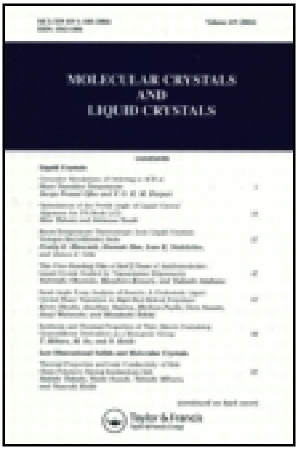

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

To cite this article: Y. Marinov, N. Shonova, S. Naydenova & A. G. Petrov (2000): Surface Dissipation of Energy in Homeotropic Nematic Layers, Weakly Anchored on Various Self-Assembled Substrates, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 351:1, 411-417

To link to this article: http://dx.doi.org/10.1080/10587250008023292

Mol. Cryst. and Liq. Cryst., 2000, Vol. 351, pp. 411-417
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Surface Dissipation of Energy in Homeotropic Nematic Layers, Weakly Anchored on Various Self-Assembled Substrates

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Homeotropic nematic layers of MBBA, oriented by self-assembled layers (on glass substrates) of dilauroyl phosphatidyl choline (DLPC), cetyl trimethyl-amonium bromide (CTAB) and silane orienting agent (ODS-E), were studied by phase-sensitive flexoelectric spectroscopy method. DLPC solutions in chloroform provided multilayers with different thickness on dipped glass substrates, depending on bulk DLPC concentration. CTAB solutions in water provided, on the other hand, just monolayers, with surface density depending on pulling speed of substrates. Finally, ODS-E solutions provided orienting layers that can be cross-linked at elevated temperatures. The viscoelastic spectra of these layers contained information about surface dissipation of orientational energy under variable structure of orienting layers that may, or may not, dissolve partially in the nematic.

Keywords: flexoelectric spectroscopy; weak anchoring; surface viscosity

INTRODUCTION

Earlier, first experimental observation of nematic surface viscosity by the method of flexoelectric spectroscopy was reported[1] and temperature dependence of surface viscosity of MBBA/CTAB interface was systematically investigated[2]. Knowledge of surface viscosity coefficient reveals important dynamic aspects of the orientational interaction nematic-substrate and of the surface dissipation of energy. This is important for nematic liquid crystals in thin layers, but also for nematics in confined geometries[3,4]. Surface dissipation in confined geometries was investigated recently[5]. Some theoretical aspects of surface viscosity and its relation to bulk orientational viscosity were also explored[6,7].

Flexoelectric spectroscopy method, based on a device for generation and amplification of flexoelectrooptic oscillations of light passing through a homeotropic nematic layer, was described elsewhere[1,2]. Experimentally, we measured the 1st harmonic in the flexoelectrically modulated light intensity, passing through the homeotropic layer subjected to a horizontal dc+ac electric field following a slow frequency sweep, provided by a computer-interfaced lock-in amplifier (SR830). Theoretically, the problem for the description of these oscillations was solved earlier[2,8]. The 1st harmonic vs. frequency spectrum includes surface anchoring (b), bulk viscosity (γ_l^*) and surface viscosity (κ) contributions:

$$I_\omega(\omega) = \frac{A}{\omega}\,\frac{1 - \frac{B}{d}\frac{1}{\sqrt{\omega}}}{\sqrt{\left(1 + \frac{B}{b}\frac{1}{\sqrt{\omega}}\right)^2 + \left(1 - D\sqrt{\omega}\right)^2}}$$

(1)

where

$$A \propto \frac{2e_{3x}^{*4}\,E_l\,E_0^3\,d^3}{3K_{33}^3\,\gamma_l^*\left(l + d\ 2b\right)^3};\quad B = \sqrt{\frac{2K_{33}}{\gamma_l^*}};\quad D = \kappa\sqrt{\frac{2}{K_{33}\gamma_l^*}};\quad b = \frac{K_{33}}{C}.$$

Here $e_{3x}^* = e_{3x} + m_p$ is the bend flexocoefficient *plus* surface polarization, K_{33} is the bend elastic constant, γ_1^* is the rotational viscosity of the nematic, corrected for the back-flow, κ is the surface viscosity and C is the anchoring energy. By fitting the above expression to the experimentally obtained flexoelectric spectra we can find the parameter D, i.e. surface viscosity κ, providing independent data about K_{33} and γ_1^* are available[9]. In the frequency range under study (above 1 Hz) the effect of terms containing the parameter B are negligible (including finite extrapolation length b effect in the denominator).

MATERIALS AND METHODS

Nematic layers of MBBA (T_C = 43°C) obtained from Reachim were studied throughout. The nematic material was sandwiched between two glass plates with homeotropic treatment of the glass surfaces. Earlier, CTAB monolayers were used as orientants[2]. The CTAB monolayer films were self-assembled by dipping the precleaned substrates into water solutions of the surfactant CTAB (Merck 99% p.a.) at $1.6\cdot10^{-5}$ M concentration in bidistilled water for 10 min. The plates were then withdrawn with two different speeds (i.e., 0.6 cm/min or 2 cm/min) to obtain densely packed or loosely packed orienting monolayers for homeotropic MBBA anchoring[2,10]. Presently, self-assembled multilayers of DLPC (Fluka) dissolved in chloroform were also employed. Bulk lipid concentration was varied in the range 1-100 μM in order to vary the multilayer thickness[11]. Glass plates were dipped in chloroform solution for 20 min and then air-dried at 50°C. For comparison, cross-linked orienting layers of silanes were also studied. 0.1 vol % of ODS-E (Chisso) was dissolved in 9:1 iso-propyl alcohol/water and glass plates were dipped in the solution for several hours under continuous stirring. The plates were then rinsed with distilled water and polymerized at 110°C for 1 hour.

Liquid crystal cells were assembled with 100 μm thick Cu-foil spacers serving as electrodes. The samples were sealed by Araldite (epoxy-glue). The inter-electrode distance was 2 mm. Cells were placed in a Mettler FP82 heating stage for varying the temperature. After filling the cell the MBBA clearing point was usually reduced to 41°C. A horizontal electric field directed at 45° versus crossed polarizers was applied to the nematic layer by means of the copper spacers. The frequency dependence of transmitted light modulation depth was obtained by means of a "flexoelectric spectrometer"[2].

RESULTS AND DISCUSSION

The 1st harmonic flexoelectric spectra of MBBA anchored on a loose CTAB monolayer (2 cm/min pulling velocity) at different temperatures in the nematic range were reported elsewhere[2]. The shape of the spectra closely followed theoretical predictions: in the lower end $I_\omega \propto \omega^1$ and in the higher end $I_\omega \propto \omega^{1.5}$.

At lower pulling velocity (0.6 cm/min) good homeotropic orientation was also obtained. However, in comparison with the loosely covered substrates at higher pulling speeds, a middle frequency plateau appeared on the spectral curves, not explainable by the present theory. This interesting phenomenon is now observed also with orienting (multi)layers of lecithin, self-assembled by dipping in chloroform

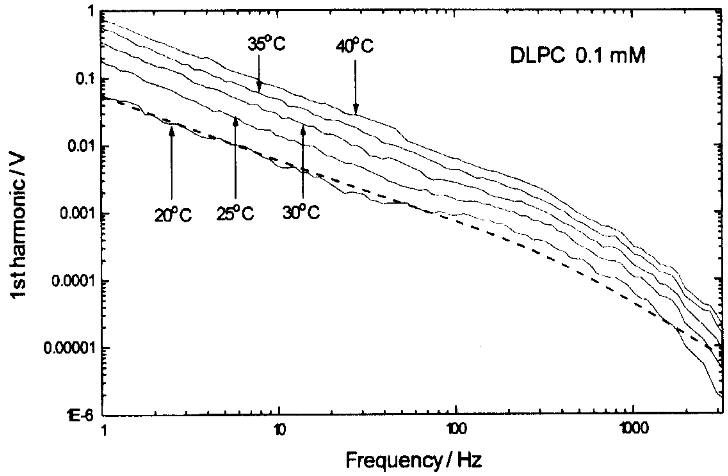

FIGURE 1 Frequency dependence of the 1st harmonic of flexoelectrically modulated transmitted light through a homeotropic nematic layer of MBBA at different temperatures. Homeotropic orientation by self-assembled DLPC layers (bulk concentration 0.1M). Layer thickness is 100 μm, electrode distance is 2mm, a.c.voltage is 30 V_{pp}, d.c. bias is 15 V. For clarity only one (unsuccessful) attempt to fit the spectrum by the theory (Eq.1) at 20°C is shown on the graph.

solution (Fig. 1):

It was suggested that the middle frequency plateau may be due to the formation of a gradient of excess desorbed surfactant close to the substrate. In order to prove this, control experiments with cross-linked ODS-E silane orienting layers were performed, where polymerization of silane monomers would presumably preclude the desorption of orientants. Results obtained proved this idea (Fig. 2). The shape of spectra is totally different, middle frequency plateau is absent, and the linear shape (in log-log coordinates) with just one break (cross-over

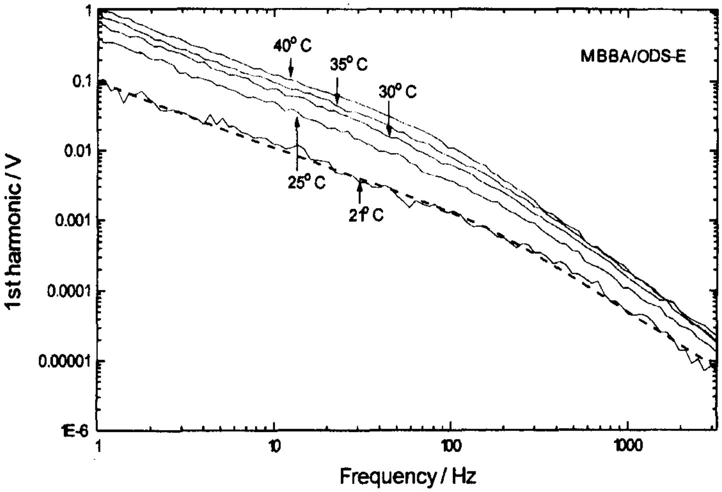

FIGURE 2 Frequency dependence of the 1st harmonic of flexoelectrically modulated transmitted light through a homeotropic nematic layer of MBBA at different temperatures. Homeotropic orientation by cross-linked ODS-E coatings. Layer thickness is 100 μm, electrode distance is 2mm, a.c.voltage is 20 V_{pp}, d.c. bias is 10 V. For clarity only one fit of the spectrum at 21 °C is shown on the graph.

frequency) is fully explainable in terms of surface viscosity. Same type of spectra with just one break were observed earlier with MBBA/DMOAP interfaces[1].

It is seen that the cross-over frequency decreases with increasing the temperature. By means of a two-parameter fitting procedure (i.e., by neglecting terms containing parameter B), the values of parameter D were extracted and surface viscosity was calculated. To this aim data for γ_1^* and K_{33} for the corresponding relative temperatures of MBBA were interpolated from Figs. 9 and 10 in[9]. The calculated values of κ ranged from $3\cdot10^{-8}$ (±5%) J s m^{-2} at 21°C down to $1\cdot10^{-8}$ (±5%) J s m^{-2} at 40°C. These values are a factor of 2 higher than the surface viscosity of CTAB/MBBA interface[9]. They also tend to vary from sample to sample, apparently being correlated to the strength of anchoring: e.g., in a cell with 1st harmonic values in the range [50 mV - 300 mV] at 1 Hz (lower than those on Fig. 2, i.e., with a stronger anchoring) the κ values ranged from $3.8\cdot10^{-8}$ (±5%) J s m^{-2} at 21°C down to $2.1\cdot10^{-8}$ (±5%) J s m^{-2} at 39°C.

CONCLUSION

Experimental results on the surface dissipation of orientational energy in homeotropic nematics demonstrate a good agreement with the theory in the case of a minor amount of orienting substance on the substrates, but a disagreement in case of excess monomeric orientant. A conclusion is drawn that the disagreement may be due to the monomer desorption and built-up of a surfactant gradient near the substrate. This is confirmed by the subsequent finding that with polymerized orienting layers the agreement is again fulfilled. To further theoretically corroborate this conclusion a non-trivial extension of the existing theory by including order parameter gradients near the substrates (caused by the gradients in orientant concentration) has to be done.

Acknowledgments

This work is supported by INCO-COPERNICUS (ERBIC15-CT96-0744) joint project and by the National Fund "Scientific Studies"of Bulgaria (Project F519).

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