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Optically Aligned Ferroelectric Liquid Crystals**

By Yue Zhao* and Nadine Paiement

Ferroelectric liquid crystals (FLCs) have a chiral smectic-C phase, S_C^* , in which each layer has a permanent electric polarization that is confined in the plane of the layer and perpendicular to the director (molecular orientation direction) tilted by an angle from the layer normal. Normally in a bulk FLC, the chirality leads to rotation of the directors of the successive layers, and the induced helical structure cancels the polarization vectors from each other over a pitch length. Therefore, to observe and make use of the spontaneous polarization of FLCs, the key condition is to suppress the helical structure in the S_C^* phase by aligning molecules in one direction. There has been a considerable interest in developing FLC technologies over the last two decades, because FLCs have important advantages over other liquid crystals (LCs) for use in electronic and photonic devices, mainly due to the fast switching speed of FLCs in an electric field. However, until now, the only technique for the suppression of the helix in the S_C^*

phase, which leads to successful commercialization of FLC devices, is the surface-stabilized FLC (SSFLC) discovered by Clark and Lagerwall in 1980.^[1] In this communication we report a new strategy that needs no rubbed surfaces to align and stabilize FLCs. An azobenzene diacrylate monomer is dissolved in a FLC host, polymerized and irradiated with linearly polarized light; the photoalignment of azobenzene results in an anisotropic polymer network that subsequently accomplishes both the induction and stabilization of the FLC orientation in the S_C^* phase.

To make SSFLCs, the FLC compound (or mixture) is introduced into an electrooptic cell whose inner surfaces, coated with indium tin oxide (ITO), are parallelly rubbed, and whose gap is less than the helical pitch of the S_C^* phase. Under these conditions, the helical structure cannot develop in the S_C^* phase, while rubbed surfaces can impose a uniaxial orientation on the FLC molecules. With a desirable bookshelf geometry, where the layers are perpendicular to the binding plates and the molecules are oriented at the tilt angle θ with respect to the surface rubbing direction, the spontaneous polarization is normal to the binding plates. The direction of this polarization may switch between two (up and down) states in response to change in the polarity of the electric field applied across the cell, leading to the in-plane switching of the FLC molecules by an angle of 2θ . Under crossed polarizers, such switching may create the dark and bright states, which is the basis for FLC devices. The lack of major breakthroughs in the commercialization of SSFLCs is mainly explained by complications in the fabrication process and the difficulty of inducing and sustaining a uniform alignment;^[2] their weak shock resistance is another drawback.^[3] Since the discovery of SSFLCs, considerable efforts have been made to develop new techniques for the alignment and stabilization of FLCs by external effects other than rubbed surfaces. Representative studies include polymer-dispersed FLCs,^[4] microphase-stabilized FLCs,^[5] and ferroelectric elastomers,^[6,7] for which a mechanical shear is generally employed to induce the alignment.

In the present study, we succeeded in aligning FLCs by light and fixing the molecular orientation by a polymer network, without the use of rubbed surfaces. This work was based on a new optical approach recently developed in our laboratory for nematic LCs,^[8-10] which makes use of the well-known photoisomerization-induced orientation of azobenzene molecules when exposed to linearly polarized light.^[11,12] Our approach uses a diacrylate monomer bearing an azobenzene group in its structure to accomplish both the induction and stabilization of the LC orientation. One of the findings on nematic LCs is that when an azobenzene diacrylate monomer is dissolved in the LC host, thermally induced polymerization in the isotropic phase of the LC under irradiation with linearly polarized light can result in an aligned azobenzene polymer network,^[9] and that on cooling under irradiation, a long-range uniaxial LC orientation is induced by the anisotropic network in the nematic phase. We investigated the usability of this optical approach for FLCs on the basis of the following consideration. For a FLC having a chiral nematic, N^* , and a smec-

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tic- A , S_A , phase prior to the formation of the S_C^* phase, which often is the case, if an anisotropic azobenzene network is obtained by irradiation and polymerization in the isotropic phase of the FLC, on cooling, the anisotropic network may induce a uniaxial molecular orientation in the N^* phase, and retain this orientation upon subsequent phase transitions into the S_A and S_C^* phases, thus preventing the helical structure from occurring in the S_C^* phase; the network then provides the orientation stability for the FLC. As a matter of fact, the orientation stability provided by an anisotropic polymer network to various types of LC^[13,14] including FLCs,^[2] has been well demonstrated; but in all the reported systems, rubbed surfaces were needed to promote the initial LC orientation before polymerization of a reactive monomer was performed in the oriented LC to obtain the stabilizing anisotropic network.

In our study, we used a FLC host, CS-1031, purchased from CHISSO Corporation (Japan), which is a FLC mixture having the following phase transition temperatures: Cr -12°C S_C^* , 60°C S_A , 85°C N^* , 97°C Iso. The helical pitch of CS-1031 is $37\ \mu\text{m}$ in the N^* phase and $3\ \mu\text{m}$ in the S_C^* phase. The azobenzene diacrylate monomer used has the chemical structure shown below, whose synthesis has already been reported.^[8]

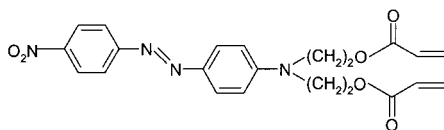


Figure 1 presents a set of polarized optical micrographs, taken on a Leitz MP-microscope, which show the formation of the bulk alignment of FLCs by the action of an optically aligned azobenzene network. The sample, a thin film ($\sim 5\ \mu\text{m}$) cast between two CaF_2 windows, contains 5 wt.-% of the azobenzene network. When cooled from the isotropic phase into the N^* phase (92°C), a birefringent mixture is obtained (Fig. 1a). On further cooling into the S_A phase (80°C), the three photos (Fig. 1b–d), taken within about 1 min, show the growth of aligned domains in the direction perpendicular to the polarization of the irradiation light used during the preparation. Figure 1e shows that this bulk alignment is retained when cooled into the S_C^* (50°C). The alignment is not as uniform as what can be achieved by rubbed surfaces under slow cooling; the apparent pattern formation may be related to the polymer network that generates more defects. As will be seen below, the domain alignment direction is the FLC molecular orientation direction. The pictures in Figure 1 were taken by setting an angle of 5° between the alignment direction and

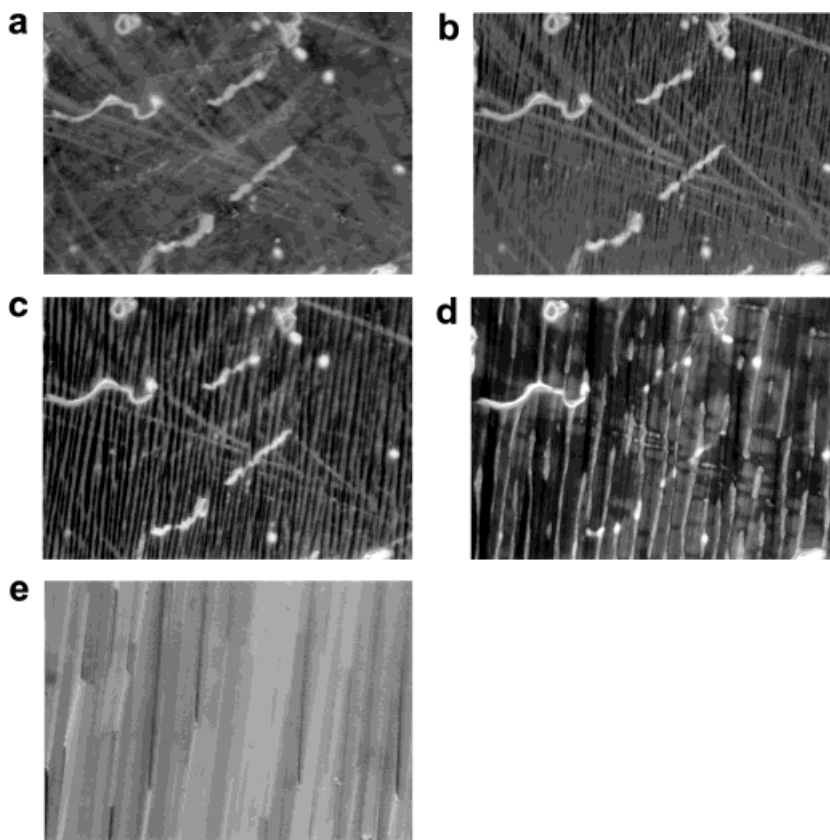


Fig. 1. Polarized optical micrographs for a sample containing 5 wt.-% of azobenzene network on cooling from the isotropic phase into a) the N^* phase (92°C); b–d) the S_A phase (80°C); and e) the S_C^* phase (50°C). The bulk alignment is perpendicular to the polarization of the irradiation light used for optical alignment during the preparation by thermal polymerization. The three photos of the S_A phase were taken within 1 min of each other, and all photos cover an area of $550\ \mu\text{m} \times 390\ \mu\text{m}$.

crossed polarizers in order to avoid the extinction so that the aligned domains can be viewed. The mixture showed no characteristic texture before polymerization, after being spread between two windows (picture not shown).

The azobenzene network induces and stabilizes a long-range FLC molecular orientation, as revealed by polarized infrared measurements (using a Bomem MB-200 Fourier transform infrared, FTIR, spectrometer). Figure 2 shows the results for a sample containing 10 % of azobenzene network, where the absorbance of the phenyl band at $1430\ \text{cm}^{-1}$ is plotted as a function of the angle between the electric vector of the infrared beam and the normal to the polarization of the irradiation light. The sampling area for taking the infrared spectra covered the entire film (about 10 mm in diameter). In the isotropic phase, the constant absorbance indicates the absence of any orientation. When cooled into the N^* phase, the angle-dependent absorbance indicates a long-range molecular orientation of FLCs in the expected direction. This average orientation is enhanced in the S_A and S_C^* phases with, within experimental error, no change in the orientation direction. At this point, the exact geometry in these samples is unknown. Nevertheless, microscopy investigations suggest the formation of chevrons, with the smectic layers tilted with respect to the cell surfaces. A change in the tilt of smectic layers was also

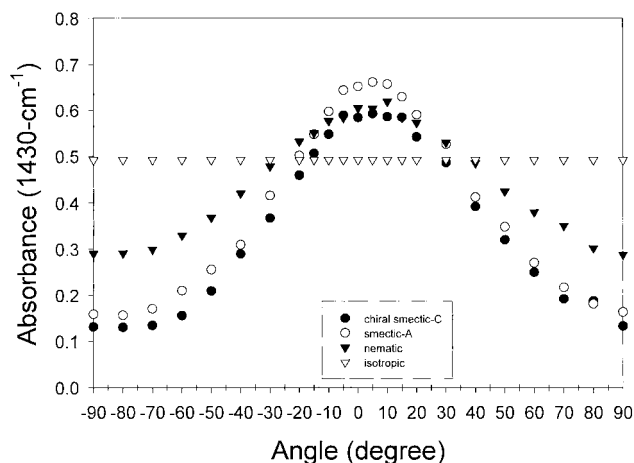


Fig. 2. Polarized infrared measurements for a sample containing 10 % of azobenzene network on cooling from the isotropic phase (120 °C) into the N* (90 °C), S_A (80 °C), and S_C* phase (50 °C). The plots are the absorbance of the 1430 cm⁻¹ band vs. angle between the electric vector of the infrared beam and the normal to the polarization of the irradiation light used for optical alignment during preparation by thermal polymerization.

observed in the S_C* phase, following cooling from the isotropic phase, which resulted in an increased phase separation of the network from the aligned FLCs. Detailed studies on the geometry will be reported later. In all aligned samples, the FLC orientation is stabilized by the network and completely reversible upon repeated heating-cooling cycles. Another interesting feature is that in contrast to SSFLCs, for which a uniform bulk alignment in the S_C* phase generally is achievable by very slow cooling of the FLC from its isotropic phase,^[15] for these optically aligned FLCs the formation of a bulk alignment apparently is insensitive to the cooling rate. Even by cooling the sample rapidly from the isotropic phase to room temperature, alignment is quickly induced by the network.

As mentioned earlier, an irradiation-induced anisotropy of the azobenzene network during polymerization in the isotropic phase should be responsible for the FLC alignment. Unfortunately, we could not confirm this initial network alignment, as we were unable to carry out polarized ultraviolet (UV) measurements in the course of polymerization under irradiation. Nevertheless, after a sample was prepared, the anisotropy of its network could be examined from polarized UV spectra taken in the various phases. Figure 3 shows the results for the sample containing 10 % of azobenzene network on cooling from the isotropic phase, the spectra being recorded at the same temperatures as in Figure 2, with the electric vector of the beam parallel (dashed lines) and perpendicular (solid lines) to the polarization direction of the irradiation light used during the preparation process. In the isotropic phase, though it is difficult to assess the dichroism of the absorption band of the azobenzene moieties because of the weak absorption, which may be related to the high temperature, the dichroism seems to be small. Once cooled into the N* phase, the dichroism becomes clear, indicating an alignment of the azobenzene groups in the expected direction. The azobenzene network remains aligned in the S_A and S_C*

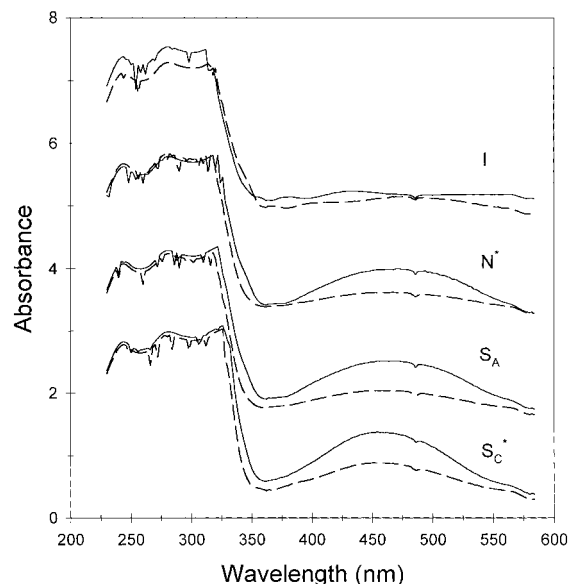


Fig. 3. Polarized UV spectra for a sample containing 10 % of azobenzene network on cooling from the isotropic phase (120 °C) into the N* (90 °C), S_A (80 °C), and S_C* phase (50 °C). The spectra were recorded with the electric vector of the beam parallel (dashed lines) and perpendicular (solid lines) to the polarization of the irradiation light used during the preparation process.

phases. Similar results were obtained for all samples. Judging from the UV spectra, the network anisotropy in the isotropic phase seems to be weak, but in the LC phases both FLC molecules and azobenzene groups on the network are aligned. Combined with the infrared results for the FLC orientation (Fig. 2), it appears that the initial, irradiation-induced, and perhaps weakly, oriented network is enough to bring the FLC molecules to align in the same direction in the N* phase. In turn, the oriented FLC host has a feedback effect on the network as it rearranges to adapt to the anisotropic environment, resulting in the enhanced azobenzene orientation (Fig. 3).

For these optically aligned and network-stabilized FLCs, switching was observed in the S_C* phase. A photodetector (Displaytech) was mounted on the polarizing microscope, and a digital oscilloscope (Tektronix, TDS 210) was utilized to record the optical response. Figure 4 shows an example of the measurements for a film (~4 μm) containing 5 % of azoben-

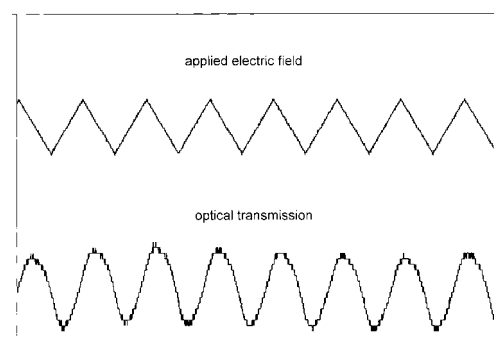


Fig. 4. Oscilloscope traces showing the switching at room temperature, in the S_C* phase, for a sample containing 5 % of azobenzene network. The applied AC field has a peak-to-peak voltage of 2 V and a frequency of 1 kHz (time scale in the figure is 7.5 ms).

zene network and cast between two ITO-coated glass plates, whose surfaces were not rubbed, but spin-coated with a thin poly(vinyl alcohol) (PVA) film. We found that the coating with a thin PVA layer, which modifies the surface tension, can improve the optical alignment of FLCs. For this particular sample, a uniform bulk alignment was obtained in the irradiated area (rectangular, about 5 mm × 10 mm). The oscilloscope trace in Figure 4 was recorded by placing the cell at the position where the maximum optical contrast was obtained during the switching. Under an alternating current (AC) field (triangle waveform, 1 kHz, peak-to-peak voltage: 2 V), the FLC molecules switch in the plane of the film, in response to the reversal of the spontaneous polarization, and results in the low and high light transmission under crossed polarizers. At the used low voltage, however, the switching is partial and the optical response varies continuously following the AC field. When the switching is complete at higher voltages (>10 V), the cell has a lower optical contrast than pure FLCs aligned by rubbed surfaces, the lowest and highest transmissions being about 8 % and 70 % for the former as compared with 5 % and 80 % for the latter. This can be explained by defects generated by the network, causing light scattering, and the high light absorption of the azobenzene moieties on the network. Otherwise, the switching behavior of the optically aligned and network-stabilized FLC was found to be comparable to pure FLCs aligned by rubbed surfaces. The switching starts at voltages below 2 V for a 5 μm cell; and the optical response is able to follow high frequencies of the AC field (>5 kHz), even though the spontaneous polarization of the FLC was reduced by the presence of the network, from 35.1 nC cm⁻² for pure FLC to 30.0 nC cm⁻² for the mixture with 5 % of network and to 23.2 nC cm⁻² for the mixture with 10 %. The observed decrease in the spontaneous polarization of the FLC host is no surprise. Generally, commercially available FLCs are carefully formulated mixtures that contain a chiral dopant for the induction of the S_C^{*} phase; the presence of a polymer network may have a disruption effect on the interaction between the chiral dopant the LC and, thus, reduces the spontaneous polarization of the S_C^{*} phase.

As compared to SSFLCs, the optically aligned and network-stabilized FLCs may have some advantages. First, the photoalignment of the azobenzene monomer or network is a bulk effect and can be made uniform along the thickness direction, which means that alignment and stabilization for samples thicker than the helical pitch is feasible, if necessary. Second, as no rubbed surfaces are needed, complications related to the rubbing process are eliminated. Third, the polymer network may improve the shock resistance of FLC cells, which is the main interest for studies on polymer-stabilized SSFLCs.^[3] The disadvantage is that the polymer network can reduce the spontaneous polarization of the FLC and thus decrease the switching speed to some extent. The network may also decrease the homogeneity of the cell and reduce the contrast ratio. The biggest challenge in the development of this optical and rubbing-free technique is to find efficient azobenzene monomers so that low concentrations would be enough to

make a network that induces and stabilizes a FLC orientation, uniformly and over large areas. Using this azobenzene monomer, we prepared samples with 3 % of network, and found that the bulk alignment was generally unstable. Ongoing studies in our laboratory include synthesis of new azobenzene monomers and investigation on various polymerization methods (thermal and photopolymerization) and conditions.

Experimental

The azobenzene monomer is non-mesogenic, and has the maximum absorption at 442 nm. To prepare a mixture of CS-1031 with the azobenzene monomer, both components were dissolved in a common solvent, tetrahydrofuran (THF), together with an initiator, 2,2'-azobisisobutyronitrile (AIBN) (~2 wt.-%), for polymerization; once a homogeneous solution was formed, the solvent was evaporated, and the mixture was dried in vacuum. Thermal polymerization was found to be successful. Typically, under irradiation with linearly polarized light at λ = 440 nm, the mixture was quickly heated to 120 °C (isotropic phase); after 10 min of polymerization, it was cooled to 50 °C (S_C^{*} phase); the irradiation was then turned off and the sample cooled to room temperature. After the preparation process, all optically aligned samples were heated into the isotropic phase, in the absence of irradiation, and the orientation stability was examined through repeated heating-cooling cycles. The irradiation source was a 1000 W Hg (Xe) lamp (Oriel), used with a polarizer and filters. The actual irradiation intensity was about 6 mW/cm².

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