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Classification

Physics Abstracts

61.30G — 61.30E — 61.25H

Short Communication

Field-induced spirals from a confined cholesteric

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Résumé. — Nous avons observé des spirales biréfringentes induites par un champ à partir d'une texture fingerprint résultante d'un polymère cholestérique en solution dans un cristal liquide nématique de faible poids molaire. Cet article décrit les conditions de nucléation de ces spirales et le rôle de différents paramètres qui déterminent leurs caractéristiques.

Abstract. — We have observed birefringent spirals induced by a field in a fingerprint texture of a cholesteric polymer in solution in a nematic low molar weight liquid crystal. This paper describes the conditions of nucleation of these spirals and the part of different parameters which determine their characteristics.

Introduction.

The observation of textures exhibiting spirals in zero electric field has often been described in large pitch cholesteric liquid crystals. Bouligand [1], from a study of polygonal fields describes several spiral types observed when the cholesteric pitch is sufficiently large. This type of structure is also observed in the more complicated cases of biological systems, by Bouligand [2] and in cholesteric droplets and spherulites by several authors [3-6]. The detailed organization of cholesteric spherulites and the different patterns that they show, such as spirals, has recently been discussed and modelled [7].

In the present paper, we consider the nucleation and the growth of spirals induced by an electric field [8]. We have made the observation in the case of several mixtures, with a cholesteric polymer in solution in a nematic or a cholesteric low molar weight liquid crystal. A such a mixture, of positive dielectric permittivity, exhibits focal-conic or fingerprint-type textures for certain concentrations. When it is submitted to an electric field we observe a filament texture which, for increasing applied voltage, evolves towards the homeotropic state characteristic of high voltages. We observe that the filaments can form spirals for voltages near the threshold

(*) U.A. CNRS 190.

corresponding to the cholesteric-homeotropic nematic transition. The filament texture (also called "fingers") is well-known in the case of cholesteric low molar weight liquid crystals [9-14]. Recently, Ribière and Oswald [14] have studied the nucleation and the growth of cholesteric fingers in an electric field but do not mention the existence of spirals. Hinov and Kukleva [15] refer to the existence of such spirals in low molar weight liquid crystal mixtures on application of a direct-current voltage and have related the phenomenon to charge injection in the electrode region where point singularities are formed.

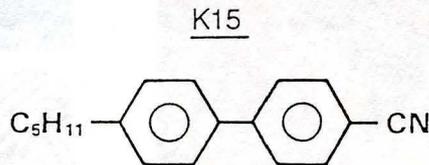
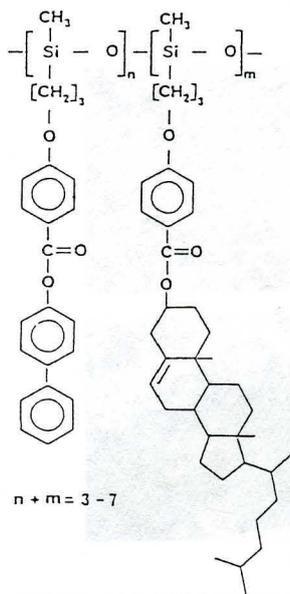
The free energy per unit volume of the cholesteric phase, including the electric field contribution and the anisotropic elasticity, is minimized to obtain the energy of a filament per unit length [14]; the authors have proposed a phase diagram for stability or metastability of the filaments formation according to the voltage values and the confinement ratio (i.e. the sample thickness/natural pitch ratio).

In order to understand the mechanism of field-induced spiral formation we investigate the role of several parameters such as the frequency of the applied voltage, the polymer concentration, the temperature and the sample thickness which modify spiral characteristics.

Experimental conditions.

The chemical formula and characteristics of the sidechain polysiloxane copolymers and the nematic liquid crystal K15 (BDH) are given in Plate 1a and b, respectively.

Liquid crystal silicones are sidechain polymers with a siloxane backbone and cholesteryl and biphenyl side groups. These copolymers were synthesized by Dr F.H. Kreuzer for the "*Consortium für Elektrochemische Industrie GMBH*". Pitch and color of reflection are determined by the molar ratio of the two sidegroups and the ring size of the backbone. Cholesteric liquid crystal silicones exhibit reflection wavelengths in the blue, green, red and near infra-red spectral region. They are solids at room temperature and have glass temperatures of about 50°C and clearing temperatures of 200°C. Polymeric materials offer a unique advantage over low molar weight substances : the required cholesteric mesophase may be attained by annealing at an elevated temperature and locking the phase into a glassy matrix by thermal quenching [16-18]. Only the copolymer corresponding to selective reflection in the blue of visible spectrum is used here, the other copolymers presenting similar results. We have obtained an excellent compatibility by mixing this polymer with the low molar weight liquid crystal cyanobiphenyl K15 for all ranges of concentration. The phase diagram (Fig. 1), obtained by optical microscopy observation of the textures and differential scanning calorimetry, exhibits a continuous and increasing variation of the cholesteric pitch when the nematic concentration increases. The selective reflection changes from blue to red for temperatures between 180°C and 70°C and polymer concentrations between 90 and 50 wt%. A large pitch (corresponding to the well-known fingerprint-type texture) is then obtained in the lower temperature range and for low polymer concentrations. Plate 2 gives the result of a contact preparation, with a concentration gradient between the two compounds, at room temperature; we see in the upper left part the smectic A phase (the cholesteric part of the polymer doesn't appear in the photo); in the lower right part we see the K15 nematic phase (black zone), in the vicinity of a zone where filaments occur. We work at 24°C and select a region of the phase diagram where the textures with filaments can be observed, corresponding to polymer concentrations of about 10 wt%. Thus, this is a large pitch zone, far from the smectic A - cholesteric transition, situated at a polymer concentration around 35 wt% at room temperature, and its fluctuations. The sample thickness is 3.5 μm . The interaction between the two compounds of the mixture seems sometimes to lead to a smectic A phase, below the cholesteric phase, reflecting a microsegregation of sidechains



- Crystal / nematic transition temperature : 24 °C.
- Nematic - isotropic transition temperature : 35,3 °C.

b)

Liquid crystal Silicone "Blue"

- Reflection wavelength : 450 nm.
- Glass transition temperature : 50 °C.
- Clearing temperature : 200 °C.

a)

PLATE 1. — Characteristics of the liquid crystals. a) Cholesteric liquid crystal copolymer. b) Nematic low molar weight liquid crystal.

and mainchains, and to homeotropic structures where the mesogens of liquid crystal and of the polymer are aligned perpendicularly to the capacitor plates. The presence of CN groups (the dipolar moment is 3.4 Debyes) can explain the important effect of the electric field. The precise arrangement of the dipoles of the two mesogens is unknown. However, at the concentrations used for study in an electric field, the nematic phase is strongly dominant (more than 80 wt%) and the dielectric anisotropy of the mixture is positive.

The textures are observed by standard means associating an optical microscope with a Mettler FP52 hot stage, equipped with optical windows, thus allowing the direct observation of the preparation during heating or cooling, between crossed polarizers and at normal incidence. The samples are contained in conventional sandwich cells; the thickness is adjusted by Mylar sheets of specified values. The thickness is not controlled after preparation but only a small error is expected due to the fluid nature of the mixture. Furthermore, using I.T.O. conducting transparent electrodes, a continuous or alternating voltage up to 200 Volts and of a few MHz can be applied.

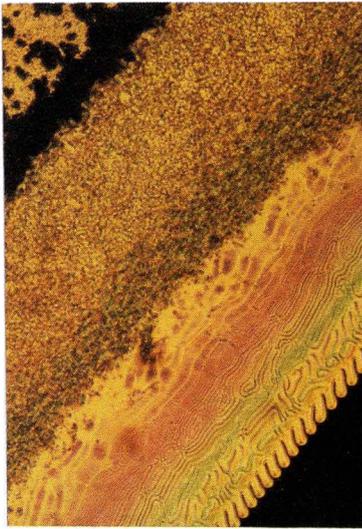


Plate 2

2 μm

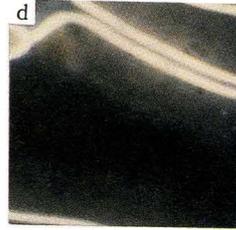
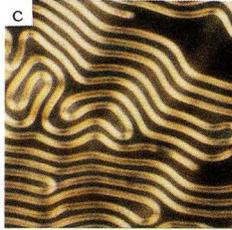
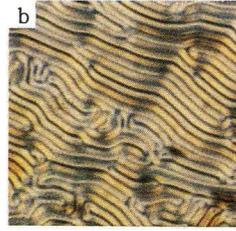
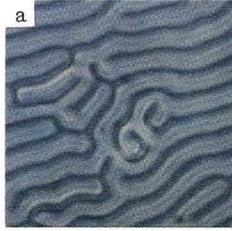


Plate 3

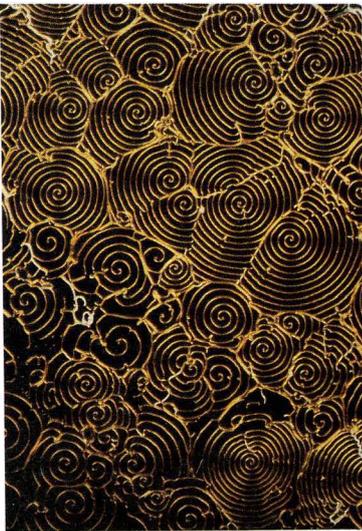


Plate 4



Plate 5

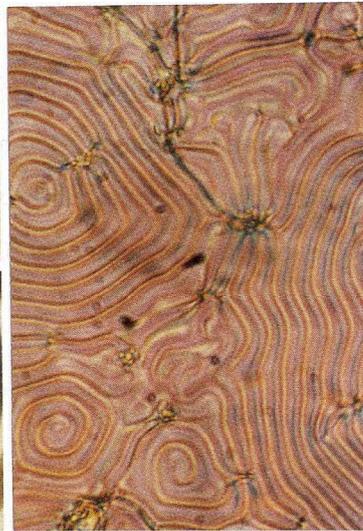


Plate 6

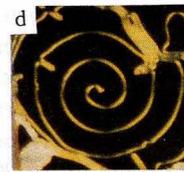
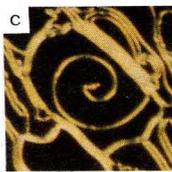
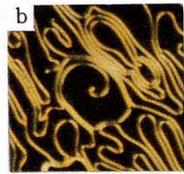
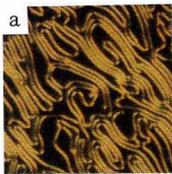


Plate 7

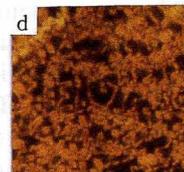
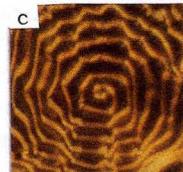
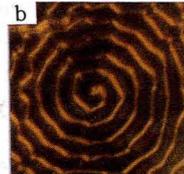


Plate 8

PLATE 2. — Contact preparation (concentration gradient) between the two compounds (at room temperature). In the upper left part: the smectic A phase (the cholesteric part of the polymer doesn't appear in the photo). In the lower right part: the nematic phase (black region) in the vicinity of the zone of filaments.

PLATE 3. — Some steps of the cholesteric-homeotropic nematic field-induced transition for $f = 20$ Hz. $T = 24$ °C. a) Fingerprint-type texture. No field. b) $V = 2.6$ V. c) $V = 4.9$ V. d) $V = 5.4$ V.

PLATE 4. — Interconnected spirals paving all the sample. $T = 24$ °C. $V = 4$ V. $f = 30$ Hz.

PLATE 5. — Two types of spirals. $T = 24$ °C. $V = 4.2$ V. $f = 20$ Hz. a) Simple spiral. b) Double spiral.

PLATE 6. — "Fixed spirals": field-induced spirals in a fingerprint matrix. The sample (SB/M24 mixture for the 9/91 wt% ratio) has been cooled from 80 °C (from a spiral texture obtained for $f = 30$ Hz and $V = 4$ V) to 24 °C (room temperature) by 0.2 °C per minute. The spirals are frozen in. When the field is switched off, the homeotropic becomes fingerprint-type.

PLATE 7. — Different steps of a spiral growth at $f = 50$ Hz and $V = 4.6$ V. $T = 24$ °C. a) $t = 0$ s. b) $t = 1$ min. 20 s. c) $t = 2$ min. 10 s. d) $t = 3$ min. 36 s.

PLATE 8. — Effect of temperature on the spiral structure. The deformation progresses from the extremity until the core. $f = 12$ Hz, $V = 4.5$ V. a) $T = 21$ °C (equilibrium temperature). b) $T = 26.7$ °C. c) $T = 30$ °C. d) $T = 34$ °C.

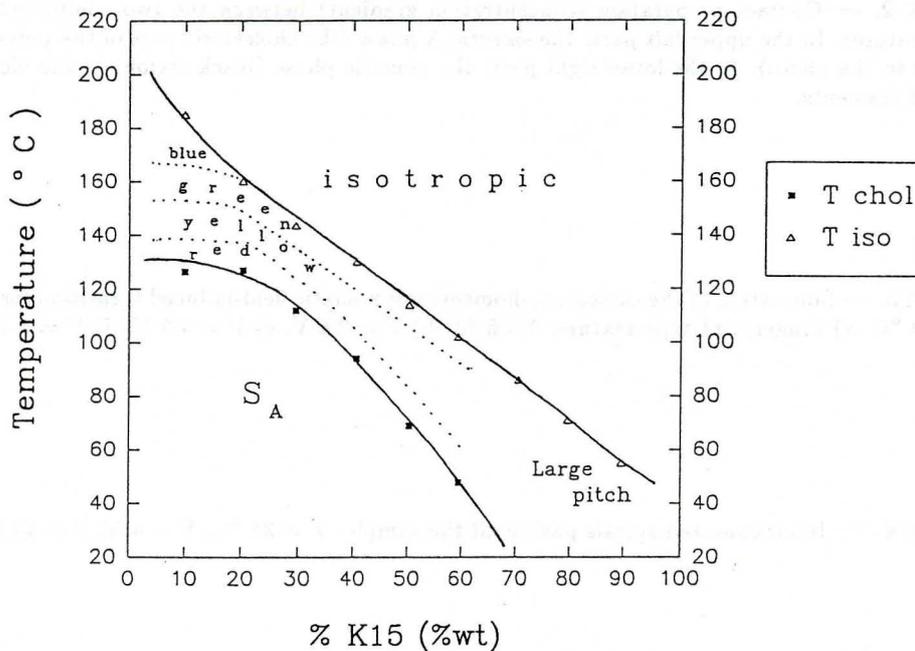


Fig. 1. — SB/K15 phase diagram. The qualitative variation of the pitch in the cholesteric region is given: selective reflection colours and large-pitch zone.

The spiral texture.

The spiral texture nucleates during the cholesteric-homeotropic nematic transition. Starting from a fingerprint-type texture, filaments embedded in a homeotropic matrix appear when the field is increased. The sample is completely homeotropic at a certain threshold voltage V_{th} . The photographs of Plate 3 show the different textures obtained at typical voltage values for this transition. For applied voltages near the threshold value (between about $3/4 V_{th}$ and V_{th}) a spiralling of the filaments occurs (see Plates 4 and 5), in less than one minute for frequencies between 5 and 40 Hz. When the homeotropic texture is preponderant this effect appears more easily. If the rate of increase of V_{th} is too rapid, the phenomenon may not be perceived. Spirals of left or right-handedness grow until paving the sample. These spirals are the last structures which resist to the field-induced homeotropic propagation.

THRESHOLD VOLTAGES. — Figure 2 represents the {Voltage, Frequency} phase diagram where there appear successively, for frequencies less than a few tens of kHz:

- a fingerprint-type texture, not modified by the electric field until about 1 V
 - filaments embedded in a dark homeotropic matrix (between 1 and 5 V)
 - the spiralled filaments for a voltage range (between about 3.5 and 5 V) below the threshold corresponding to the homeotropic one
 - lastly, the completely homeotropic state.
- At frequencies corresponding to a constant threshold voltage value, the presence of filaments

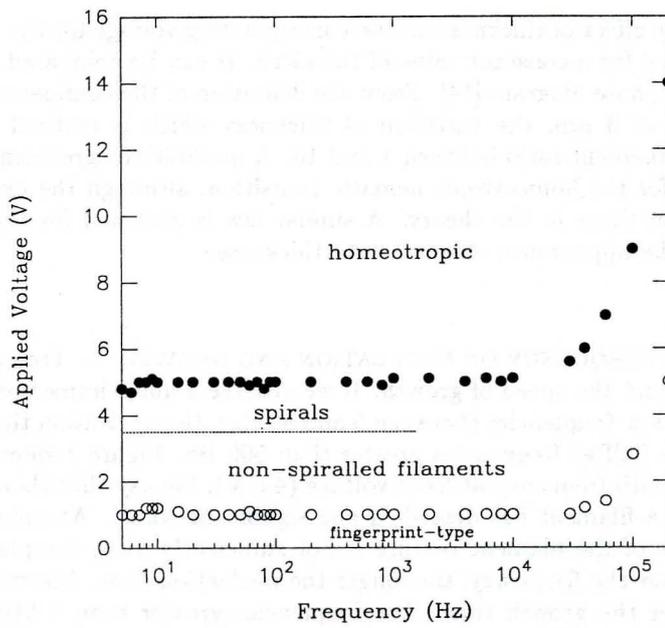


Fig. 2. — Threshold voltage versus frequency. The cholesteric-homeotropic transition is given by the different phases; the zone of spiralled filaments is traced.

can be explained by the model described in [14]. On the other hand, for more elevated frequencies, dielectric effects modifying the threshold values must be taken into account, which could explain the $f^{1/2}$ variation above about 20 kHz.

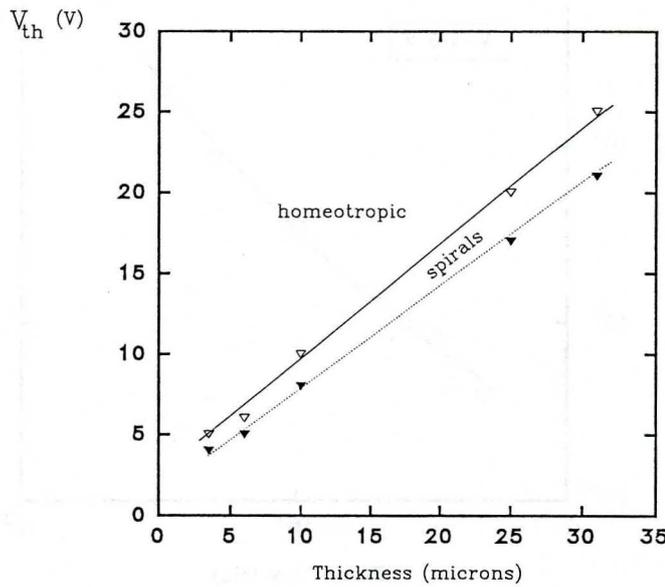


Fig. 3. — Threshold voltage (complete homeotropic) and zone for spirals versus the sample thickness.

Figure 3 shows the effect of thickness on the corresponding voltage for the spirals formation. This curve is obtained for a constant value of the pitch. It can be compared to the theoretical curve describing the phase diagram [14]. From the definition of the confinement ratio $C = d/p$, at a constant pitch of $3 \mu\text{m}$, the variation of thickness which is realized corresponds to a variation of the confinement ratio between 1 and 10. A qualitative agreement with theoretical prediction is found for the homeotropic nematic transition, although the experimental values for C are larger than those in the theory. A similar law is obtained for the variation of the critical voltage for the appearance of spiral with thickness.

INFLUENCE OF THE FREQUENCY ON NUCLEATION AND GROWTH. — Frequency affects both the nucleation time and the speed of growth. If we observe a quasi-immediate nucleation (less than one minute) at low frequencies (between 5 and 40 Hz), the nucleation time can reach more than one hour and a half at frequencies greater than 500 Hz. Figure 4 shows the variation of the nucleation time with frequency at fixed voltage (4.6 V). We say that there exists one spiral in the sample when a filament has described one significant whorl. At certain frequencies, if the observation time of the filament texture is not sufficiently long, the phenomenon can be overlooked: the higher the frequency, the longer the nucleation time. Likewise, the higher the frequency, the higher the growth time. For frequencies greater than 1 kHz it is difficult to observe spirals nucleating either because the time of nucleation diverges or this corresponds to a dielectric-type regime forbidding the spiral formation. Plate 7 gives a typical example of the growth time.

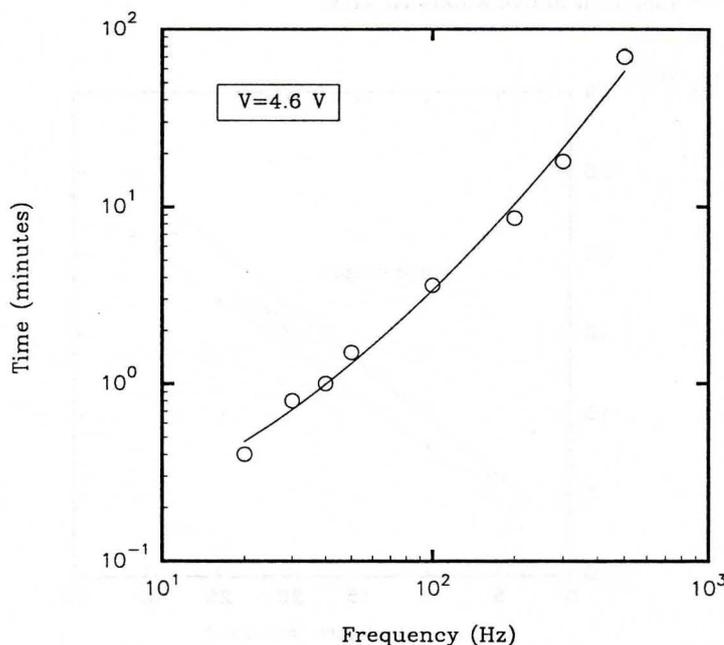


Fig. 4. — Nucleation time of spirals versus the frequency at fixed voltage (4.6 V).

Voltages immediately below V_{th} , where we observe spirals, correspond to metastable isolated filaments [14]; when an applied voltage brings the cholesteric sample in this zone of the phase diagram, there is formation of a filament embryo with different extremities [14]. This embryo can collapse or remain if the corresponding energy is greater than a critical value. Nucleation in this zone is directly linked to the frequency of the A.C. field. At high frequencies, the probability of nucleation is smaller than at low frequencies. However, when the spiralled filaments are formed, they are more stable at high frequencies, *i.e.* a weak increase of the applied voltage destroys less easily the spiral structure, by expanding the homeotropic, than at low frequencies. At high frequencies the nucleus created by the local deformation due to the electric field cannot grow quickly enough, but at lower frequencies, the nucleus grows and expands with the field. This interpretation is in agreement with the observation of two different filament tips, showing at low frequency, a modification of birefringence along the filament which oscillates from one tip to the other. Another hypothesis is given by Hinov and Kukleva [15]. These authors have observed left-handed and right-handed spiral patterns in thin samples of large-pitch cholesteric in cholesteric-MBBA mixtures of low molar weight liquid crystals, on application of a D.C. voltage for long times. The nucleation is explained by possible gradient flexoelectric generation of point singularities, through the accumulation of injected charges by the electrodes, which could also explain the growth. If the injection of charges through the electrodes plays an important role in the D.C. regime, it becomes negligible as soon as the frequency exceeds a few cycles, which could explain the longer nucleation time at high frequencies, where spirals are also observed. A detailed study of this point is in progress.

INFLUENCE OF THE CONCENTRATION. — At fixed concentration, the threshold voltage for the nucleation of spirals is about three-quarters of the threshold value corresponding to the homeotropic configuration. When the concentration is modified, this relation is conserved qualitatively in the frequency range considered (when the formation of spirals is quasi immediate). When the polymer concentration increases, all other parameters being unchanged, we observe an increase of the threshold voltage for the complete homeotropic arrangement and of the threshold value for the nucleation of spirals (Fig. 5); therefore, when the pitch decreases at lower nematic concentration, the cholesteric structure is more twisted and a higher voltage must be applied to untwist the helix. This result is in agreement with the phase diagram given by Ribière and Oswald describing the variation of the different voltages for stability or metastability of the filaments with the confinement ratio $C = d/p$ (where d is the sample thickness and p the natural pitch of the cholesteric sample). The threshold voltage increases with C ; when C is greater than a critical value (1.25 for the theoretical model) we note a linear variation between V and C . Since the cholesteric pitch decrease with concentration c of the chiral compound, for the small concentration we observe a law like $p = c^{-a}$ [19]; thus, we expect a variation of V_{th} as c^a , that is obtained in the case of figure 5 with $a = 1$. Note that this study only considers one thickness and a threshold voltage which varies on a limited concentration scale.

A final conclusion with respect to the quantitative aspect is therefore difficult.

TEMPERATURE EFFECT. — At fixed voltage (4.5 V) we examine, for several frequencies, how the temperature can destroy the spiralling of the filaments. We consider, at every frequency, a zone in the sample where several spirals have nucleated. When we increase the temperature, we observe that the spiralled filament undulates progressively from the extremity to the core, which is the last part to be destroyed (Plate 8). The variation of the temperature at which

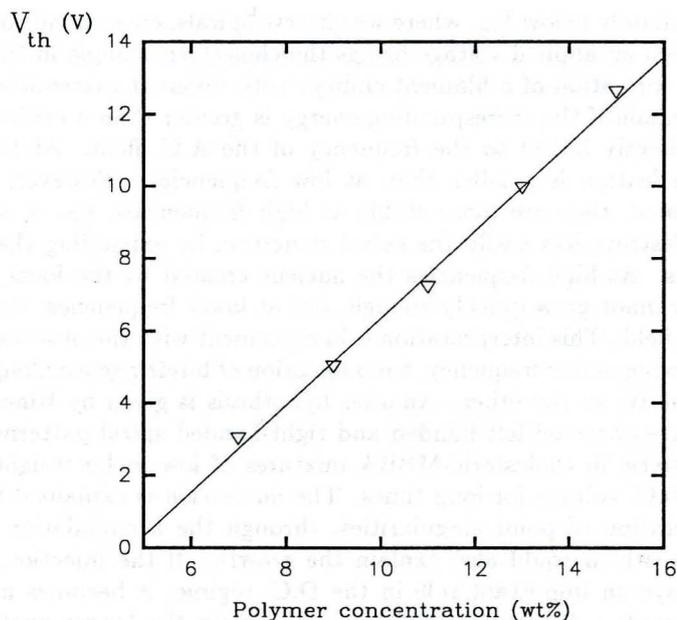


Fig. 5. — Variation of the threshold voltage for the cholesteric-homeotropic nematic transition versus the polymer concentration.

spirals are destroyed in a certain frequency range is represented on figure 6. We note that spirals are more stable at high frequency. We find again that if the nucleation time is longer when the frequency is increased, the spiralled structure is more stable.

ANCHORING EFFECT. — There exists a natural tendency to a homeotropic orientation with the SB/K15 mixture. We have studied the effect of a surface treatment producing planar anchoring. We have coated the electrodes with a thin film of a solution of polyvinyl alcohol in water and, then, rubbed it with a paper along a defined direction. The filament texture is observed over the entire sample. When we apply a field, the threshold voltage for the homeotropic state increases by about 1 V. No spiral formation is observed. In some zones (grooves) where the film has been removed, filaments seem to curve but spirals cannot nucleate on account of geometric limitations.

We have made some tests with a few surfactants inducing a homeotropic anchoring (like ZLI-3124 or a solution of lauryl sodium sulfate in water) but we have obtained no conclusive results; hence, a more exhaustive study is necessary.

FIXING OF THE STRUCTURE WITH SPIRALLING FILAMENTS. — The use of a polymer solution is of interest because it allows to freeze in a structure by a quench which brings the mixture below its glass transition temperature. Samples can then be studied by electron microscopy. The SB/K15 mixture with 9/91 wt% of concentration is solid below room temperature. We have then used other similar mixtures in which the nematic low molar weight composition is chosen with higher temperatures for the isotropic/nematic transition. Plate 6 shows a fixed

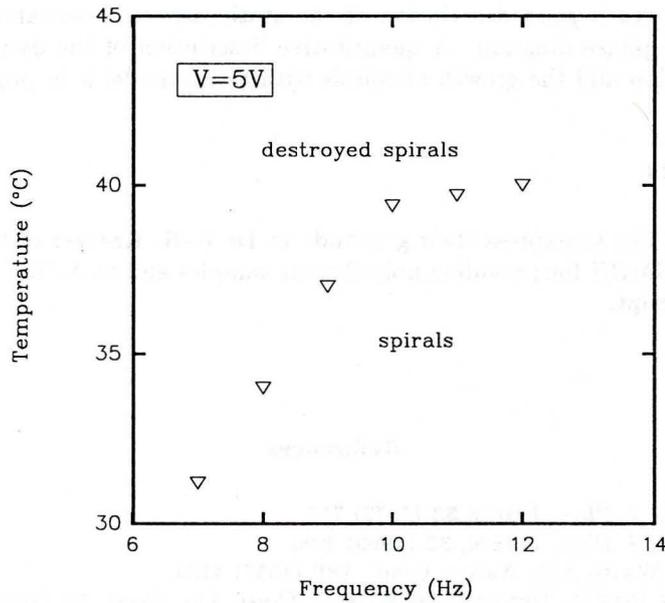


Fig. 6. — Effect of the temperature on spiral structure *versus* the frequency at fixed voltage (5 V). For an increase of the temperature, the spiralled filament undulates progressively from the extremity until the core.

structure obtained with the SB/M24 mixture at 9/91 wt%. M24 is a cyanobiphenyl furnished by BDH having the following transition temperatures:

$$T(K - S_A) = 54.5 \text{ } ^\circ\text{C}$$

$$T(S_A\text{-nematic}) = 67 \text{ } ^\circ\text{C}.$$

$$T(\text{nematic-isotropic}) = 80 \text{ } ^\circ\text{C}.$$

For the SB/M24 mixture at 9/91 wt%, the transition temperatures are:

$$T(K - S_A) = 53 \text{ } ^\circ\text{C}.$$

$$T(S_A\text{-fingerprint type cholesteric}) = 66 \text{ } ^\circ\text{C}.$$

$$T(\text{cholesteric-isotropic}) = 87 \text{ } ^\circ\text{C}.$$

The electric field was applied during cooling at $0.2 \text{ } ^\circ\text{C}$ per minute from a temperature where the spirals are observed until room temperature. After removing the voltage, the structure with spiralled filaments remains fixed. In the example considered here, the metastable structure is retained for about ten minutes. However, using a mixture composed of cholesteric polymer SB with another compound and obtaining a higher melting point than with M24, it is possible to get a more stable memory effect.

Conclusion.

The spiral configuration of cholesteric filaments, perhaps linked to the twisted direction of the molecules inside the filament [8], has been studied in relation to several parameters such as voltage, frequency, sample thickness, temperature... The behavior of a large-pitch cholesteric liquid crystal in the presence of an electric field is well described by Ribière and Oswald

[14]. The model gives a good description of the static aspects associated to the {Voltage, Confinement ratio} phase diagram. A quantitative description of the dynamical phenomena such as the nucleation and the growth of spirals within this model is in progress.

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