector filters (by using the Bragg reflexion properties of the cholesteric phase, adjusted by an electric field), notch filters and devices for polarization rotation.

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