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VIP Liquid Crystals

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A Lyotropic Chiral Smectic C Liquid Crystal with Polar Electrooptic Switching**

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Dedicated to Professor Helmut Bertagnolli on the occasion of his 70th birthday

Thermotropic and lyotropic liquid crystals are often treated separately, in research as well as in applications. While thermotropic phases are formed by mesogenic molecules in a certain temperature range, lyotropic phases are built up by aggregates of nonmesogenic amphiphilic molecules in the presence of a solvent. Even though the building blocks of thermotropics and lyotropics are rather different, they form a common state of matter with liquid-crystalline phases of similar structure and symmetry. For example, the thermotropic smectic A phase (SmA),[1] which is shown in Figure 1 a, has a well-known lyotropic analogue, the so called lamellar L_α phase[2] (Figure 1 b). On account of this, it is astonishing that some thermotropic phases have not been observed in lyotopics and vice versa. A significant example of this is the smectic C phase (SmC),[3] which consists of 1D stacks of 2D fluid layers (Figure 1 c). In these layers the molecules are ordered along the common direction of the director **n**, which is tilted with respect to the layer normal **k** by the tilt angle θ. This tilt direction is long-range correlated over macroscopic distances. In thermotropic liquid crystals this is one of the most common and best investigated phases, as the chiral variant, SmC*, which is formed by chiral molecules, is of great scientific and technological interest[4] because it shows a spontaneous polarization $\mathbf{P_S}$[5,6] and macroscopic chirality in the form of a helical twist of the tilt direction with pitch p.[5]

In contrast, the lyotropic analogue to the SmC phase (Figure 1 d) is almost unknown. There are very few reports of this phase[7] and even fewer in which the existence of this lamellar tilted and fluid phase is definitely proven, for example, by X-ray diffraction.[8] Furthermore, there has never been a report of a lyotropic chiral SmC* phase. Thus, many important questions arise concerning the constraints in the formation of a lyotropic SmC phase and about possible chirality effects in a lyotropic SmC* phase. For example, it is unclear if and how there can be a long-range transmittance of the tilt direction through the solvent layers, as there is no direct contact between the tilted molecules. Moreover, it is questionable if the chirality of the individual smectic layers and also the helical correlation could be communicated through the intermediatory achiral solvent. To answer these questions, molecules were devised which possess a relatively bulky polar head group containing ethylene glycol units, an element known from a lyotropic SmC liquid crystal investigated by Schafheutle and Finkelmann,[8] and which at the same time carry an element of chirality. Now, we report the observation of the first chiral SmC* phase which forms in the presence of a solvent.

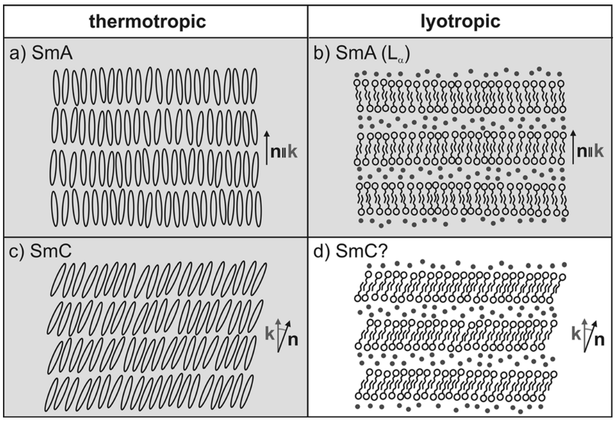

Figure 1. Schematic picture of a) the well-known thermotropic SmA phase composed of calamitic mesogens with indicated directions of director **n** and layer normal **k**, b) the lyotropic analogue of the SmA phase, L_α, composed of bilayers of amphiphilic molecules separated by solvent molecules (●), c) the thermotropic SmC phase, and d) the very uncommon lyotropic SmC phase.

The chemical structure of the investigated mesogen **1** is shown in Figure 2 (the synthesis is described in the Supporting Information). The molecule combines typical structural elements of thermotropic and lyotropic liquid crystals. On the one hand it possesses an ethylene glycol unit and a chiral diol head group which allow the molecule to mix with polar solvents,[9] and on the other hand it contains an SmC-promoting phenylpyrimidine core.[10]

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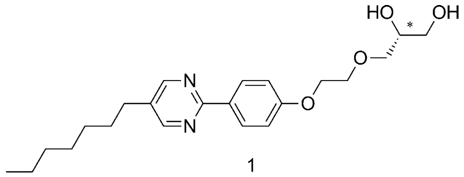

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Figure 2. Chemical structure of the investigated diol **1**.

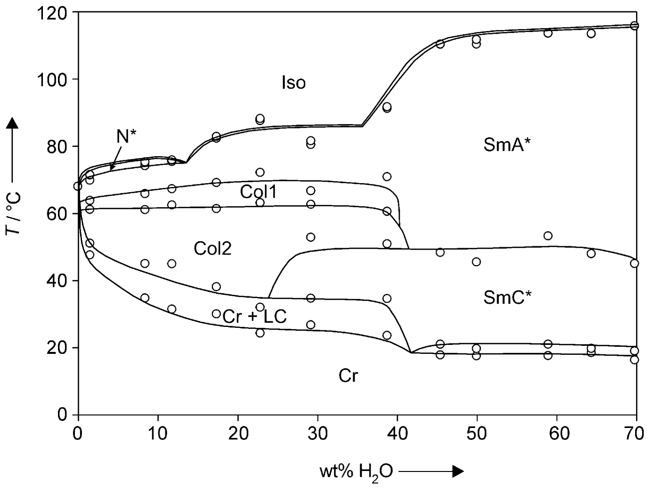

Figure 3. Phase diagrams of the diol **1**/water systems.

In the absence of solvent, diol **1** exhibits no enantiotropic liquid-crystalline phases, only a monotropic chiral nematic phase (N*) on cooling. In mixtures with water, it shows several different lyotropic mesophases (Figure 3). Very small amounts of the solvent turn the N* phase into an enantiotropic but still quite narrow phase. Furthermore, two columnar phases, Col1 and Col2, can be observed. The dominating phase of the diol **1**/water system is a lyotropic SmA* phase. At water concentrations above 20 wt%, an enantiotropic phase occurs, which will later be shown to be a lyotropic SmC* phase. The fact that this phase appears only in the presence of a solvent has to be emphasized, because this demonstrates that the phase is not an artifact of a thermotropic SmC* phase but a real lyotropic phase. The phase diagram for mixtures with formamide (see the Supporting Information) shows a similar behavior, with the same phases occurring. However, the two columnar phases and the SmC* phase are now monotropic.

The first evidence to confirm the existence of the lyotropic SmC* phase is the observation of SmC*-characteristic textures by polarized optical microscopy. The representative texture images in Figure 4 show schlieren and broken-fan textures as well as zigzag defects,[11] which are all very typical of an SmC or SmC* phase. Furthermore, the spontaneous tilt domains in Figure 4c,d suggest that this is a surface-stabilized ferroelectric SmC* phase.[6]

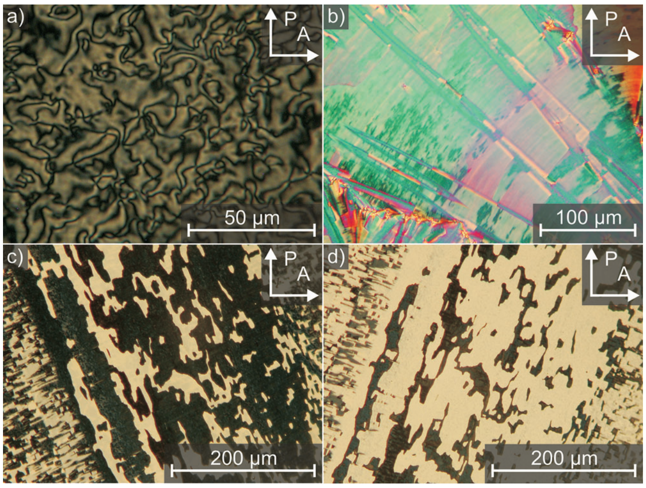

Figure 4. Texture images between crossed polarizers (P, A) of the lyotropic SmC* phase showing a) a schlieren texture (42 wt% water, 60 °C), b) a broken fan texture with zigzag defect lines (65 wt% water, 46 °C), c) and d) domains with opposite tilt directions in the surface-stabilized state of a 1.6 µm cell (17 wt% formamide, 28 °C).

Further evidence of the existence of a lyotropic SmC* phase can be obtained by means of X-ray diffraction. In Figure 5a the temperature dependence of the smectic layer spacing *d* of a sample with 64 wt% water is depicted. The layer spacing of the SmA* phase shows negative thermal expansion, with a maximum *d* value around the SmA*–SmC* transition. Below this temperature the layer spacing greatly decreases. This behavior is characteristic of an SmC or SmC* phase, due to the increasing tilt angle θ with decreasing temperatures.[12] Perhaps the most direct proof of a lyotropic SmC-analogue structure is given by the 2D diffraction pattern from a monodomain sample[13] (Figure 5b). The sharp fundamental and higher-order pseudo-Bragg peaks in the inner

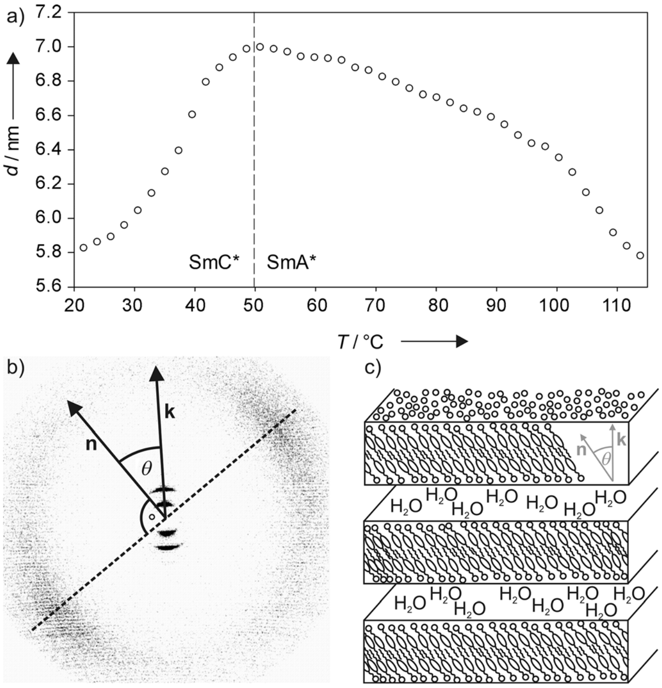

Figure 5. a) Temperature-dependent layer spacing *d* across the lyotropic SmA*–SmC* transition (64 wt% water), b) 2D diffraction pattern of a monodomain SmC* sample (42 wt% water, 38 °C), and c) schematic image of the lyotropic SmC phase.

small-angle regime originate from the long-range lamellar order along a single direction of **k**. The pair of diffuse outer wide-angle scattering maxima indicates the fluid intralayer order of the orientationally ordered diol molecules. In SmA and L_α phases, the diffuse maxima are perpendicular to the layer peaks and rotate in the same direction by θ after cooling into the SmC phase, thus indicating the non-zero average tilt of the long molecular axes with respect to the layer normal **k** ($\theta \approx 37°$ in Figure 5b).

Considering the molecular length $l = 2.5$ nm[14] of **1** and a layer spacing of $d = 7.0$ nm (Figure 5a), the solvent layer at the onset of the SmA*–SmC* transition is at least 2.0 nm thick and becomes even thicker in the case of partial double layers. A schematic image of the lyotropic SmC structure which is consistent with the X-ray data is shown in Figure 5c.

The important question now is, does this phase, being composed of chiral molecules, also exhibit the macroscopic chirality effects of the thermotropic SmC* phase? Such behavior can be demonstrated explicitly by the observation of periodic pitch lines arising from a spiraling director on the tilt cone (Figure 6d). Indeed, pitch lines appear in mixtures of the diol **1**/water system (Figure 6a) when a sealed sample is equilibrated for several weeks. The pitch of the SmC* phase for the pictured sample with 59 wt% water at 36°C is $p =$ 4.7 μm. The pitch lines appear much more clearly in mixtures with formamide (Figure 6b), in which the pitch develops within seconds. The temperature dependence of the pitch measured directly in a sample with 32 wt% formamide is plotted in Figure 6c and shows a rapid increase as the SmC*–SmA* transition is approached. The helicity provides clear evidence that the lyotropic SmC* phase exhibits macroscopic chirality and that the helical twist of the tilt direction is communicated between adjacent molecular double layers across the solvent layer in between. The reason behind the different temporal evolution of this interlayer interaction with different solvents is quite remarkable and still has to be understood.

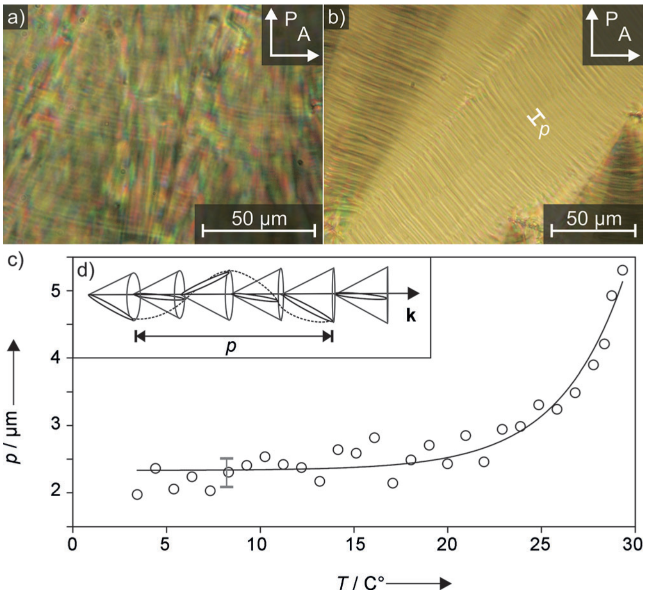

Figure 6. a) Pitch lines of a sample with 59 wt% water at 36°C and b) of a sample with 32 wt% formamide at 30°C. c) Pitch values of the latter sample derived directly from the texture images plotted against temperature and d) model of the SmC* phase illustrating the helical distortion of the tilt direction.

Another important aspect of this lyotropic SmC* phase is the occurrence of a spontaneous polarization in analogy to the thermotropic phase and thus the possibility of polarity-dependent switching between the two surface-stabilized states of the tilt direction (see Figure 4c,d). Such investigations are very challenging with lyotropic liquid crystals, because of the high electric conductivity of the solvents and the unconventional preparation process of the samples. Nevertheless, it was possible to make some preliminary measurements to demonstrate that the lyotropic SmC* phase exhibits a polar electrooptic effect in an alternating electric field. The change in the texture of the lyotropic SmC* phase, following the reversal in the direction of an applied electric field, is shown in Figures 7a,b. The observed polarity-dependent electrooptic effect is analogous to the polar electrooptic effect in ferroelectric SmC* liquid crystals, where the field-induced reversal of the spontaneous polarization reverses the tilt direction. Saturated switching as occurs in thermotropic SmC* phases is not observed here, because of the large conductivity and threat of dielectric breakdown. This polar switching process can be followed dynamically by using a photomultiplier to record the change

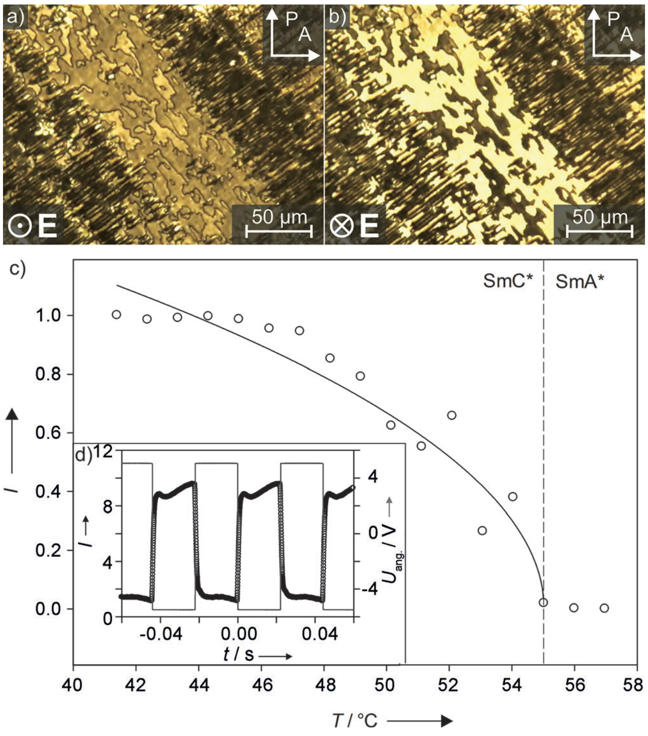

Figure 7. The lyotropic SmC* phase under the influence of an electric field. a) and b) show texture images with reversed directions of an applied electric field with $U = 5$ V μm^{-1} and $f = 0.5$ Hz (18 wt% formamide, 25°C). c) Temperature dependence of the change of transmitted light intensity of a sample with 64 wt% water and d) exemplary transmission change (○) at 44°C together with the applied square-wave voltage (——).

of transmitted light intensity as a function of the applied voltage (Figure 7d). The plot demonstrates clearly that the switching is of polar and not of dielectric nature, in which the transmission—and thus the tilt direction—does not depend on the voltage polarity. The temperature dependence of the change of transmitted intensity is depicted in Figure 7c, thus illustrating that switching ceases above $T_C = 55$ °C, which matches the transition to the lyotropic SmA* phase. This finding indicates that the observed effect is not due to possible solvent-related processes such as electroconvection, but is an intrinsic effect of the lyotropic SmC* phase and scales with the observed tilt angle. Prior to this example, polar switching of a lyotropic liquid crystal has only been observed in the case of discotic mesophases.[15] Moreover, the related piezoelectric effect was found in a lamellar L_{α} phase under viscous shear stress.[16]

In conclusion, we demonstrate the first lyotropic surface-stabilized ferroelectric SmC* phase and present evidence for its existence through texture studies, X-ray diffraction, pitch measurements, and polarity-dependent director switching. Furthermore, we demonstrate that this phase possesses macroscopic chirality effects, that is, helical pitch lines and a polar electrooptic effect, which implies communication of chirality between the molecular double layers across the intermediatory layers of solvent molecules. Following the widespread notation of lyotropic phases by Luzzati and co-workers,[17] we suggest this new lamellar phase should be denoted $L^*_{\alpha'}$, where the index α' indicates a tilted fluid phase and—according to IUPAC recommendations[18]—the superscript * indicates the chirality of the molecules.

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Keywords: chirality · ferroelectricity · helical structures · liquid crystals · lyotropics

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Communications

Liquid Crystals

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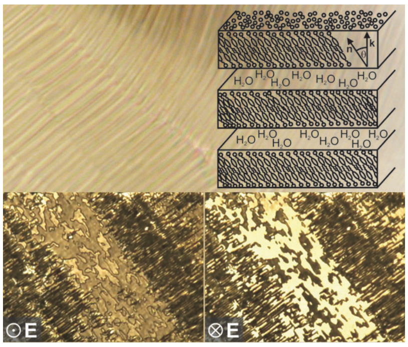
A Lyotropic Chiral Smectic C Liquid Crystal with Polar Electrooptic Switching



A lyotropic analogue of the ferroelectric smectic C* phase has been found. The lyotropic smectic C* phase shows macroscopic chirality effects, such as a helical ground state and polarity-dependent electrooptic switching, thus indicating the presence of a spontaneous electric polarization. The helicity implies communication of the chiral director twist across the achiral solvent layers separating adjacent layers of the chiral mesogens.