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Spontaneously created ring structures in free-standing liquid crystal films and their dependence on temperature and material parameters

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A rotating electric field can induce a spontaneous formation of ring structures in free-standing ferroelectric liquid crystal films. A phase delay between the field rotation and the director movement on the smectic cone is the reason for the ring creation. The appearance of these structures depends on the field parameters, on the material parameters of the liquid crystal compound used, and on the temperature. The temperature dependence of the pattern formation and of material parameters (spontaneous polarization, rotational viscosity, pitch) have been investigated in more detail. It could be shown that the rotational viscosity of the liquid crystal is the most important parameter with respect to the influence of temperature. The experimental results are compared with the theoretical interpretation of the ring formation.

1. Introduction

In free-standing films of ferroelectric liquid crystals (FLCs), systems of 2π-walls forming closed circular loops can be created by an electric field applied in the film plane [1]. These walls collapse and eventually disappear. In the S_C^* phase, the formation of stable systems of dark and bright rings (π-walls) may be brought about by a rotating electric field applied parallel to the film surfaces using a four-electrode set-up [2–5]. The appearance of these ring systems depends on the field parameters (strength E and rotational frequency ω), as well as on the material parameters of the FLC material, e.g. the pitch p.

In the tilted S_C^* phase, the electric field induces the well known rotational motion of the director on the smectic cone (Goldstone-mode). For low frequencies, this director rotation can be seen directly due to the motion of the optical axis in the conoscopic picture. Usually, a disordered switching of different dark and bright domains in a schlieren-like texture, which is visible between crossed polarizers, takes place in the film for low voltages. When a high voltage is applied, the director follows the rotating field synchronously over the whole film area, and, as a consequence, a homogeneous orientation is present (figure 1). This homogeneous switching of the whole film stops below a boundary line $E_{sync/async} = f(\omega)$. Systems of dark and bright rings, arrangements of π-walls as shown in figure 2, appear immediately after the application of a field with the corresponding parameters or after crossing the boundary line. In an exactly defined region of field parameters, the ring structure is stable, and one ring system occupies the whole film area (full ring system) [3]. Critical curves $V_{crit} = f(\omega)$ bound this quasi-stationary region. There are two such critical curves, an upper one and a lower one. Outside the critical curves, small ring systems occur, often more than one simultaneously.

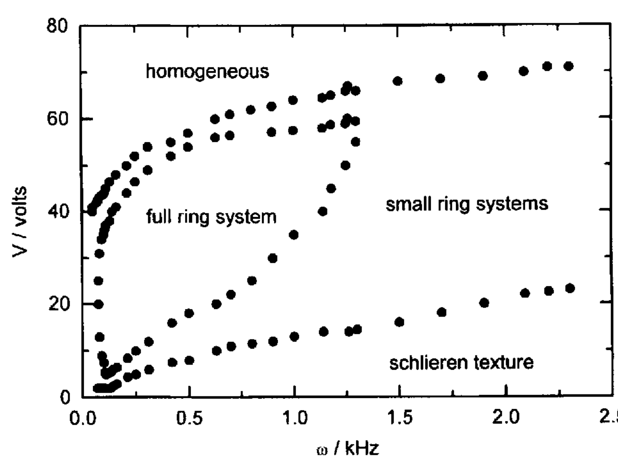

Figure 1. Dependence of the spontaneous structure formation on frequency ω and applied voltage V; mixture of FLC 6430 (60 wt.%) and 90–917B (40 wt.%), temperature $T = 26°C$.

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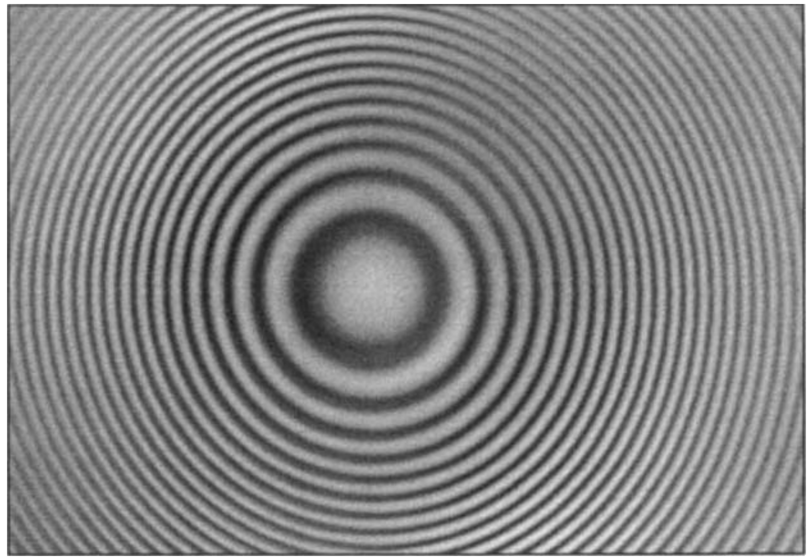

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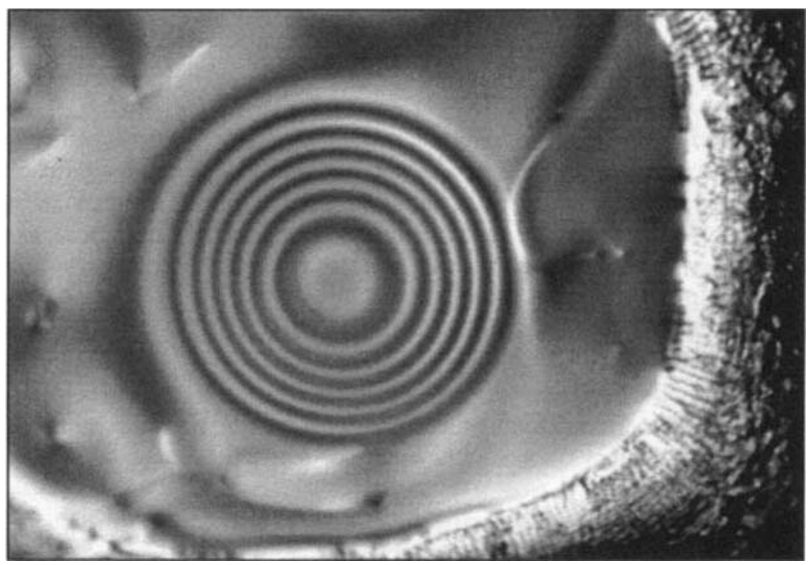


(b)

Figure 2. Ring patterns in free-standing films of FLC mixture FE1; (a) full ring system; (b) one small ring system.

A phase delay of the director orientation with respect to the rotating electric field might be the reason for the spontaneous formation of these structures [3]. A first theoretical treatment of the pattern creation supports this model for the interpretation of the appearance of ring systems [6]. However, similar ring patterns have been observed in free-standing films without applied fields [7]. A circular flow present in the film probably induces the pattern. For special field parameters, we also observed a circular flow in the film [2]. In this paper we discuss the question whether the pattern formation in rotating fields is induced by the flow or by the phase delay. Additionally, the structure of the ring systems has to be explained: are they static patterns, or does the director continue the motion on the smectic cone, as assumed in a first model [2]?

Recently, we observed that the creation of the ring systems is influenced by the temperature [3, 4]. Here, we study the variations of the spontaneous pattern formation and of the material parameters of the FLC (spontaneous polarization P_S, rotational viscosity η, and pitch p) with the temperature in more detail. From the results of this analysis it will be possible to find out the most important parameter for the temperature dependence of the structure formation. Moreover, the influence of the value of the pitch is investigated, and a comparison of experimental results with the theoretical treatment of the pattern creation [6] is given.

2. Experimental

Free-standing S_C* films stretched over a hole in a substrate were investigated. The smectic layers align themselves parallel to the free surfaces of the film. Four electrodes were arranged perpendicular to each other on the sample as shown in figure 3 [3]. They make it possible to apply a rotating electric field parallel to the FLC film, either by two sinusoidal waves, with a phase shift of 90° between the pairs of opposite electrodes, or by using sequences of rectangular impulses from all electrodes. In the second case, the impulse diagram for one electrode is drawn in figure 4. The sequence for the opposite electrode starts with the negative value $-V_A$, and for the two other electrodes the cycle begins with the field-free state. Usually, the rectangular impulses were used for the experimental investigations. A more detailed description of the experimental set-up is given elsewhere [3, 4]. In the experiments presented here, the free-standing films had a diameter of about 1 mm and a thickness of 300–500 nm. The upper limit of the field strength was $E_{max} = 3\,\mathrm{kV\,cm^{-1}}$, and ω was varied between 1 Hz and 10 kHz.

The experiments were carried out on the hot stage of a microscope using crossed polarizers. The microscope was equipped with a charge coupled device (CCD) camera (Hitachi KP-C551) with video recording of the microscopic pictures. The exposure time for a micrograph could be changed between 20 ms and 250 µs. The

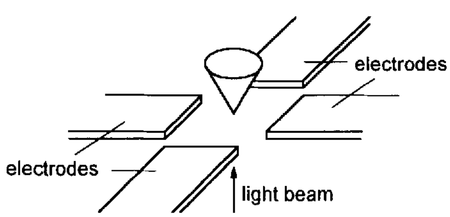


Figure 3. Experimental set-up; the free-standing film is situated between the electrodes, and the cone indicates the possible director movement.

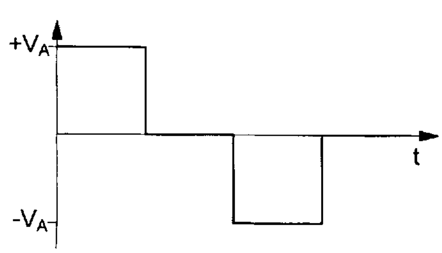


Figure 4. Impulse sequence applied to one of the electrodes.

Table 1. Composition of the mixtures of FLC-6430 with 90-917B and values of the pitch p and spontaneous polarisation P_s at 24°C.

FLC mixture	Content of FLC 6430/ wt.%	p/µm	P_s/nC cm^{-2}
FLC-6430	100	0·43	79·1
Mixture I	60	1·7	35·9
Mixture II	40	1·8	23·8
Mixture III	20	2·6	9·7
Mixture IV	13	3·9	7·5

optical transmission change was recorded by a photodetector connected with an oscilloscope. For the investigation of the circular flow, sequences of micrographs with dust particles on the film surface were transferred into a personal computer. Then, the velocity of the particles was calculated using the image processing software GLOBAL LAB® *Image*.

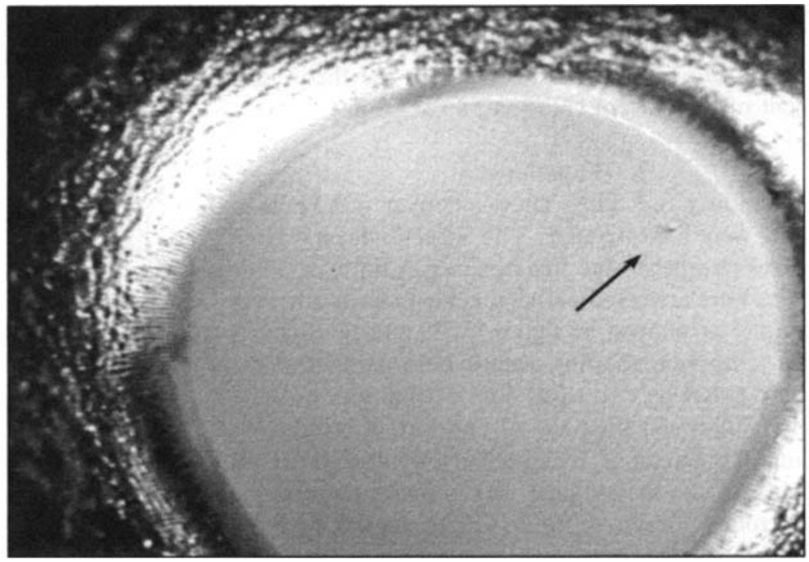
The pitch values of the liquid crystals studied were derived from the unwinding lines in sandwich cells. The distance between the lines is p [8]. These measurements were performed using again the image processing software. The spontaneous polarization was also determined in cells by the polarization reversal current method [9], and optical switching times were derived from transmission curves of free-standing films. The rotational viscosity can be calculated from P_S and the switching times [10, 11]. In the present experiments, we investigated a basic chiral substance (FLC-6430, Hoffmann-La Roche) and different mixtures of this substance with the non-chiral compound 90-917B (E. Merck). The compositions of the mixtures, as well as the values of p and P_S at room temperature are given in table 1. Additionally, the FLC mixtures FE1 and 15/2 (both from MLU, Halle) were used in some experiments.

3. Results and discussion

3.1. *Circular flow and pattern formation*

An FLC film that was well prepared for the investigations exhibited a uniform thickness over nearly the whole area. However, near the substrate the thickness increased rapidly, and a striped pattern was often visible [2, 12]. Figure 5 shows a free-standing film oriented homogenously in the area of uniform thickness. Outside this area, the thicker part can be recognised.

For low ω and high E one observes a field-induced rotational motion of the striped pattern into the direction of field rotation. Moreover, small dust particles, which are on the film by accident, move on a circular pathway in the same direction [2, 4]. These observations lead to the assumption that the rotating field induces a circular flow in the free-standing film. The limiting field parameters for which the visible motion stops are given by



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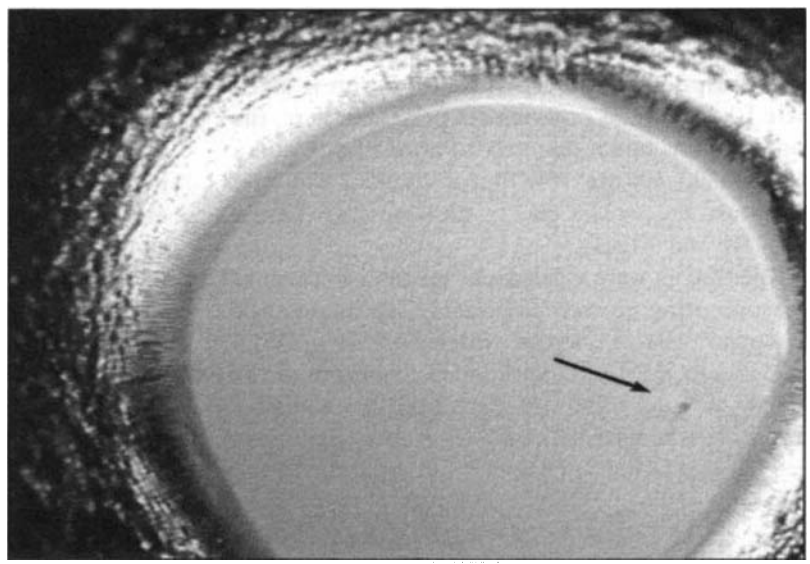


(b)

Figure 5. Free-standing film of FLC mixture FE1; homogeneous thickness in the central part and increasing thickness outside; a dust particle, marked by arrows, is moving in a circular path into the direction of field rotation.

the upper curve in figure 6. The motion takes place evidently far away from the region of spontaneous structure formation, at least for the FLC used here. However, it had to be made certain that simple observations are sufficient to detect the termination of the motion. For this purpose, we measured the velocity of dust particles—one is shown in figure 5—with decreasing voltage. The reduction in the velocity of the dust particles, v_d, with the applied voltage is shown in figure 7 for different field frequencies. The nearly linear decrease of v_d and the termination of the circular flow for $V>0$ are obvious. The intersection points between the extrapolated straight lines and the V-axis are drawn (open circles) in figure 6. They are situated very close to the upper curve. In this way, the cessation of circular flow for the field parameters denoted by this curve is confirmed.

Certainly, there are some examples of FLC mixtures where a circular motion is visible in the region of field-induced pattern formation. However, this behaviour is not the general one. The investigations presented here led us to the conclusion that the circular flow cannot be the reason for the spontaneous structure formation in rotating electric fields. The flow appears in the same experimental system which gives the ring creation and is probably caused by a coupling between director motion and macroscopic flow.

For a study of the ring structure, several series of micrographs were acquired using the short exposure

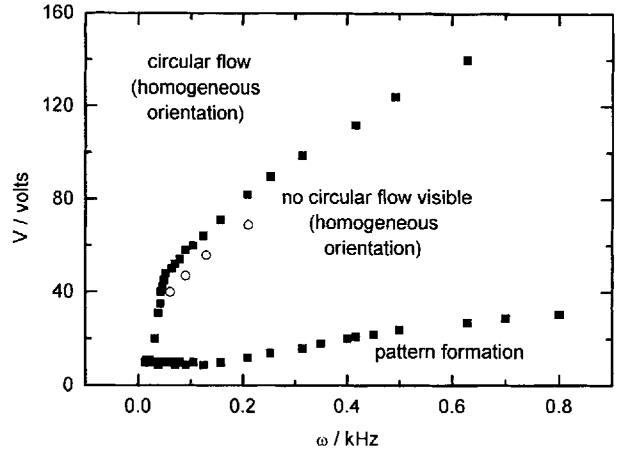


Figure 6. Visible circular motion in a free-standing film (mixture FE1) and its dependence on the field parameters V and ω; O—the results of a more detailed analysis (cf. text and figure 7).

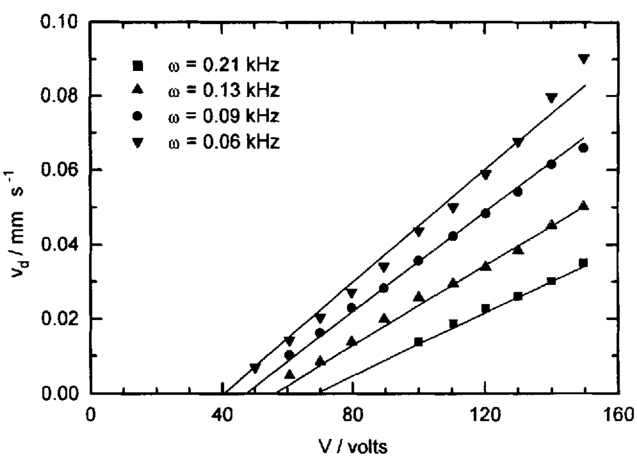


Figure 7. Dependence of the velocity of a small dust particle, v_d, on the applied voltage V for different frequencies; the same free-standing film as in figure 6.

time of 250 μs, which is several times shorter than the typical director reorientation time under our experimental conditions in free-standing films [11]. Such investigations make it possible to observe the field-induced director motion on the smectic cone. Using polarized light, a variation of intensity from one micrograph to the next suggests a change of the director orientation. A uniform intensity change takes place for the region of homogeneous orientation in the V-ω-diagram, and this confirms the synchronous director switching over the whole film area.

In the region of pattern formation, a temporal change of the spatial distribution of dark and bright rings could not be observed. Figure 8 shows two contrast enhanced micrographs from one series. Therefore, the rings are static deformations of the director field. They are visible in polarized and in non-polarized light. However, in the centre of the ring system, an intensity change indicates a director rotation on the cone.

These observations lead to the model shown in figure 9. The continuous spatial variation of transmission suggests that a ring system is composed of π- or 2π-walls. From the experiment, we are not able to decide between these two possibilities. However, theoretical treatment of the pattern formation predicts 2π-walls [6]. In the centre of the system, the director rotates with the applied field, contrary to the static deformations in the rings. After the first spontaneous formation of a whole ring system, new rings are created in the centre [3, 4] due to the continuous director rotation. The rings are moving outwards, in the direction of the border of the substrate. The spatial movement of the walls is accompanied by a slow local change of director orientation.

3.2. *Comparison between theory and experiment*

A first theoretical description of spontaneous pattern creation in the film starts from basic equations for the free energy. The resulting dynamic equation is [6]

$$\eta \frac{\partial \alpha}{\partial t} = \eta\omega - |E|\cdot|P_s|\sin\alpha + K\nabla^2\alpha, \qquad (1)$$

where K is an elastic constant, α is the lag angle $(\omega t - \varphi)$, and φ is the azimuthal angle of the director. Here, a continuously rotating field was assumed. This corresponds to the experimental situation of two sinusoidal waves shifted by phase.

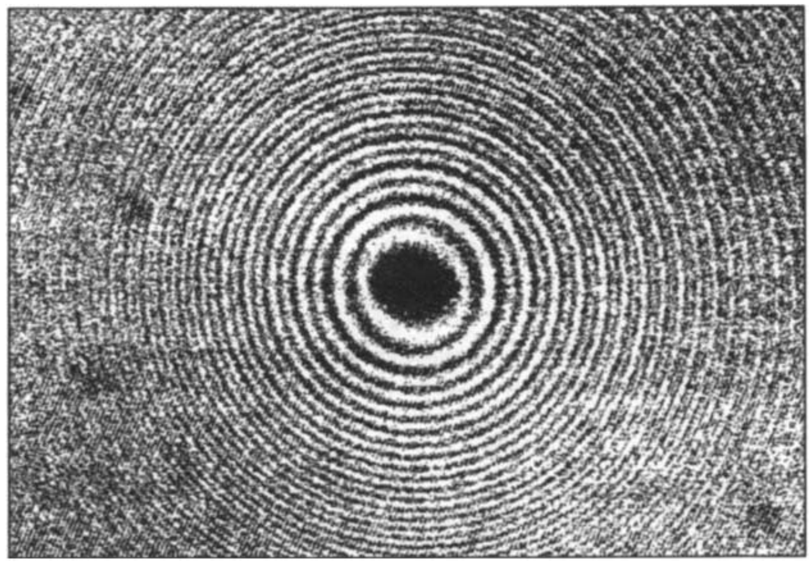
Equation (1) is similar to, but still a little more complicated than the over-damped sine–Gordon equation, which describes a soliton-like behaviour and has no analytical solutions [6]. The assumption of a homogeneous orientation simplifies equation (1) to

$$\tau \frac{\partial \alpha}{\partial t} = \omega\tau - \sin\alpha \qquad (2)$$

with the specific system time $\tau = \eta/(|E|\cdot|P_S|)$. Equation (2) has two solutions: one for $\omega\tau < 1$ where the director follows the applied field synchronously with a constant lag angle α, and a second for $\omega\tau > 1$ where the lag angle increases periodically [6]. The value $\omega\tau = 1$ defines the border between the synchronous regime and the asynchronous one. A pattern formation can occur only in the asynchronous regime. If the helix unwinding is taken into consideration, for $d \leq p$ this border is given by [6]

$$E_{\text{sync/async}} = \frac{\omega\eta}{P_S} + \left\{\frac{\pi}{4}\int_0^{d/p} [2(1-\cos\pi x)^{1/2}]\,dx\right\}^{-2} \frac{\pi^2 K t_0^2}{16 P_S}, \qquad (3)$$

where d is the film thickness, and $t_0 = 2\pi/p$. For $d > p$



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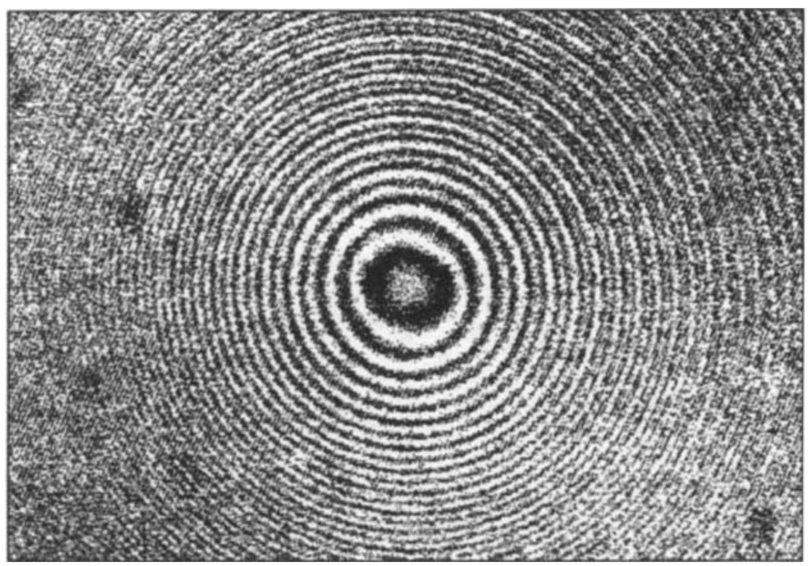

(*b*)

Figure 8. Consecutive micro graphs of a full ring system; mixture FE1, exposure time 250 μs.

the expression in brackets is equal to one, and the second term in equation (3) corresponds to the known relation for the helix unwinding [13].

Equation (3) describes the dependence of $E_{sync/async}$ on ω, which shows qualitatively the same behaviour as the upper experimental curve in figure 1. In figure 10 the experimental boundary between the homogeneous orientation (synchronous regime) and the region of pattern formation (asynchronous regime) is shown for both types of applied field. Both curves are situated very close together. This suggests that for the creation of ring systems, the rotation of the field itself is important, rather than the special field characteristics (continuously rotating or jumping).

In figure 10 the boundary calculated by equation (3) for the FLC mixture 15/2 is also shown. For the calculation, the following parameters of the FLC were used [11]: $\eta = 89$ mPa s, $P_S = 34{\cdot}7$ nC cm^{-2}, $p = 2{\cdot}3$ μm, $d =$ 500 nm, tilt angle $\theta = 12°$, and the distance between the electrodes $h = 1{\cdot}21$ mm. The curve was fitted with respect to the elastic coefficient because no data were available. The best fit was obtained for $K = 7 \times 10^{-14}$ N. A division by the scaling factor $(\sin 2\theta)^2/4$ [6] yields $1{\cdot}7 \times 10^{-12}$ N. The qualitative agreement with the experimental data is quite good. The differences may result from the omission of the dielectric term in the theory.

For very low values of the spontaneous polarization, one observes the opposite slope of the experimental

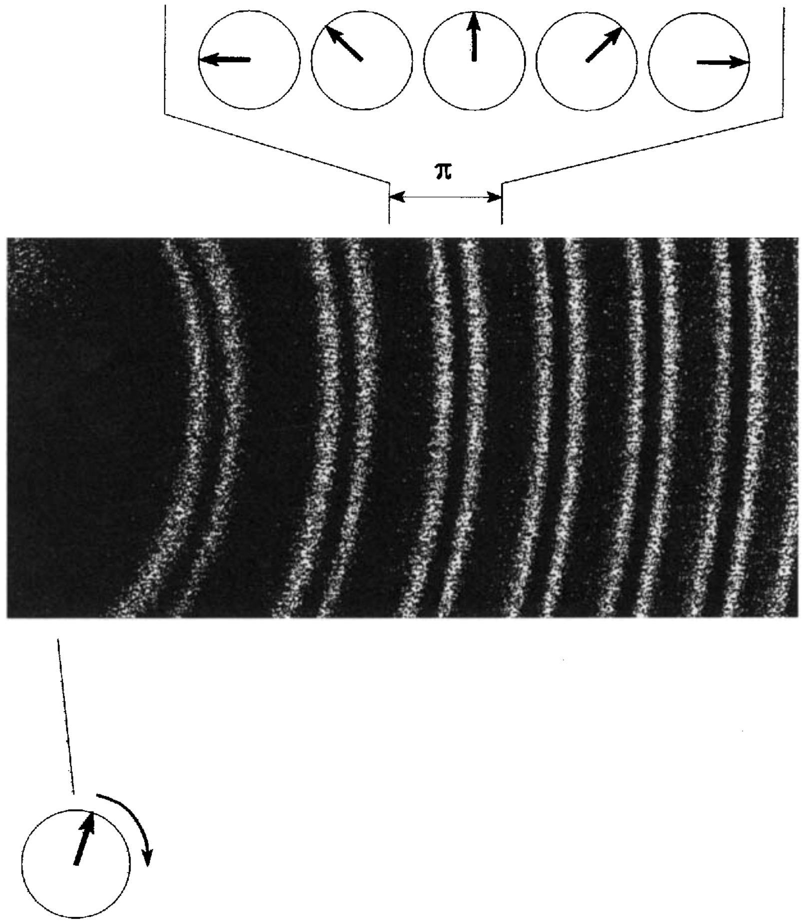

Figure 9. Ring system and the corresponding director distribution.

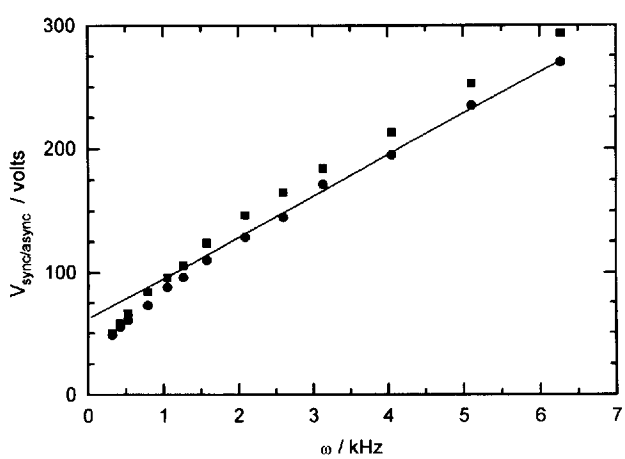

Figure 10. Boundary between homogeneous orientation and pattern formation for sinusoidal waves (●) and sequences of rectangular impulses (■); the straight line is the fit by equation (3), mixture 15/2.

curves (decreasing with increasing frequency) [4]. This behaviour cannot be explained by equation (3) which always yields curves with a positive slope. This disagreement is probably also caused by neglect of the dielectric properties in the theoretical description.

The comparison given here shows that equation (3) describes the boundary between homogeneous orientation and pattern formation, at least qualitatively. The other curves obtained experimentally (upper and lower critical curves, the boundary to the schlieren texture) are still without a theoretical explanation.

However, other experimental observations can be discussed using existing theory, e.g. the dependence of the upper critical curve of the quasi-stationary region on the pitch. This investigation, and most of the others, was not carried out for the boundary to the homogeneous orientation, but for the upper critical curve, which is almost parallel to this line. Disturbances of the homogeneous order often occur near the border to the substrate during the experimental determination of the boundary between the regions of the homogeneous orientation and the pattern formation. It is difficult to decide whether they indicate the beginning of the structure creation, or the influence of the substrate disturbs the homogeneous order. Contrary to this uncertainty, the upper critical curve is well defined because, in full ring systems, the width of the rings decreases with increasing distance from the centre of the system, whereas in small systems, the ring width is constant [5, 14]. In figure 11 the critical voltage V_{crit}, the value of the critical curve for a fixed frequency, is shown as a function of p. At first, the critical voltage decreases nearly independently of frequency, and, after that, V_{crit} increases with a strong dependence on ω. Variation of ω and p in equation (3) yields the picture presented in figure 12. The position of the minimum of the curve depends only on the film thickness; it characterizes the transition from the behaviour for $d > p$ to that for $d \leqslant p$. Indeed, there is only a qualitative agreement between figures 11 and 12 because they are connected with

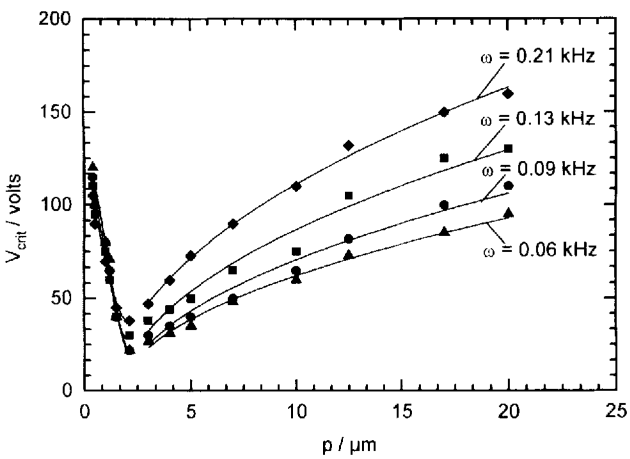

Figure 11. Dependence of the critical voltage V_{crit} on the pitch p; mixture I.

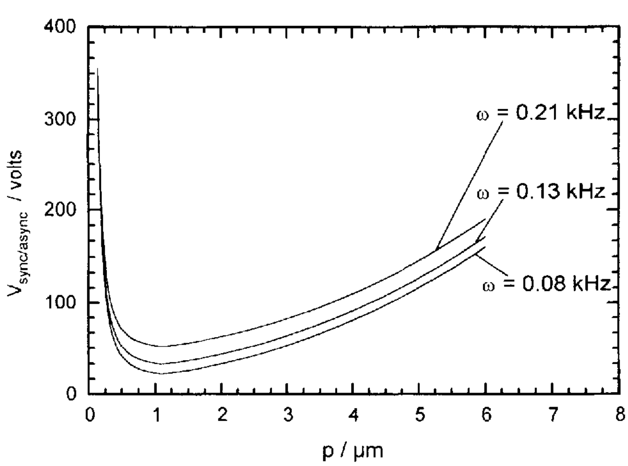

Figure 12. Variation of p and ω in equation (3); material parameters of mixture I.

different boundaries in the V-ω-diagram, as already mentioned. However, the experimental results could hardly be understood without the theoretical simulation of the inherent tendencies.

3.3. *Dependence of the pattern formation on temperature and material parameters*

On heating, a continuous displacement of the upper critical curve to lower voltages can be observed, as shown for mixture I in figure 13 (cf. also figure 1). Contrary to this strong influence of temperature on the upper critical values, the lower critical curve and the border to the region of schlieren texture depend only weakly on temperature. Therefore, a reduction in size of the quasi-stationary region with a full ring system takes place. The boundary between homogeneous orientation and pattern formation shows a behaviour which is similar to that of the upper critical curve. The decrease of the upper critical voltage (for $\omega = 310$ Hz) is shown in figure 14 for all FLC mixtures investigated.

The results of the measurement of P_S are presented in figure 15. A decrease of the spontaneous polarization with increasing temperature was found for all mixtures. At the phase transition from the S_C^* to the S_A phase, the spontaneous polarization becomes zero. The basic chiral mixture is the only one that shows a stronger temperature dependence. The influence of temperature becomes weaker with increase in the content of non-chiral compound in the mixture.

The rotational viscosity characterizes the molecular mobility on the smectic cone. It is well known that decrease in temperature causes an increase in viscosity. From independent measurements of the spontaneous polarization and of optical switching times, it is possible to calculate the viscosity of the liquid crystalline materials [11]. The results are given in figure 16. The expected increase for decreasing temperature was found for all mixtures investigated and the basic chiral substance. The viscosity values show a nearly Arrhenius-type behaviour away from the phase transition into the S_A phase. The activation energies E_V are given in table 2.

The change of p with variation in temperature is shown in figure 17 for mixture I. The other substances investigated have a similar behaviour. In the S_C^* phase a strong temperature dependence of the pitch could not be observed. The elastic coefficient K is one of the material parameters in equation (3) and is, therefore, also important for the pattern formation in free-standing films. However, its temperature dependence was not studied because known methods for the estimation of K (e.g. calculation from the voltage of helix unwinding [13]) are too inaccurate for this purpose.

A comparison of the temperature dependence of P_S, p, and η for mixture I is depicted in figure 17. The

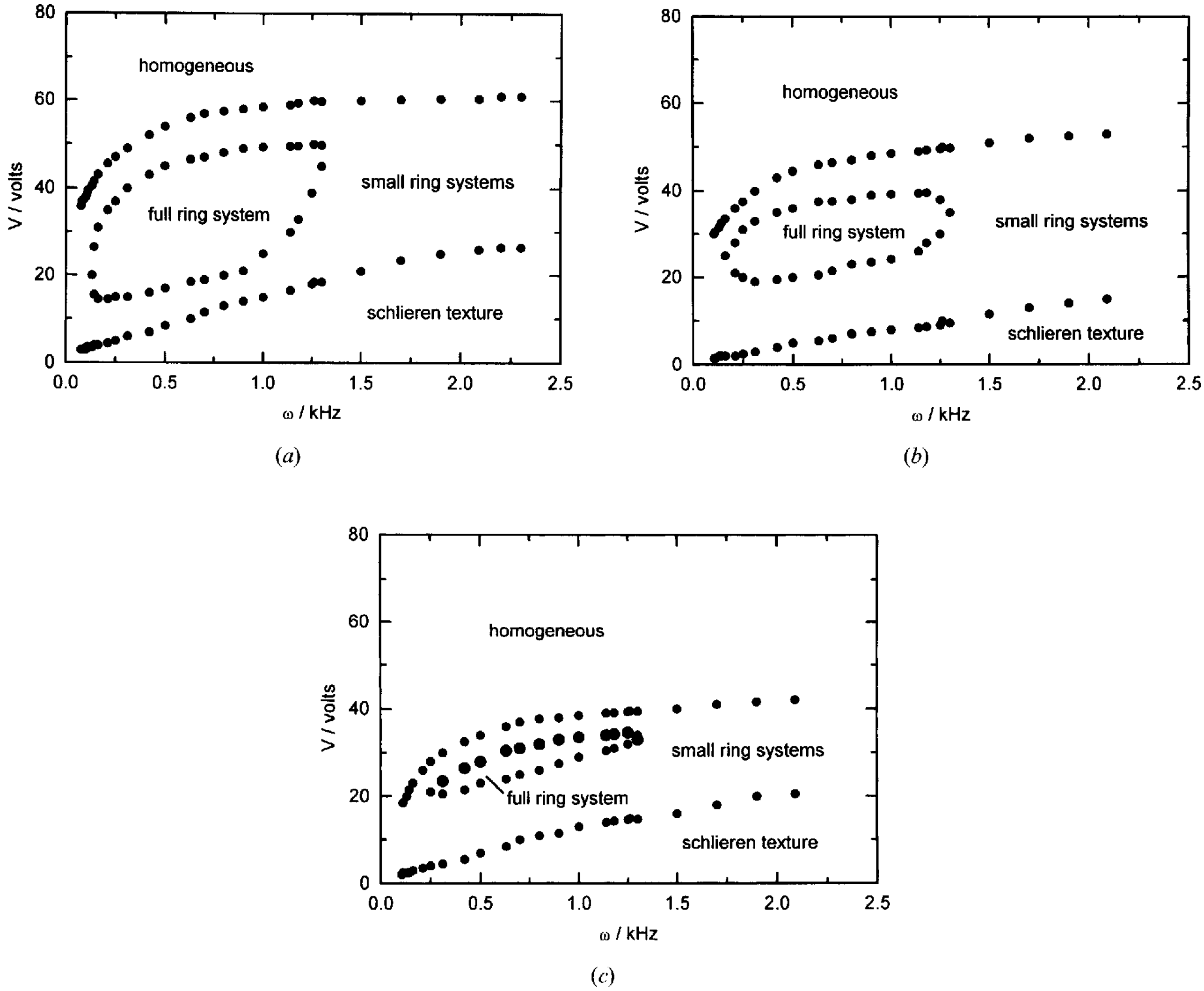

Figure 13. Dependence of the spontaneous structure formation on frequency ω and voltage V in mixture I for different temperatures; (*a*) $T=30°C$, (*b*) $T=33°C$, and (*c*) $T=43°C$.

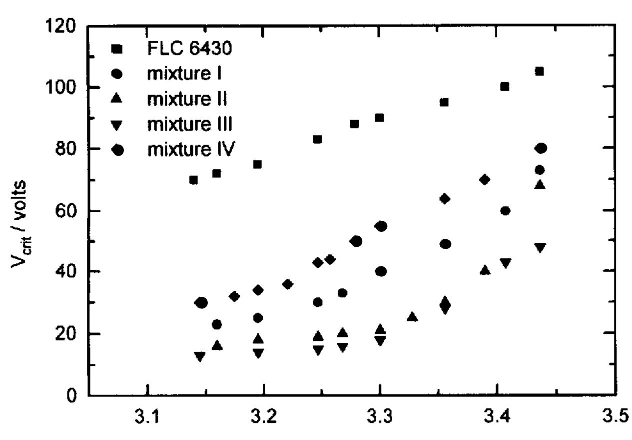

Figure 14. Dependence of the critical voltage V_{crit} on the temperature T for $\omega=310$ Hz.

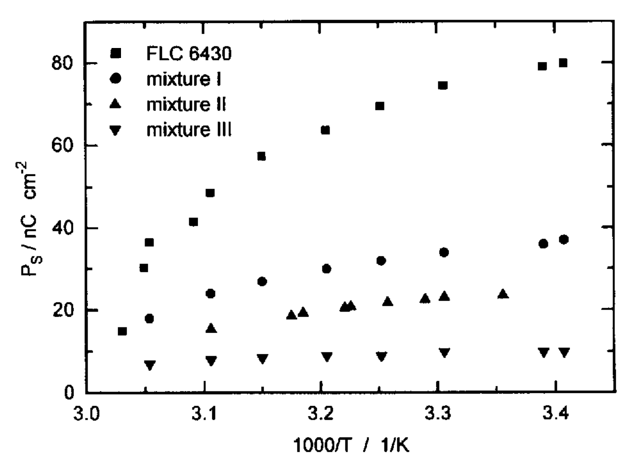

Figure 15. Dependence of the spontaneous polarization P_s on the temperature T.

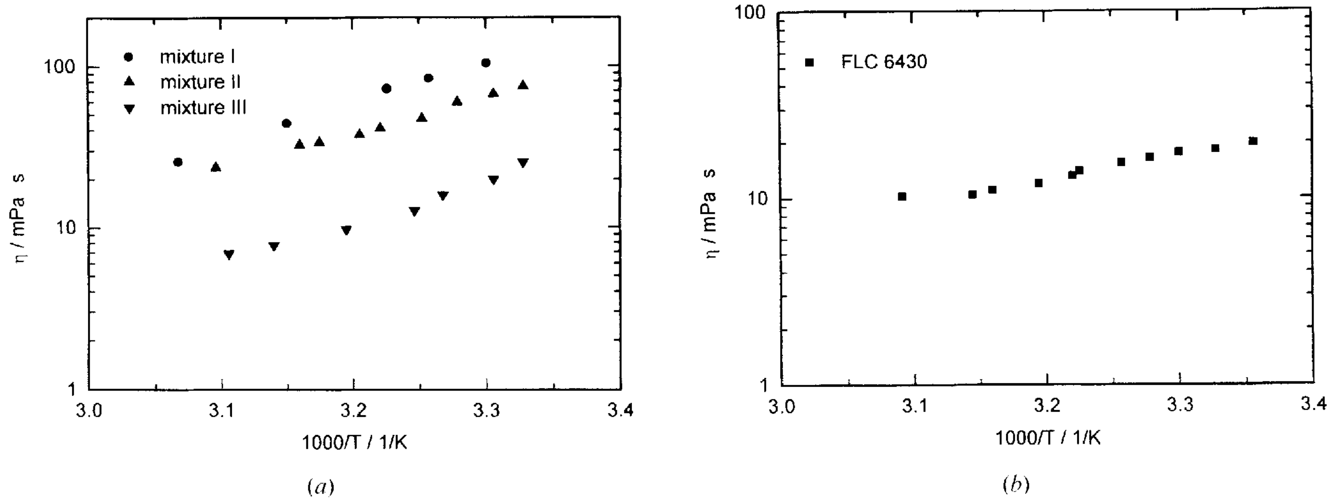

Figure 16. Dependence of the rotational viscosity η on the temperature T; (a) for mixtures I, II, and III; (b) for the substance FLC 6430.

Table 2. Activation energies E_v of some of the substances investigated.

FLC mixture	E_v/kJ mol^{-1}
FLC-6430	45·9
Mixture I	50·3
Mixture II	41·4
Mixture III	48·1

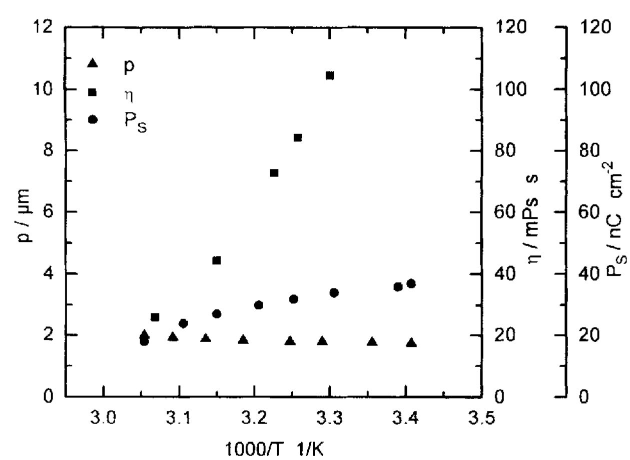

Figure 17. Dependence of pitch p, rotational viscosity η, and spontaneous polarization P_s on temperature T for mixture I.

viscosity is obviously the only parameter which exhibits a strong temperature dependence. The changes of the pitch and of the spontaneous polarization with temperature variation are very small in comparison to that of the viscosity. We obtained similar results for the other mixtures investigated. Only for the basic chiral substance does the P_S show a stronger temperature dependence, but it remains smaller than the variation of η. Therefore, we consider that the temperature dependence of the spontaneous structure creation is essentially influenced only by the viscosity. The temperature dependence of the boundary between homogeneous orientation and pattern formation was calculated through equation (3) using the experimentally derived values of $\eta(T)$ and the parameters $\omega = 310\,\mathrm{Hz}$, $d = 530\,\mathrm{nm}$, $h = 1{\cdot}21\,\mathrm{mm}$, and $K = 8{\cdot}3 \times 10^{-14}\,\mathrm{N}$. The results are shown in figure 18. For comparison, values obtained directly from the V-ω-diagrams are also presented. Both relate to curves which are very similar. The scatter of the experimental results is caused by the difficulties in determination of the boundary between homogeneous orientation and pattern formation, as mentioned above. The comparison given here demonstrates again the importance of η for the

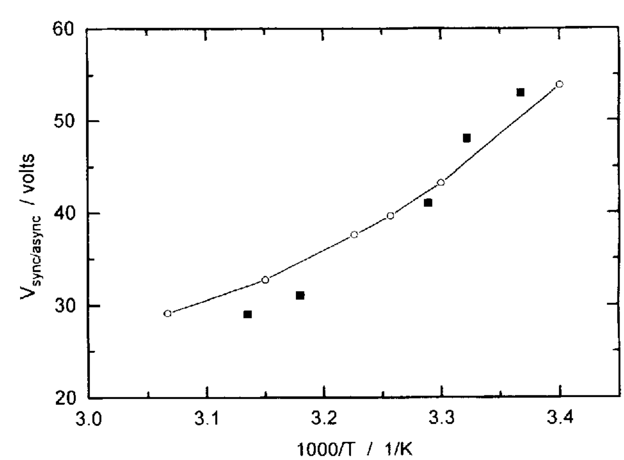

Figure 18. Dependence of the boundary between homogeneous orientation and pattern formation ($V_{sync/async}$ for $\omega = 310\,\mathrm{Hz}$) on temperature; experimental points (■) and calculated curve, mixture I.

general behaviour of the pattern formation in free-standing films and its dependence on temperature.

4. Conclusion

In conclusion, it has been shown that for free-standing films in a rotating electric field, the circular flow is not the reason for the spontaneous formation of ring structures. The phase delay between the field and the director is responsible for this structure creation. The dark and bright rings are systems of 2π-walls, and the field-induced director motion on the smectic cone is suppressed by the formation of the walls. The theoretical description of the pattern formation [6] is useful for an understanding of the general behaviour of free-standing films in rotating fields, and can explain some experimental results. However, an extension is necessary, e.g. the introduction of the dielectric term. The structure formation is influenced by temperature, and the rotational viscosity is the most important material parameter connected with this dependence.

Additionally, an unexpected spontaneous formation of ring structures was observed in the non-chiral smectic phases S_C, crystal G and S_I. A detailed discussion of these results will be published elsewhere [14]. It seems that the presence of a director pattern which is tilted with respect to the field, and not a finite value of the spontaneous polarization, is a necessary condition for the formation of the ring systems [12]. In the non-tilted S_A phase, structure formation could not be observed within the limits of the fields we applied.

After the initial creation, the further development of the ring structures shows a strong dependence on the viscoelastic properties of the liquid crystalline material [5]. Hence, spontaneous structure formation is in principle a viscoelastic effect.

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