Freedericksz transition in polymeric hexatic liquid crystals

P. Schiller; K. Camara; G. Pelzl; U. Emmerling; J. Lindau; F. Zeitler

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Fréedericksz transition in polymeric hexatic liquid crystals

by P. SCHILLER*, K. CAMARA, G. PELZL, U. EMMERLING, J. LINDAU
and F. ZEITLER

Martin-Luther-Universität Halle, Institut für Physikalische Chemie, Mühlpforte 1,
D 06108 Halle/S., Germany

The threshold voltage for the Fréedericksz transition of a polymer hexatic liquid crystal depends on the film thickness. This behaviour is attributed to the coupling of the director and the bonds defined by the hexatic order. We fit the results of a simple elastic continuum model to threshold data. The fit is suitable for the estimation of several material constants.

1. Introduction

In a few hexatic smectic phases, long molecules are tilted towards the smectic layer planes [1, 2]. The tilt can be characterized by a unit vector **n** called the director, which is parallel to the direction of the molecular long axes. A macroscopically non-homogeneous director configuration produces an elastic torque, which can be described by a continuum theory. A further degree of freedom is attributed to the bond-orientational order. The bonds are defined as the lines connecting the centres of gravity of neighbouring molecules. Although a crystalline lattice does not exist, the local hexagon consisting of the six nearest neighbours of a particle in a smectic layer is aligned macroscopically. The smectic I, F and L phases are distinguished by the director orientation with respect to the bonds. In the smectic I phase, the director is tilted towards an apex of the local hexagon, while in the smectic F phase the tilt direction is locked halfway between two local bonds. The smectic L phase is defined by an asymmetrical tilt direction [2].

If elastic distortions occur, the angle θ between the director and the smectic layer normal remains constant, but the projection of the director onto the smectic layer plane could be turned far away from the initial position after applying a relatively weak torque. Thus the azimuthal angle ϕ is sufficient to locate the director (figure 1). The rotation of the local hexagon from its initial position is characterized by an angle η. Since there is a coupling between the director and the bonds, distortions of the director field also cause distortions of the bond-net. It was found both theoretically [3] and experimentally [4] that the hexatic order has some influence on electrically driven instabilities of thin films.

The Fréedericksz transition, originally observed in nematic layers [5], also occurs in smectic C films [6, 7].
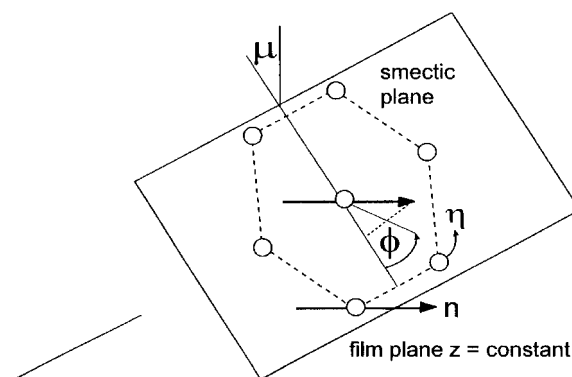

Figure 1. Director and bond reorientation in a planar film of the smectic F phase. The angles η and ϕ define the rotation of the director **n** and the hexagon of the bonds from their initial position. The z-plane is parallel to the bounding plates of the film. The angle μ is enclosed between the film normal and the smectic layer (layer tilt).

Applying an electric field to a suitably prepared planar oriented sample, elastic distortions appear for a voltage exceeding a certain threshold value. A mathematical model for the Fréedericksz transition of the hexatic smectic F phase should be similar to the corresponding model for the smectic I phase [3, 4]. Figure 1 refers to the smectic F phase. Applying a sufficiently high electric field across a planar film (parallel to the z-axis), the director reorientation (ϕ) should be accompanied by a reorientation of the bonds (η). To describe these field-induced director and bond reorientations the free energy [4]

$$F = \frac{1}{2}\int_{-d/2}^{d/2} dz \left[K_1(\partial_z \phi)^2 + K_6(\partial_z \eta)^2 + H(\phi - \eta)^2 - \Delta\varepsilon_{\text{eff}}(U/d)^2 \phi^2 \right] \tag{1}$$

is a suitable starting point, where d is the film thickness, K_1 and K_6 are effective elastic constants for director and

*Author for correspondence.

bond rotations, the coefficient H defines the strength of the director–bond coupling, $\Delta\varepsilon_{\mathrm{eff}} > 0$ is the effective dielectric anisotropy and U is the applied voltage. The effective dielectric anisotropy $\Delta\varepsilon_{\mathrm{eff}}$ depends on the layer tilt angle μ and the three principal values of the dielectric tensor. Assuming fixed bond and director angles at the boundaries—$\phi(z = -d/2) = \phi(z = d/2) = 0$ and $\eta(z = -d/2) = \eta(z = d/2) = 0$—a threshold voltage at which distortions start to grow can be evaluated by minimizing the free energy (1). Due to the coupling of the director and the bonds, this threshold depends on the sample thickness d. The square of the threshold voltage U_{C}^2 can be written as [4]

$$U_{\mathrm{C}}^2 = U_0^2 \left[1 + (d/d_0)^2 - \frac{(d/d_0)^4}{K_6/K_1 + (d/d_0)^2} \right] \qquad (2)$$
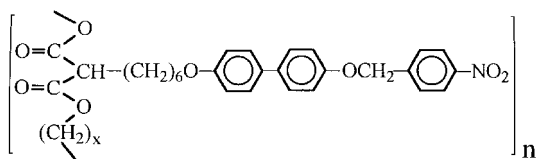
where

$$U_0 = \left(\frac{\pi^2 K_1}{\Delta\varepsilon_{\mathrm{eff}}} \right)^{1/2} \quad \text{and} \quad d_0 = \left(\frac{\pi^2 K_1}{H} \right)^{1/2}.$$

A plot of U_{C}^2 versus d^2 allows determination of some material constants which are coefficients in the free energy (1).

2. Experimental results

The experimental set-up for the determination of the threshold voltage is the same as that described in reference [4]. A voltage was applied to the bounding plates of a liquid crystalline film with a uniform director alignment parallel to the substrates (planar orientation). Increasing the voltage, the intensity of the light transmitted through the film was measured by using a polarizing microscope equipped with a photomultiplier. The threshold voltage was obtained from the transmission–voltage curve.

A fairly good planar orientation of smectic polymer liquid crystals can be achieved by cooling down from the aligned nematic phase. In this paper we consider planar smectic C and smectic F films formed by the side group polymer (P6)

where the spacer length chosen was $x = 6$. The phase sequence of P6 was found to be

Cr 30 SmX 82 SmF 94 SmC 128 N_{re} 129·5

SmA 131 N 147 I (°C).
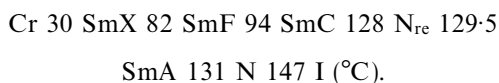
The symbol N_{re} indicates a re-entrant nematic phase. As the structure of the smectic X phase (SmX) was not

clarified unambiguously, we do not discuss the threshold behaviour of this phase. It is interesting now to compare the material constants for the polymer P6 with the corresponding results for the compound M
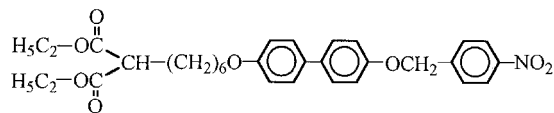
which has the phase sequence

Cr 69 SmX 66·5 SmF 75 SmC 94 N 110 I (°C).
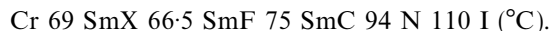
The low molar mass compound M has a structure quite similar to that of the mesogenic unit of the polymer. Figure 2 illustrates the dependence of the threshold on the temperature for planar films with thickness $d = 6\,\mu\mathrm{m}$. The threshold voltage of the low molar mass liquid crystal film is found to be somewhat lower than the threshold of the polymer film.

More interesting is the dependence of the threshold on the film thickness. In figures 3 and 4, the square of U_{C} is plotted versus the square of d for eight different samples ($d = 2$, 4, 6, 10, 15, 25, 40 and $50\,\mu\mathrm{m}$). The threshold voltage of the nematic sample is nearly independent of the film thickness, but there is a characteristic dependence for smectic C and smectic F films. We have used equation (2) to fit the experimental data. Theoretical arguments suggest that U_0 should have nearly the same value for the smectic C and the smectic F phase, as long as the tilt angle θ remains constant [4]. Actually, optical and X-ray diffraction experiments revealed that the angle $\theta \approx 30°$ does not change significantly in the temperature range of our experiments. Therefore it was reasonable to determine U_0 by using the threshold data for the smectic C phase, since for this phase U_0 is not much different from the Fréedericksz
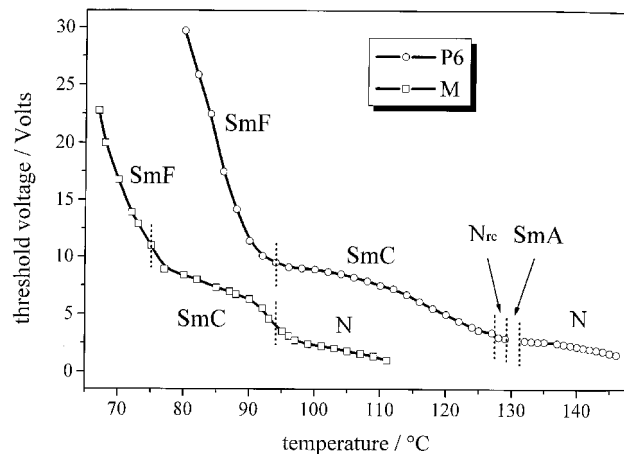

Figure 2. Fréedericksz threshold for films of the polymer P6 and the low molar mass liquid crystalline material M as a function of the temperature ($d = 6\,\mu\mathrm{m}$).
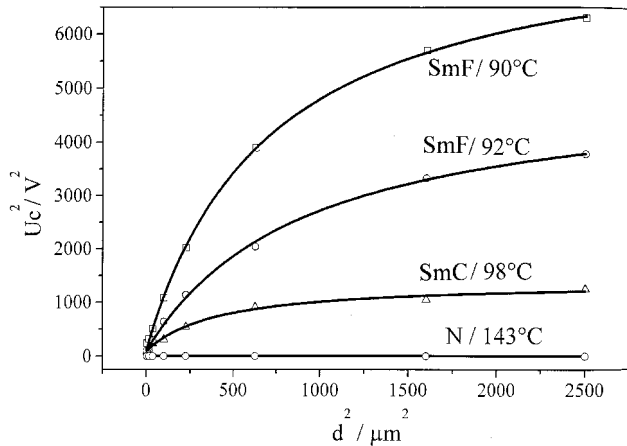
Figure 3. The square of the threshold voltage for the Fréedericksz transition of the polymer P6 plotted against the square of the film thickness. The experimental data are fitted by using equation (2).
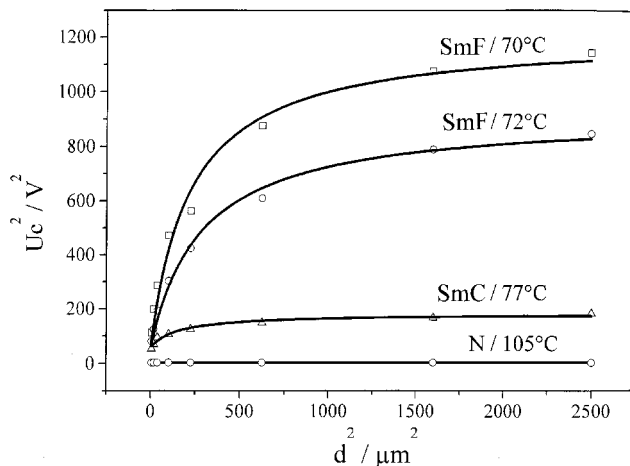

Figure 4. The same plot as in figure 3 for the low molar mass compound M.

Table.

Phase	$\vartheta/°C$[a]	U_0/V	$d_0/\mu m$	K_6/K_1	$(H/K_1)/10^{10}\,m^{-2}$
P6					
SmC	98	9·3	5·3	14·9	35·1
SmF	92	9·3	4·0	58·1	61·7
SmF	90	9·3	2·7	91·5	135·4
M					
SmC	77	8·0	10·0	2·3	9·9
SmF	72	8·0	4·7	13·5	44·7
SmF	70	8·0	3·5	22·8	80·6

[a] Temperature of observation.

Therefore the experimental results support the general concept [1] based on a finite coupling of the director to the bond-net. The statement that $K_6 \gg K_1$ agrees well with the conclusions drawn from light scattering experiments [8] for free-standing films. Furthermore, our measurements support the assumption that the values of the elastic constant K_1 for the smectic F phase and the smectic C phase do not differ much as long as the tilt angle θ remains approximately constant [4]. Comparing the results for the low molar mass liquid crystal and the polymer (see the table), no significant differences in the general behaviour were detected. In accordance with X-ray experiments [9], some bond-orientational order was proven to exist even in the smectic C phase. This observation indicates that the smectic C phase belongs to the hexatic liquid crystalline class of phases.

threshold U_C. Then there are only two free parameters available (d_0 and K_6/K_1) to fit the experimental data for the smectic F phase. The fitted constants of the polymer P6 and the non-polymeric substance M are summarized in the table below.

Unfortunately, the experimental data are not sufficient to extract the values for the material constants K_1, K_6 and H, because the effective dielectric constant $\Delta\varepsilon_{eff}$ is unknown. Using the data in the last column of the table and assuming that $K_1 \approx 10^{-10} \ldots 10^{-11}$ N, the value of the coupling constant H could be roughly estimated.

3. Conclusions

The simple equation (2) provides a fairly accurate description for the threshold behaviour of the Fréedericksz transition in hexatic phases with tilted molecules.

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