

Self-assembled cholesteric liquid crystal gels: preparation and scattering-based electrooptical switching

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Two gelator compounds were used to prepare self-assembled cholesteric liquid crystal (CLC) gels. The presence of a physical network formed by the fibrous aggregates of the gelators in the CLC host creates inhomogeneous domains and generates a highly scattering state. The scattering-based electrooptical switching effects of the CLC gels were investigated by changing a number of parameters such as the texture of the CLC in which the aggregation of the gelator occurs, the concentration of gelator and the concentration of chiral dopant. The resulting network of aggregates determines the electrooptical response as it affects the light scattering by the CLC domains in the field-off state and the degree of CLC alignment as well as the light scattering by the network in the field-on state.

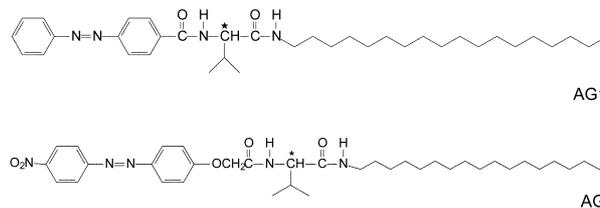
Introduction

New liquid crystalline materials that allow reversible changes in optical transmittance upon application of an electric field are of interest for the development of liquid crystal (LC) displays. In particular, electrooptical switching between a light scattering and an optically transparent state, without the use of polarizers, is attractive for applications in large-area display technology.^{1,2} A number of LC displays based on light scattering have been demonstrated, which include polymer-dispersed liquid crystals (PDLCs),^{3,4} polymer-stabilized cholesteric liquid crystals (PSCLCs),^{5,6} polymer-filled nematics (PFNs)^{7,8} and liquid crystals containing dispersed dendrimers.⁹ In all the systems, light scattering is caused by an optical heterogeneity of the material, generally formed in the absence of an electric field, while the transparent state is obtained by applying an a.c. field that induces the required optical homogeneity by aligning the LC molecules. However, in the case of PDLCs¹⁰ and PSCLCs,^{5,6} reverse switching modes, *i.e.*, transparent in the field-off and scattering in the field-on state, have also been designed.

A self-assembled LC gel refers to a LC contained by a dispersed non-covalent network that is formed by fibrous aggregates of an organic gelling compound called a gelator.^{11–18} When a homogeneous mixture of the gelator and LC host is cooled from the liquid phase, driven by intermolecular hydrogen bonding, the gelator molecules can self-associate into fibrous aggregates leading to gelation. These thermally reversible LC gels may have interesting properties, such as fast response to an electric field,¹³ direct casting for making twisted nematic cells,¹⁴ stabilization of polar orientation in ferroelectric liquid crystals (FLCs)¹⁵ and pitch compensation in a FLC, which facilitates the bulk alignment, followed by formation of nanometer-sized fibers.¹⁸ On the other hand, the LC gels may also be interesting to exploit for scattering-based electrooptical switching, as the physical network is generally disordered and its presence in a LC host may create the optical heterogeneity required for light scattering. In this paper, we report an investigation of the electrooptical effects of self-assembled cholesteric liquid crystals (CLCs) using two LC gelators synthesized in our laboratory.

Experimental

The two gelators used were AG1 and AG2 (see their chemical structures), whose syntheses and characterizations have been reported elsewhere.^{16,18}



The CLC host was prepared from a nematic LC, BL006, and a chiral dopant, R811 (both purchased from Merck). BL006, being a eutectic mixture of several low-molar mass LC compounds, has a large birefringence $\Delta n = 0.286$ (589 nm, 20 °C), a positive dielectric anisotropy $\Delta\epsilon = 17.3$ and a nematic to isotropic transition temperature $T_{ni} = 115$ °C. With 5% chiral dopant, the transition temperature is reduced to about 109 °C. The typical procedure for the sample preparation is as follows. BL006, R811 and the gelator were dissolved in THF to obtain a homogeneous solution; after most of the solvent had evaporated in air, the sample was dried at 40 °C in a vacuum oven. The homogeneous mixture was then heated to the isotropic liquid phase and flow-filled into non-rubbed, indium tin oxide (ITO)-coated cells (purchased from E.H.C.). The cell gap was 10 μm . Heating and cooling of the cells was carried out using a hot-stage (Instec) that could be mounted on a polarizing microscope (Leitz DMR-P). For scanning electron microscopy observations of the aggregates (Hitachi S-4700 FEG SEM), the gel samples were prepared between two ITO-coated glass slides and the LC host was extracted in hexane.

The kinetics of the gelation process are known to affect largely the size and morphology of the aggregates.^{17,18} Slow cooling always results in large fibrous or elongated aggregates of the gelator, leading to distinct areas of LC and aggregates. The consequence of this is diminished light scattering in the off-state and a low contrast from the electrooptical switch. In order to produce a finely dispersed network of thin fibres, thus

dividing the LC into many small domains, fast cooling was required. In the present study, after treatment at a predetermined temperature, the cells were removed from the hot stage quickly and placed in contact with two aluminium plates at room temperature. Using a high-speed photodetector (Displaytech) connected to a digital oscilloscope (Tektronix, TDS 420A), the electrooptical response of the cells was studied by measuring the optical transmittance with a He-Ne laser, the collection angle being 2° . A high-voltage waveform generator (WFG500, FLC Electronics) was used to apply an electric field to the cells. For the measurement of optical transmittance as a function of voltage, an a.c. field at a frequency of 1000 Hz was utilized, and at each peak-to-peak voltage the cell was retained for 30 seconds before taking the measurement.

Results and discussion

We found that the scattering-based electrooptical properties of the self-assembled CLC gels are strongly dependent on the conditions under which the aggregation process takes place. A representative example is given in Fig. 1 which shows the results obtained with a cholesteric mixture composed of 94% nematic BL006, 5% chiral dopant R811 and 1% gelator AG2. The mixture was first held at 130°C for 5 min to reach equilibrium and then cooled to 85°C , inside the cholesteric phase. At this temperature, aggregation of AG2 did not occur and a Grandjean (planar) texture, with helical axes mainly normal to the plates, was visible by polarizing microscopy. Two other LC textures could also be produced at 85°C before aggregation of the gelator, with the help of an electric field. When a voltage of 24 V was applied across the cell, a fingerprint texture was induced with randomly aligned helices in the plane of the binding plates, while as the voltage was increased to 60 V, a homeotropic texture was formed with the LC molecules aligned in the field direction and the cell appeared dark under crossed polarizers. For the aggregation of AG2 we quickly cooled the mixture from 85°C for each of the three textures. For the aggregation of the samples prepared from the homeotropic and fingerprint textures, the electric field was maintained during the cooling and at room temperature for several hours to complete the aggregation process. Several observations can be made from Fig. 1. First, the sample prepared from the homeotropic texture displays the best electrooptical response, with a very low transmittance in the field-off state (0 V) and a high transmittance reaching 80% in the field-on state (80 V). The photos in Fig. 2 show the switch of the sample (in the ITO-coated area) between the opaque and transparent states. For comparison, a cell made from the pure

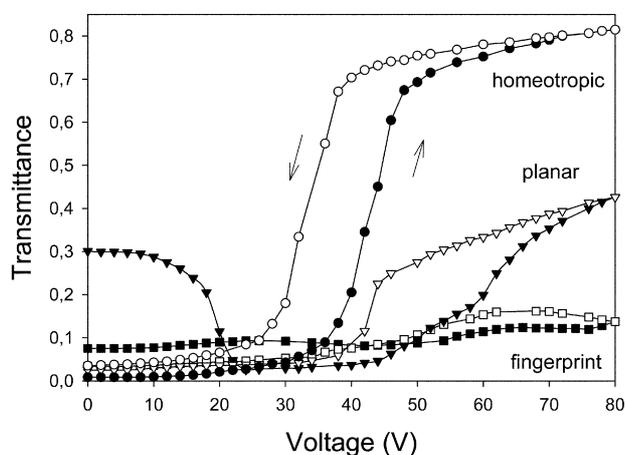


Fig. 1 Transmittance vs. applied voltage (peak-to-peak) for three samples of the mixture containing 1% of AG2, whose aggregation occurred in the homeotropic, planar and fingerprint textures, respectively.

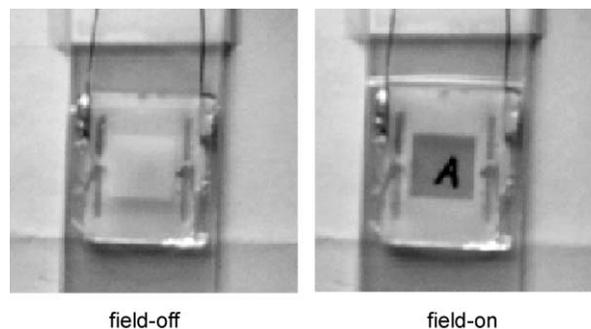


Fig. 2 Photos showing the electrooptical switch of a sample containing 1% of AG2.

nematic BL006 showed a transmittance of about 85% under homeotropic alignment (80 V). Second, in complete contrast, almost no optical contrast was observed for the sample prepared from the fingerprint texture, which exhibits strong light scattering and appears opaque before and after application of the field. Third, the sample prepared from the Grandjean texture behaves differently. Despite the presence of a network of the aggregates, part of the planar texture formed at 85°C remains at room temperature, which has the consequence of reducing light scattering in the field-off state. As the applied voltage increases, transition from the planar to the fingerprint texture occurs at lower voltages, which is followed by a second transition into the homeotropic texture at higher voltages. However, as compared with the sample prepared from the homeotropic texture, the transmittance is much reduced and the transition needs higher voltages to take place. For all samples displaying electrooptical switching, a large hysteresis effect is observed for the transmittance as the voltage is decreased.

These very different electrooptical behaviors of the samples prepared from the same mixture, but under different conditions, come from different morphologies of the network of aggregates and their different interactions with the LC host. It is clear from the above results that the LC texture influences the formation of the network of aggregates, and that the network, in turn, effectively determines the electrooptical effects of the sample. This was confirmed by optical microscopy. Fig. 3 shows the photomicrographs of the three samples in the field-on state at 80 V. Indeed, for the sample cooled from the homeotropic texture (photo a), switching of the LC host is complete and what is observed in the dark background is a network of birefringent aggregates, which appear to be homogeneous and finely dispersed in the LC host. This morphology accounts for the high transmittance in the field-on state and the very low transmittance in the field-off state, as the finely dispersed thin fibrous aggregates are effective in cutting the LC into small and strongly light-scattering domains. In contrast, for the sample cooled from the Grandjean texture (photo b), the morphology is very coarse-grained. The much

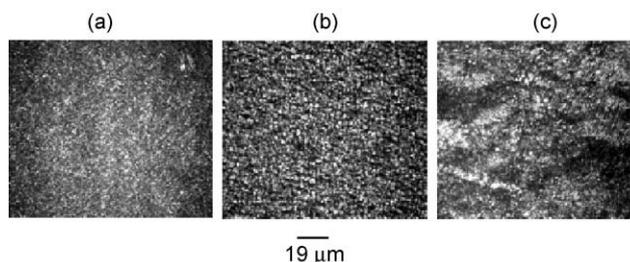


Fig. 3 Polarizing optical micrographs for the three samples used in Fig. 1 in the field-on state (80 V, peak-to-peak), whose gelation occurred in the homeotropic (a), the planar (b) and the fingerprint texture (c).

lower transmittance in the field-on state can be caused by two factors: 1) the larger and less homogeneous aggregates scatter more light, and 2) the homeotropic alignment of the LC molecules is hindered by their strong interactions with the aggregates, as is revealed by the significant increase in the switching voltage. Finally, for the sample cooled from the fingerprint texture (photo c), the remaining fingerprint texture indicates that the interactions between the aggregates and the LC are so strong that the alignment of the LC is limited in the field-on state, which explains the absence of effective electro-optical switching.

The aggregates of AG2 were viewed on a scanning electron microscope (SEM) after removing the LC host in a hexane solution. The representative SEM pictures in Fig. 4 show some noticeable differences for samples prepared under different conditions. For the sample in which aggregation occurred in the homeotropic texture (photo a), the resulting network of aggregates seems to have quite an open structure, whereas for the aggregation in the Grandjean (planar) texture (photo b) the network appears dense and contains flat, tape-like aggregates. For the sake of comparison, another sample was rapidly cooled from 130 °C to room temperature without being held at 85 °C for a specific LC texture (photo c); the resulting aggregates are rod-like nanofibres (about 50 nm in diameter). The SEM observations indicate that the size and the shape and the general morphology of the aggregates are influenced by the LC texture and the kinetics of the aggregation process. It should be pointed out, however, that the SEM images may not reveal precisely the structure or the state of arrangement of the aggregates in the CLC gels before the removal of the LC host, since changes such as the collapse or stacking of aggregates may occur during the extraction process, which may also explain the absence of any fibrils oriented perpendicular to the substrates for the sample prepared under homeotropic alignment (photo a).

The electrooptical switching of the CLC gel prepared from the homeotropic texture appears to be stable. Fig. 5 shows the response of the mixture with 1% AG2 to a number of field-on (10 s, 80 V) and field-off (10 s, 0 V) cycles. Also shown is its dynamic response to a pulse wave of 80 ms, from which the switching time, being defined as the time period required for transmission change between 10 and 90% of the maximum transmittance, could be estimated. The turn-on time is about 7 ms and the turn-off time is about 11 ms. For other samples with different concentrations of AG2 or using AG1 as the gelator, similar turn-on and turn-off times were obtained. A notable difference between the physical networks of aggregates in these self-assembled CLC gels and the covalent polymer networks in PSCLCs^{5,6} is that in the latter system the turn-off time is much shorter than the turn-on time. This is likely to be a reflection of a much stronger stabilizing or memory effect provided by a covalent network to the LC host as compared with a physical network. Indeed, in the case of PSCLCs, the covalent network formed in the planar texture is able to stabilize the highly transparent texture, which is the condition for the reverse mode of switching,^{5,6} while as shown in Fig. 1,

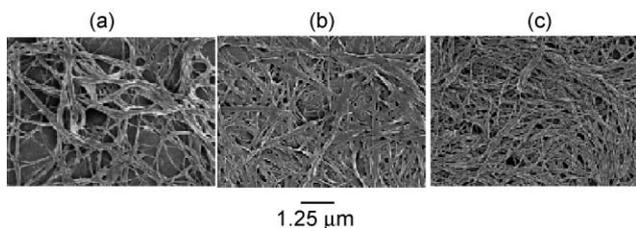


Fig. 4 SEM pictures of the aggregates of AG2 for the samples containing 1% of AG2: gelation in the homeotropic texture (a), gelation in the planar texture (b) and gelation during fast cooling from the isotropic liquid phase to room temperature (c).

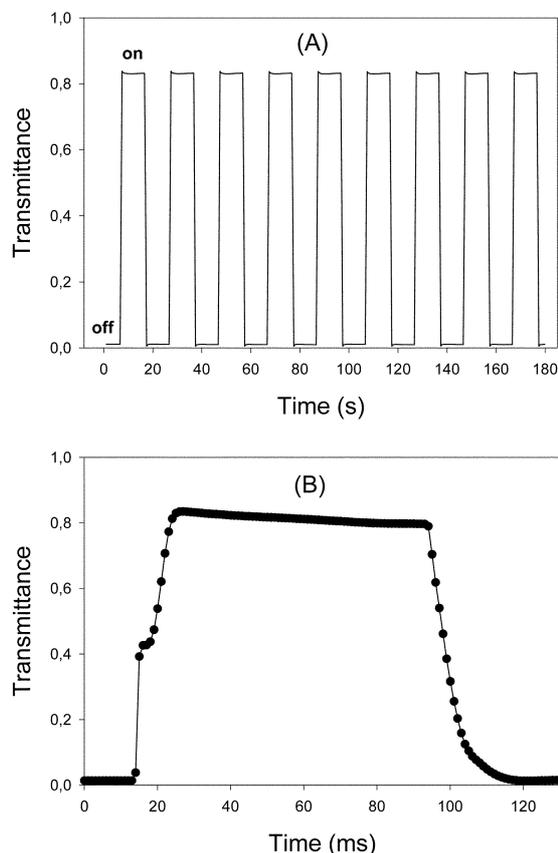


Fig. 5 Electrooptical switch of a sample containing 1% of AG2: response to a number of cycles between the field-off (0 V) and the field-on (80 V, peak-to-peak) states (a) and dynamic response to a pulse of 80 ms (b).

uniform planar textures cannot be retained by networks of aggregates.

The gelator AG2 was also used to investigate the influence of the concentration of gelator, *i.e.*, the concentration of the network, on the electrooptical properties of the CLC gels. Fig. 6 shows the results obtained for three mixtures containing 0.5, 1 and 3% AG2, with the concentration of the chiral dopant R811 kept constant at 5%. All samples prepared were cooled from the homeotropic texture. As compared with 1% AG2, the mixture with 0.5% AG2 switches at a slightly lower voltage and displays a similar high transmittance. Its scattering state, however, is less efficient, which corresponds to a significant

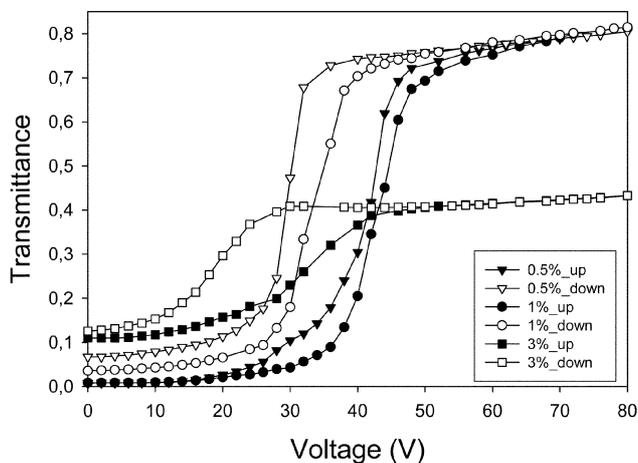


Fig. 6 Transmittance vs. applied voltage (peak-to-peak) for mixtures containing 0.5, 1 and 3% of AG2, respectively. The aggregation occurred in the homeotropic texture for all samples.

decrease in optical contrast. On the other hand, when the concentration of AG2 is raised to 3%, both light scattering in the field-off state and the transmittance in the field-on state are very much reduced. This is no surprise considering the heterogeneity associated with an increased network volume. The decrease in the switching voltage for this mixture indicates that although there are more aggregates the effective interaction between the network and the CLC is diminished. Note that the pure CLC (BL006 doped with 5% R811) containing no AG2 switches at about 10 V under the conditions used. For the pure CLC in the field-off state, a focal conic texture with randomly aligned helices scatters light,¹⁹ but the scattering is lower than in the CLC gels and is unstable.

We also prepared CLC gels using the gelator AG1 and studied their electrooptical properties. Similar behaviors were observed in most cases. The difference between the two gelators is that the transmittance achieved in the field-on state is generally lower for samples with AG1 than those with AG2 (the highest transmittance was observed with 0.5% AG1). Fig. 7 shows the results obtained with AG1 which illustrate the influence of the helical pitch of the CLC on the electrooptical switching. This experiment was performed using three mixtures containing 3, 5 and 7% chiral dopant and 1% AG1. All samples were prepared by cooling the homeotropic texture induced at 85 °C, as described above. The pitches of the three mixtures at 85 °C, estimated from the fingerprint texture induced by applying a voltage of 24 V, are 6.5, 2.8 and 1.6 μm, respectively. It is seen, from Fig. 7, that a decrease in the pitch has two consequences: 1) an increase in the optical contrast as a result of enhanced light scattering in the field-off state and increased transmittance in the field-on state, and 2) an increase in the switching voltage. While the effect on the switching voltage is easily understandable as it is more difficult to unwind more twisted helices, the effect on the transmittance in the field-on state needs more analyses. The SEM pictures of the aggregates of AG1 in the three samples after removal of the LC host are presented in Fig. 8. Again, the sample displaying the highest transmittance in the field-on state contains a network of aggregates with an open structure (photo c), in contrast with the more densely packed aggregates found in the sample showing the lowest transmittance (photo a). As compared with the aggregates of AG2 (Fig. 4), these aggregates appear to be shorter, straighter and have a slightly larger diameter (around 100 nm). In principle, as the three samples have the same concentration of gelator and as the aggregation takes place under the same homeotropic texture, in which all helices are unwound, the aggregates formed would be expected to be similar regardless of the concentration of the chiral agent

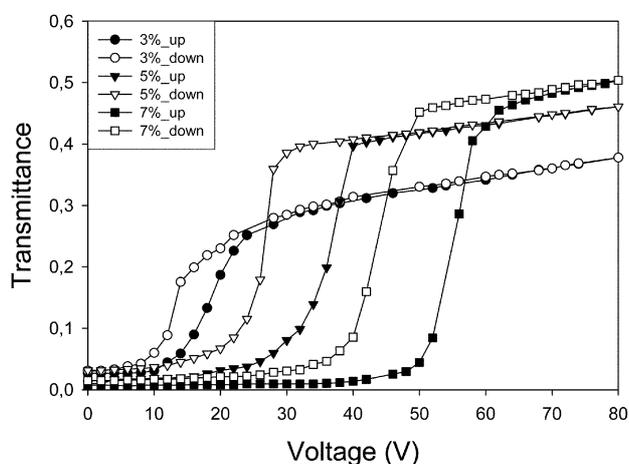


Fig. 7 Transmittance vs. applied voltage (peak-to-peak) for mixtures containing 1% of AG1 with 3, 5 and 7% of chiral agent R811, respectively. The aggregation occurred in the homeotropic texture for all samples.

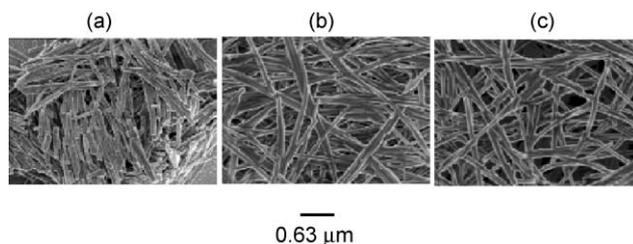


Fig. 8 SEM pictures of the aggregates of AG1 for the samples containing 1% of AG1 with 3% (a), 5% (b) and 7% of R811 (c).

R811. The results shown in Fig. 7 imply that the aggregation process of the gelator may be affected by the concentration of the chiral agent. As a matter of fact, the two gelators are chiral compounds and may behave as additional chiral dopant in the mixtures.^{17,18} It is thus no surprise that the kinetics of the aggregation process are influenced by the total concentration of the chiral agents present in the mixture, resulting in different networks of aggregates. The participation of the gelator in the induction of the cholesteric phase can also be seen from the electrooptical results of the three samples shown in Fig. 6, containing 5% R811 with, respectively, 0.5, 1 and 3% AG2. Their pitches at 85 °C, measured from the fingerprint textures, were found to be 4.9, 3.4 and 2.4 μm. It should be mentioned that if the nematic LC is mixed only with AG1 or AG2, a cholesteric phase could be induced before aggregation of the gelator, but this cholesteric phase reverts back to the simple nematic phase after the aggregation process as the gelator molecules are separated from the LC host. In that case, the polydomain structure of the nematic LC does not scatter light as strongly as the cholesteric LC.

Conclusions

The self-assembled and easily prepared CLC gels may be interesting materials for scattering-based electrooptical switching. While a highly scattering state can readily be obtained in the field-off state by adjusting the physical network of the fibrous aggregates of the gelator, the required high optical transmittance in the field-on state necessitates much more control. The key is to form a homogeneous and finely dispersed network that does not scatter much light by itself and does not prevent the alignment of LC molecules in an electric field. By making the aggregation process occur in the homeotropic texture of the LC host, under an applied voltage, seems to be the best way to obtain such a network. Much work remains to be carried out in the search for new gelators that are effective in producing high optical contrast, yet that have little interaction with the CLC host, which allows for switching at low voltages and reduces the hysteresis effect.

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