

Temperature-Induced Orientational Transition of Nematics on the Surface of a Ferroelectric Crystal

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Received July 10, 2002

A temperature-induced orientational transition is investigated in a mixture of nematic liquid crystals on the surface of a cleavage of a ferroelectric triglycine sulfate crystal. The transition has been observed by the variation of the polarized absorbance components of a dye introduced into the nematic matrix with increasing temperature. The reorientation of molecules in the liquid crystal volume confined by solid walls is due to competition between dispersion and polar forces at the surface and the decrease in the electric field of the substrate up to its complete disappearance at the ferroelectric Curie point. © 2002 MAIK “Nauka/Interperiodica”.

PACS numbers: 61.30.Gd; 64.70.Md; 77.84.Nh

The alignment of liquid crystal molecules confined by solid walls can be due to the competition of two or more independent factors favorable to homeotropic or planar texture [1]. If the competing factors differ in their temperature dependence, an orientational transition from one texture to the other can take place. A transition from planar to homeotropic alignment with varying temperature under conditions of a competition between van der Waals and short-range anchoring forces on the surface was observed previously [2]. The competition of polar and dispersion van der Waals forces of the substrate also favors the orientational transition [3]. At the same time, the electric field of the substrate substantially affects the alignment of the liquid crystal because of its dielectric anisotropy and enhances the polar effects at the confining surfaces [4]. The competing effect of dielectric, polar, and dispersion forces can be effectively observed on the orienting surfaces of ferroelectrics. The spontaneous polarization field of a ferroelectric single crystal depends on temperature and vanishes at the point of its phase transition to a nonpolar state. If the liquid crystal is chosen so that its temperature of the transition to an isotropic liquid is above the Curie point, the alignment of the nematic can be traced until the electric field of the substrate completely disappears. The polar and surface polarization effects on the energy of nematic anchoring to the ferroelectric surface were discovered recently [5].

In this work the behavior of a mixture of nematic liquid crystals is studied on the surface of a cleavage of a ferroelectric triglycine sulfate (TGS) crystal. An orientational transition in the bulk of the liquid crystal layer due to variations of the competing forces at the surface with temperature is reported.

Polar and nonpolar substrates were used in the experiment for orienting liquid crystals. Areas of TGS cleavages containing “–” domains served as polar sub-

strates. A liquid crystal was placed in the space between two coaxially oriented cleavages [6] separated by wire spacers 20 μm in diameter. Mixture B ((2/3) MBBA + (1/3) EBBA) was used as the liquid crystal in order to extend the temperature range of the existence of the mesophase [7]. An observation using a polarization microscope demonstrated that the mixture existed as a nematic phase up to 51.5°C, that is, above the ferroelectric phase transition temperature (49°C). With the aim of visualizing the orientational effects under conditions of the intrinsic birefringence of the substrates, the anthraquinone dye KD-10 [6] was added to the mixture in the amount of 0.3 wt %, whose absorption band maximum coincided with the He–Ne laser wavelength ($\lambda = 632.8$ nm). Observations by polarization microscopy led to the conclusion that the nematic mixture is in a planar alignment along the crystallographic axis c of TGS. Absorption spectra D_{\parallel} and D_{\perp} of the KD-10 dye in the nematic phase of mixture B at a fixed temperature (23°C) are presented in Fig. 1. The large value of the dichroic ratio $D_{\parallel}/D_{\perp} = 7$ at the He–Ne laser wavelength provides the possibility of reliably observing the orientational effects. TGS cleavage plates made a small contribution to polarized absorbance components. This contribution was determined in samples that did not contain a liquid-crystal mixture and a dye and was taken into account in the experiment. The spectrum was obtained on an SF-20 spectrophotometer connected to a computer. Nonpolar substrates were glass plates treated by depositing a polymer film of poly(vinyl alcohol) on them. It is known [8] that such a treatment gives a nonpolar surface layer and provides a homogeneous alignment of nematics. The substrates were oriented uniaxially (that is, the directions of their easy orientation axes coincided) and were separated by Teflon spacers 20 μm thick. Mixture B with the KD-10 dye was poured in the gap between the substrates in the isotropic phase.

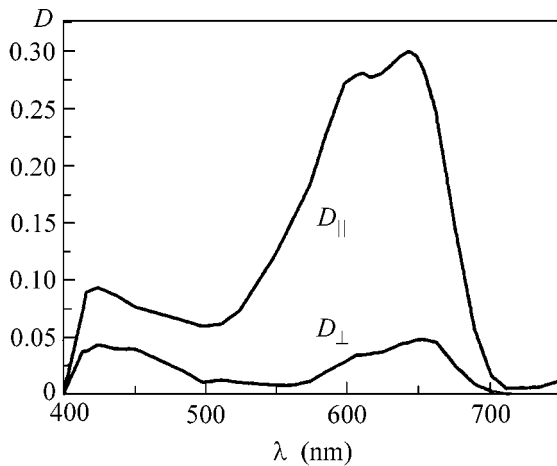


Fig. 1. Polarized absorption spectra D_{\parallel} and D_{\perp} of the KD-10 dye in nematic mixture B between TGS cleavages in a 20- μm gap at a temperature of 23°C.

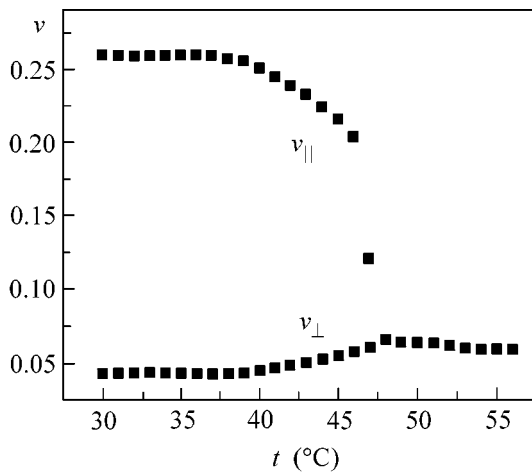


Fig. 2. Absorbance components v_{\parallel} and v_{\perp} of the KD-10 dye at the He-Ne laser wavelength in nematic mixture B between two polar surfaces of TGS cleavages in a 20- μm gap as functions of temperature.

The orientational texture of the liquid crystal mixture was studied by placing the samples in a thermostated cell. The temperature was scanned by a thermostat and was measured by a copper–constantan thermocouple. A He–Ne laser beam passed through the sample so that the direction of its polarization coincided with the director n of the nematic mixture and the crystallographic axes of the TGS plates. The intensity I_{\parallel} of the modulated signal was taken from a photodiode and was measured by a selective nanovoltmeter. Next, the sample was rotated around the laser beam through 90°, and the temperature dependence of I_{\perp} was recorded. The magnitude of I_0 corresponded to the intensity of the laser radiation passed through the sample area free of the liquid crystal mixture. The experimental procedure with the use of laser radiation allowed the state of a sample to be controlled by a polarization microscope

while scanning the temperature so as to exclude the possible motion of domain walls on TGS cleavage surfaces [9]. The mixture absorbance components corresponding to the dye absorption band maximum for the light polarization directions parallel and perpendicular to the director were calculated by the equations $v_{\parallel} = \log(I_0/I_{\parallel})$ and $v_{\perp} = \log(I_0/I_{\perp})$ [7].

The absorbance components v_{\parallel} and v_{\perp} of the dye at the He–Ne laser wavelength are given in Fig. 2 as functions of temperature for nematic mixture B on polar surfaces. The experimental data in Fig. 2 demonstrate a significant decrease in v_{\parallel} and an insignificant increase in v_{\perp} in the vicinity of the ferroelectric phase transition. The components become equal on the transition of TGS to the nonpolar state (49°C). The temperature dependence of v_{\parallel} and v_{\perp} is shown in Fig. 3 for mixture B on nonpolar substrates. The curves draw closer together up to the point of the phase transition of the nematic mixture to the isotropic liquid (51.5°C). The difference in the run of the polarized absorbance components on polar and nonpolar surfaces points to an orientational effect, which accompanies the decrease in the order parameter of the liquid crystal with increasing temperature. The v_{\parallel} and v_{\perp} components on polar substrates are equal to each other above the point of the phase transition of the ferroelectric to the nonpolar state, in which the electric field of the substrate disappears, but below the point of the phase transition of the nematic mixture to the isotropic liquid, up to which this mixture retains its liquid crystal properties. This fact allows the conclusion that the nematics undergo an orientational transition from the planar to homeotropic texture.

In order to analyze the experimental data, let us consider processes at the boundary of the liquid crystal layer. On the TGS cleavage surface, the electric field of the spontaneous polarization of the ferroelectric “packs” the molecules of the nematic mixture, because of its negative dielectric anisotropy, in the substrate plane [9]. The field may turn out to be nonuniform across the thickness of the polarized layer of the liquid crystal λ_D with the average dielectric constant ϵ and to make a contribution to the surface energy proportional to the quadrupole density q [9] and the density σ of charges adsorbed on the surface [4]. The total contribution of the electric field to the surface energy, depending on the deflection angle θ of the liquid crystal director from the normal to the surface, was $f_e = (-\pi\Delta\epsilon\sigma\lambda_D/\epsilon^2 + 4\pi q/\epsilon)\cos^2\theta = w_e\cos^2\theta$ [4]. Van der Waals dispersion forces of the substrate favors the planar texture, because these forces are responsible for the difference in the alignment of nematics on the “+” and “-” domains of TGS [9]. The anisotropic part of the surface energy for dispersion forces, without taking into account correlations between molecular orientations and assuming the equality of the order parameter in the bulk and at the surface of the liquid crystal cell, can be represented in the form $f_d = w_d\cos^2\theta$ [3]. Thus,

the contributions of the electric field and dispersion forces to the surface energy of nematics have the same angular dependences. In addition, these forces give rise to unidirectional moments on the surface. The temperature dependences of the spontaneous polarization vector of the ferroelectric [10] and the order parameter of nematics on glass surfaces [11] qualitatively coincide and cannot generate the reorientation threshold of the liquid crystal [1]. These features allow us not to consider the competition of the given factors in our experiment. At the same time, the asymmetric action of the liquid crystal–solid interface and the character of the interaction of the ends of molecules with the TGS cleavage surface [9] may give rise to a polar moment favorable to the homeotropic alignment of nematics. The surface induces a polar order parameter, which contributes to the surface energy $f_p = -w_p \cos \theta$ [3]. The coefficient w_p also takes into account surface polarization. This polarization is due to ordering of molecular dipoles and interacts with the electric field of the substrate [12]. Competition between the polar f_p and dispersion f_d factors leads to a temperature-induced orientational transition in nematics [13]. The minimization of the free energy carried out in [3] gave $\cos \theta = 1$ if $w_p > w_d$ and $\cos \theta = w_p/w_d$ at $w_p < w_d$. Because the temperature dependences of w_p and w_d are different, an orientational transition may occur from planar to homeotropic texture. Suppose that in our case $w_p < w_d$. Polar moments favor homeotropic alignment. However, both the electric field and surface dispersion forces tend to orient the director of nematics in the planar geometry. As the electric field of the ferroelectric decreases with increasing temperature and completely disappears above the Curie point, the competition of dispersion and polar forces lead to the homeotropic texture. Another contribution to the surface energy should also be taken into account. This contribution is due to the gradient of the scalar order parameter of the liquid crystal at the surface, which can be represented in the form $f_q = w_q \cos^4 \theta$ [14]. The coefficients w_p and w_d differ in their temperature dependence, and an orientational transition of the nematic is possible. However, the contribution of f_q commonly turns out to be small [4]. It was this instance that did not allow the significant difference in the anchoring coefficients of MBBA on the TGS cleavage surfaces for the planar and homeotropic alignments to be explained using this mechanism [5, 15].

Thus, an orientational transition of nematic mixture B from the planar texture to the homeotropic one was observed. The alignment was a consequence of the competition of three contending factors: the electric field of the ferroelectric tends to “lay” liquid crystal molecules in the substrate plane and the van der Waals anchoring forces favor the planar alignment, whereas the polar effects give rise to the homeotropic texture. The transition is due to a difference in the temperature dependence of the competing factors and a decrease in

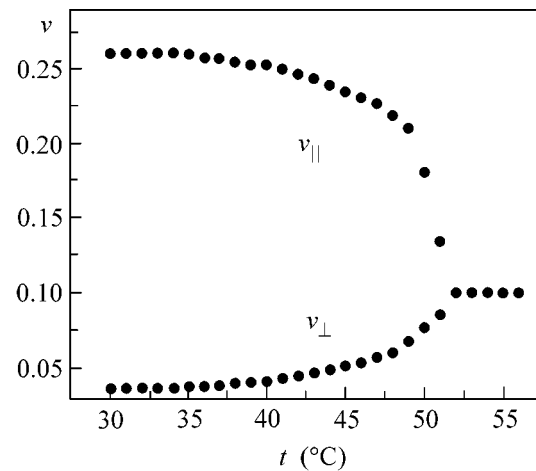


Fig. 3. Absorbance components v_{\parallel} and v_{\perp} of the KD-10 dye at the He–Ne laser wavelength in nematic mixture B between two nonpolar glass surfaces in a 20- μm gap as functions of temperature.

the electric field of the substrate down to its complete disappearance at the Curie point of the ferroelectric.

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Translated by A. Bagatur'yants