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Yue Zhao^a; Li Guan^a

^a Département de Chimie, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1; and Centre de recherche en science et ingénierie des macromolécules (CERSIM), Université Laval, Québec, Canada G1K 7P4,

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Use of a gelator in a ferroelectric liquid crystal: pitch compensation and nanofibres

YUE ZHAO* and LI GUAN

Département de Chimie, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1; and Centre de recherche en science et ingénierie des macromolécules (CERSIM), Université Laval, Québec, Canada G1K 7P4

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A new azobenzene-containing gelator for liquid crystals, AG2, was synthesized and used to prepare a ferroelectric liquid crystal (FLC) gel. The FLC gel shows interesting features. On cooling from the isotropic phase into the N* phase, the dissolved AG2 acts as a chiral dopant and has a compensation effect on the helical pitch of the N* phase. With 0.5 wt % of AG2 in the FLC host, a homogeneous alignment of the FLC molecules is formed in the N* phase, ensuring the bulk alignment in the SmC* phase, even on quenching the mixture from the isotropic phase. This alignment under fast cooling contrasts sharply with the slow cooling rate required for the alignment of a pure FLC. After formation of the bulk alignment, the aggregation of AG2 occurs in the lower temperature SmA or SmC* phases, and the gelator molecules self-assemble into nanometer-sized fibres (about 100 nm diameter) that are aligned and located between the smectic layers. As the gelator is microphase-separated from the FLC in the SmC* phase, it exerts little disruption on the electro-optic properties of the FLC cell.

1. Introduction

Self-assembled liquid crystal (LC) gels are a new type of functional material that may have interesting properties [1–3]. These LCs are generally prepared by dissolving a gelator compound in a LC host and cooling the mixture from the homogeneous liquid state. During cooling, driven by specific intermolecular interactions such as hydrogen bonding, the gelator molecules can self-aggregate into fibrous entities that form a non-covalent network dispersed in the LC host. The physical networks in self-assembled LC gels can be reversibly dissociated by heating, and reformed by cooling, which is different from the covalently crosslinked polymer networks in polymer-stabilized LCs or covalent LC gels [4–6]. Most studies of self-assembled LC gels have used nematic and smectic LCs [1–3]. Recently, a study on ferroelectric liquid crystals (FLCs) was reported, showing that the physical network can stabilize a polar orientation state induced by applying a d.c. field across the electrooptic cell with mechanical shearing [7]. As new materials, the new functions and utilities of self-assembled LC gels remain to be exploited.

In this paper, we report an interesting feature observed for a self-assembled FLC gel using a new chiral gelator AG2. The dissolved AG2 may compensate the helical pitch of the chiral nematic (N*) phase before its aggre-

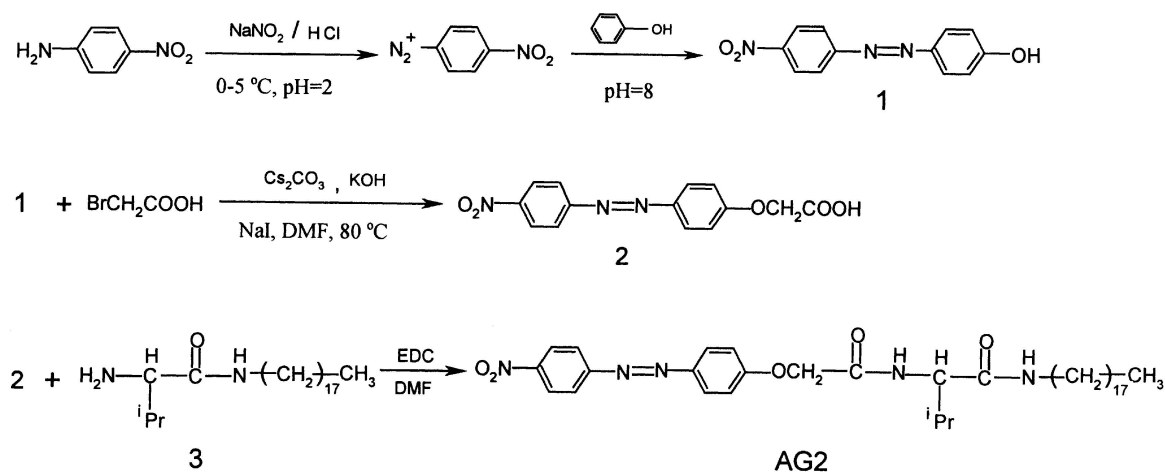
gation and, consequently, allows for a uniform bulk alignment to be achieved in the chiral smectic (SmC*) phase on fast cooling, even quenching, from the isotropic phase inside electro-optic cells with rubbed surfaces. Generally, to prepare a surface-stabilized FLC [8], slow cooling is needed for obtaining the bulk alignment. Afterwards, the aggregation of AG2 occurs at lower temperatures, resulting in aligned, nanometer-sized fibres located between the smectic layers. As the gelator is microphase-separated from the FLC host in the SmC* phase, it causes little disruption on the electro-optic properties of the FLC host.

2. Experimental

2.1. Synthesis

The synthetic route to the new gelator AG2 is shown in the scheme. The gelator has a chiral centre and two amide groups for intermolecular hydrogen bonding. All reagents were purchased from Aldrich or Sigma and used without further purification. Dry solvents were freshly distilled under anhydrous conditions. The reactions were monitored by thin layer chromatography (TLC), and the compounds were characterized using ¹H NMR (Bruker AC-F 300), differential scanning calorimetry (Perkin-Elmer, DSC7), mass spectroscopy (Micromass ZAB-1F), infrared spectroscopy (Bomen MB-102 FTIR), and UV-Vis spectroscopy (HP-8452A).

* Author for correspondence; e-mail: yue.zhao@usherbrooke.ca



Scheme. Synthesis of the gelator.

Compound **1** was obtained by the standard coupling reaction between a diazo compound and a phenol. The crude product was purified by recrystallization from ethanol. The preparation of compound **3** has been reported elsewhere [2*a*].

For the synthesis of compound **2**, a solution of compound **1** (450 mg, 1.8 mmol), bromoacetic acid (250 mg, 1.8 mmol), NaI (60 mg), Cs₂CO₃ (1.3 g, 4 mmol), and KOH (200 mg, 4 mmol) in dry DMF was stirred at 80 °C for two days. The mixture was then poured into 100 ml of water and the pH adjusted to 7; un-reacted **1** formed a red deposit and was filtered out. The aqueous solution was then washed with ethyl acetate until the solution became light coloured. Further adjustment of the pH of the aqueous solution to 6 gave a yellow deposit from which compound **2** was collected (yield: 60%).

For the preparation of gelator AG2, a solution of compound **2** (165 mg, 0.5 mmol), compound **3** (182 mg, 0.5 mmol), and EDC (77 mg, 0.5 mmol) was stirred at room temperature for 24 h. The reacted mixture was poured into 50 ml of water and extracted three times with CHCl₃. The collected CHCl₃ solution was dried with MgSO₄. After evaporation of the solvent, the mixture was purified by column chromatography on silica gel (hexane/ethyl acetate) to collect AG2 (light yellow solid m.p. 209 °C). ¹H NMR (δ/ppm) (chloroform-*d*): 8.36 (2H, d), 8.02 (4H, d), 7.12 (2H, d), 7.09 (1H, d), 5.72 (1H, t), 4.62 (2H, d), 4.23 (1H, t), 3.23 (2H, m), 2.15 (1H, m), 1.50 (2H, m), 1.24 (30H, brs), 0.95 (6H, d), 0.88 (3H, t). IR (ν/cm⁻¹, KBr): 1639 (C–O of aromatic amide), 1667 (C–O of alkyl amide), 3281 (N–H of urethanes and amides). MS (*m/e*): 651 (M⁺); UV (λ/nm) (THF): 370 (π → π*, azobenzene).

2. Preparation and characterization of the gels

The FLC host was purchased from Chisso Corporation (Japan). It is a FLC mixture with the following phase transition temperatures: Cr–12 °C SmC* 60 °C SmA

85 °C N* 97 °C I. The helical pitch in the N* phase is reported to be 37 μm at just above the N*–SmA phase transition, while the pitch in the SmC* phase is 3 μm. To prepare mixtures of FLC/AG2, the two components were dissolved in THF to obtain a homogeneous solution, and the solvent was then evaporated in vacuum. Parall-rubbed, indium tin oxide coated electro-optic cells were used (purchased from E.H.C, Japan), with a cell gap of 5 μm. To fill a cell, the FLC/AG2 mixture was heated into the isotropic phase and flow-filled by capillarity. Once prepared, all cells were sealed.

The FLC alignment was observed by a polarizing microscope (Leitz DMR-P) equipped with a hot stage (Instec). Before cooling for observations or measurements, all cells were heated to 160 °C for 10 min to ensure a homogeneous mixture with AG2 well dissolved in the FLC. Electro-optic behaviour (transmission–voltage) was recorded using a photodetector (Displaytech) mounted on the microscope and a digital oscilloscope (Tektronix, TDS 210), with cells placed between crossed polarizers in the position where the maximum optical contrast was obtained during switching. Scanning electron microscopy (SEM) observations were conducted on some samples after extraction of the FLC (JEOL JSC-840A).

3. Results and discussion

Figure 1 presents the phase diagram for the FLC/AG2 system, which was measured on the polarizing microscope using a cooling rate of 1 °C min⁻¹. The aggregation temperature was taken as the temperature at which the first birefringent aggregates were observed. The concentration of AG2 was set to 3 wt % and below. As expected, the aggregation temperature for AG2 decreases as its concentration is lowered. On the other hand, similar to known LC gels [1–3, 7], AG2 has little effect on the phase transition temperatures of the FLC host, mostly because of the microphase separation resulting from the

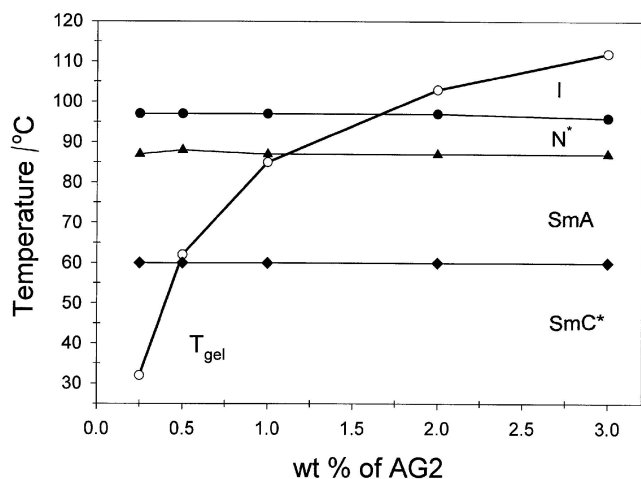


Figure 1. Phase diagram for FLC/AG2. Phases of the FLC host are indicated, and T_{gel} is the aggregation temperature of AG2.

aggregation of the gelator. Even when the aggregation occurs inside the LC phases, the small amount of AG2, less than 2%, explains the small effect on the phase transitions. It was noted that aggregation of AG2 takes place in the smectic phases when its concentration is below 1%.

The FLC/AG2 mixture displays surprisingly easy alignment of FLC inside electro-optic cells on cooling from the isotropic phase, especially for AG2 concentrations around 0.5%. In sharp contrast with the pure FLC, for which a slow cooling rate is necessary to induce a homogeneous alignment, a bulk alignment of FLC is obtained regardless of the cooling rate for the FLC/AG2 (0.5%) mixture. Figure 2 shows polarized optical micrographs taken at room temperature for this mixture subjected to two cooling conditions from 160°C: (1) the cell was removed from the hot stage and placed immediately inside a freezer for quenching (-30°C); and (2) the cell was removed from the hot stage and cooled at room temperature (it took less than 45 s for the N^* –SmA phase transition to be observed). In both cases, a bulk alignment of the FLC is achieved in the SmC* phase, figures 2(a) and 2(b). Repeated heating–cooling treatments gave rise to the same results. For the sake of comparison, figure 2 also shows micrographs for the pure FLC subjected to the same fast cooling at room temperature, not quenching (c), and to a slow cooling at a rate of $0.1^{\circ}\text{C min}^{-1}$ inside the hot stage. Under the fast cooling, no bulk alignment can be obtained, and a focal conic texture of the SmC* phase is seen. While using the very slow cooling, bulk alignment is obtained for pure FLC. It is apparent that the textures of the aligned FLC/AG2 mixture are different from that of the aligned pure FLC.

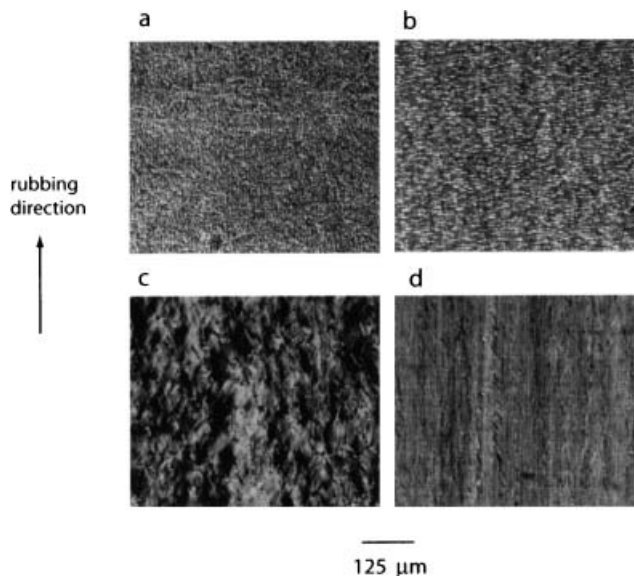


Figure 2. Polarized optical micrographs for the FLC/AG2 (0.5%) mixture subjected to (a) quenching in a freezer (-30°C), (b) fast cooling at room temperature; and for the pure FLC host subjected to (c) fast cooling at room temperature, (d) slow cooling at $0.1^{\circ}\text{C min}^{-1}$.

The mechanism for the easy bulk alignment of the FLC/AG2 mixtures under fast cooling was revealed through microscopy. It is known that a homogeneous alignment in the N^* phase, i.e. a uniaxial orientation of the FLC molecules along the rubbing direction, is a prerequisite for a bulk alignment in the lower temperature SmA and SmC* phases, figure 2(d). When the pure FLC is subjected to a very slow cooling, a planar texture in which the helices are perpendicular to the binding plates under the effect of rubbed surfaces, is observed over almost the whole temperature range of the N^* phase, indicating that the helical pitch is short, as compared with the cell gap. A homogeneous alignment is observed only at the beginning of the N^* –SmA phase transition when the helical pitch becomes much longer. Upon fast cooling, however, the FLC has no time to stay at a temperature where the helical pitch is long enough to allow for the homogeneous alignment to develop in the N^* phase and, consequently, no bulk alignment is obtained in the SmC* phase.

By contrast, in the case of the FLC/AG2 (0.5%) mixture, even under fast cooling from the isotropic phase a homogeneous alignment is observed once the sample enters the N^* phase, which ensures the bulk alignment in the subsequent smectic phases. A planar texture could be observed only at temperatures very close to the isotropic to N^* phase transition. When a voltage is applied across the cell, it destabilizes the helices so that the planar texture is transformed into a fingerprint texture, for which the helices lie in the plane of the cell.

The optical micrographs in figure 3 compare the fingerprint textures observed for the pure FLC and the FLC/AG2 (0.5%) mixture when a voltage of 10 V was applied, the photos being taken at 95°C, i.e. only 2°C into the N* phase. It is seen that the fingerprint texture of the gel sample is much larger than for the pure FLC, indicating a much longer helical pitch in the presence of AG2. This result suggests that AG2, being a chiral compound, has an effect of compensating the helical pitch of the FLC in the N* phase. From the fingerprint textures induced by a voltage, we have estimated the half-pitch length for mixtures with different concentrations of AG2 at 95°C; the results are shown in figure 4. Indeed, the half-pitch lengths of all gels investigated are longer than that of the pure FLC, but go through a maximum at the AG2 concentration of 0.5%. Acting as a chiral dopant in the N* phase, AG2 may induce a twist of opposite handedness in the FLC and unwind the helix. The compensation effect attains a peak with

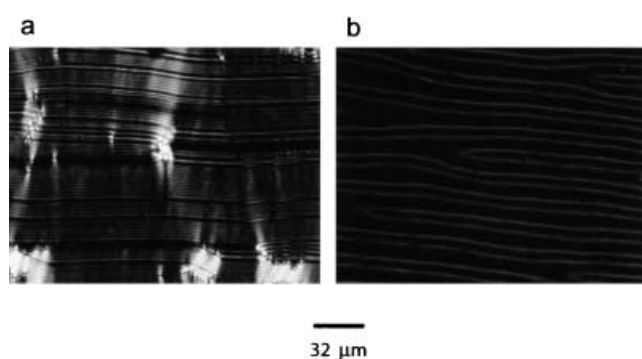


Figure 3. Polarized optical micrographs showing the fingerprint textures observed at 95°C by applying a voltage of 10 V across the cells: (a) pure FLC, (b) the FLC/AG2 (0.5%) mixture.

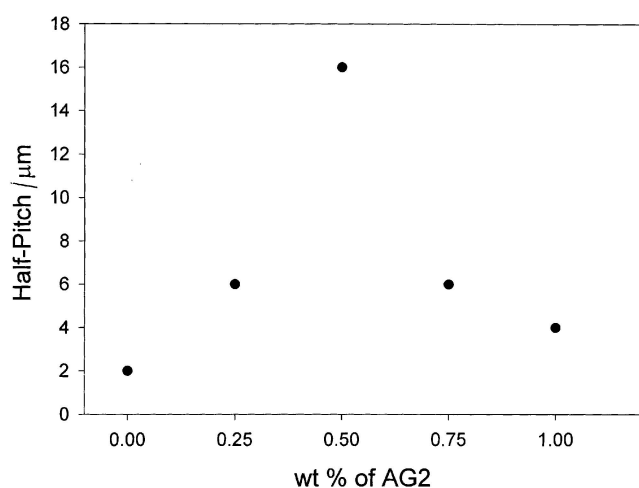


Figure 4. Half-pitch length in the N* phase as a function of the concentration of AG2.

0.5% of AG2 dissolved in the FLC, and the resulting long pitch (about 32 μm) at just below the isotropic to N* phase transition allows for the homogeneous alignment in the N* phase to be achieved, even under a very fast cooling condition such as the quenching experiment described above, figure 2(a). At gelator concentrations greater than 0.5%, the helical pitch falls, which may be an indication that the helical handedness is inverted by AG2. When the concentration of AG2 is between about 1 and 2%, aggregation occurs in the N* phase. In this case, randomly aligned fibrous aggregates disrupt the fingerprint texture so that the pitch can not be measured with certainty. In small areas where a fingerprint texture can be seen, the pitch is similar to that for the pure FLC. These observations suggest that upon aggregation most gelator molecules are phase separated from the host. As for the pitch compensation by chiral compounds, it should also be mentioned that similar effects by chiral monomers have been used to prepare covalent cholesteric LC networks [9, 10].

The apparent differences in texture, shown in figure 2, between aligned FLC/AG2 (0.5%) and pure FLC are related to the aggregation of the gelator, the result of which is the formation of fibrous hydrogen-bonded aggregates that form a non-covalent network. Aggregation of the gelator molecules is a crystallization process that is triggered by changes in temperature and affected by the cooling rate [1–3]. Figure 5 illustrates schematically the formation of the unit fibre of AG2 through intermolecular H-bonding between the amide groups. Interestingly, for the FLC/AG2 (0.5%) mixture quenched in the freezer, the aggregates of AG2 are very small and cannot be noticed from the optical micrograph, figure 2(a), while when the mixture is rapidly cooled at room temperature, relatively larger aggregates are formed and, from optical micrograph figure 2(b) they appear highly elongated and lie perpendicular to the rubbing direction, i.e. parallel to

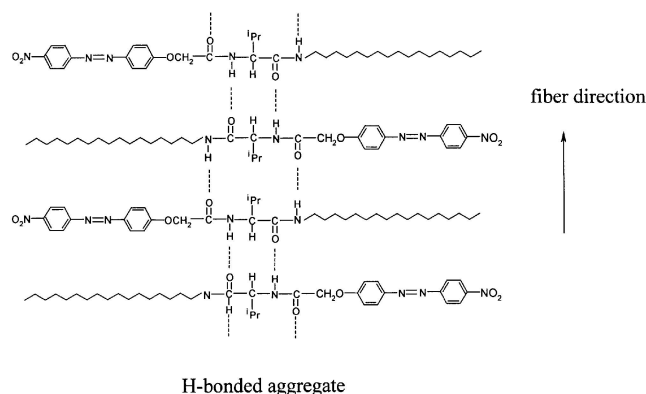


Figure 5. Schematic illustration of the unit fibre of AG2 formed through intermolecular H-bonding, whose condensation results in fibrous aggregates.

smectic layers. Electro-optic cells of the mixtures were carefully opened, and after extraction of the FLC host with hexane, the aggregates of AG2 remaining on the surfaces were examined by SEM. Figure 6 shows an example of the typical results. For the FLC/AG2 (0.5%) gel quenched in the freezer, figure 6(a), thin fibrous aggregates are aligned perpendicularly to the rubbing direction, suggesting that the non-covalent network formed under the quenching condition is mainly located between the smectic layers. The aggregates are crystalline nanometer-sized fibres with an average diameter close to 100 nm. For the mixture subjected to fast cooling at room temperature, figure 6(b), the nanofibres of AG2 are condensed into larger fibrous aggregates that are also parallel-aligned to the smectic layers of the FLC host. An interesting feature is that the nanofibres seem to be squeezed into the aggregates and become highly folded. A section of the aggregate under high magnification is given in figure 6(c) (the scale bar on the picture is 100 nm). The SEM results are well consistent with the optical micrographs in figure 2.

On fast cooling, after the pitch compensation in the N^* phase that facilitates the bulk alignment of the FLC, the gelator self-aggregates into nanofibres in the smectic phases. Because of the microphase separation, AG2 no longer acts as a chiral dopant and thus has little disruptive effect on the properties of the FLC host. Figure 7 compares the electro-optic effects for the pure FLC (curve a), whose alignment was obtained by very slow cooling at $0.1^\circ\text{C min}^{-1}$, and the FLC/AG2 (0.5%) mixture, whose alignment was obtained either by quenching in the freezer (curve b) or fast cooling at room temperature (curve c). The optical transmission is slightly reduced for the mixture; the decrease is a little greater for the sample quenched in the freezer. This result is understandable because the quenched sample contains much finer aggregates, figure 6(a), which means more interaction between the network and the FLC host. The hysteresis loop, however, is slightly narrower than the pure FLC, corresponding to a lower switching voltage.

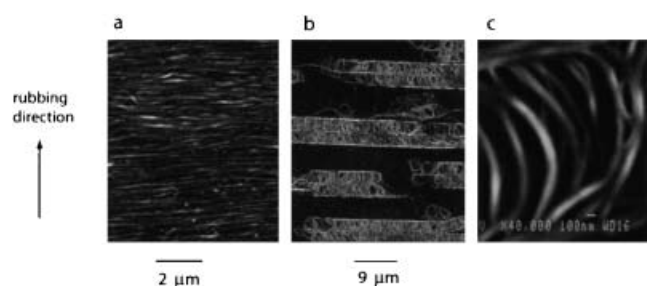


Figure 6. SEM pictures for the FLC/AG2 (0.5%) mixture: (a) subjected to quenching in a freezer, (b) cooled at room temperature, (c) nanofibres in (b). The FLC host was extracted with hexane.

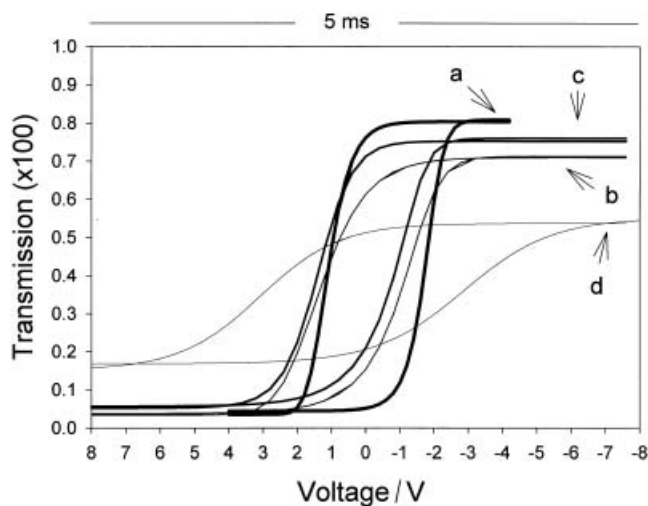


Figure 7. Electro-optic effects for (a) pure FLC aligned by slow cooling at $0.1^\circ\text{C min}^{-1}$, (b) the FLC/AG2 (0.5%) mixture aligned under quenching in a freezer, (c) the FLC/AG2 (0.5%) mixture aligned under fast cooling at room temperature, (d) the FLC/AG2 (2%) mixture subjected to fast cooling at room temperature. Applied a.c field: triangular wave, 100 Hz, 16 V of peak-to-peak voltage.

For this mixture, even in $10\ \mu\text{m}$ electro-optic cells, the long pitch leads to a homogeneous alignment in the N^* phase, and fast cooling at room temperature results in good bulk alignment. The switching behaviour is similar to that of the $5\ \mu\text{m}$ cell, with a slightly reduced optical transmission. For mixtures containing more than 0.5% of AG2, the helical pitch in the N^* phase is shorter but remains longer than that of the pure FLC (figure 4). On fast cooling, only a partial bulk alignment of the FLC host can be obtained in the SmC^* phase, while light scattering by the aggregates becomes more important. This leads to a severe reduction of the optical contrast and an increase in the switching voltage (wider hysteresis loop). Figure 7 shows an example with a sample containing 2% of AG2 (curve d). For comparison, we mention that no switching can be observed for the pure FLC after fast cooling at room temperature due to the absence of any bulk alignment. When the gelator concentration is greater than 2%, aggregation occurs in the isotropic phase before the N^* phase is reached; consequently no pitch compensation takes place in the N^* phase, and fast cooling results in no bulk alignment.

4. Conclusion

When a small amount of gelator AG2 is dissolved in a FLC host, on cooling from the isotropic phase the gelator first acts as a chiral dopant in the N^* phase of the FLC and compensates its helical pitch so that a homogeneous alignment can easily be induced under even a quenching condition, leading to bulk alignment

in the SmC* phase. After bulk alignment, the AG2 molecules self-assemble into fibrous aggregates and no longer act as a chiral dopant, thus causing no severe disruption to the FLC host. The other interesting finding of this study is that under fast cooling, the aggregates of AG2 formed in the FLC host are nanometer-sized fibres, aligned and located between the smectic layers. Considering that commercially available FLCs generally have a short helical pitch in the N* phase, and that alignment is a key issue in the preparation of surface stabilized FLCs, the attractive feature found for the FLC/AG2 gel demonstrates a useful concept or strategy. A chiral gelator can be designed first to compensate the pitch in the N* phase, which greatly facilitates the obtaining of a uniform bulk alignment in the SmC* phase, and then to self-aggregate into a non-covalent network that exerts little disruption on the electro-optic behaviour of the FLC. Moreover, in the case of polymer stabilized FLCs [5, 11], the interest of having a covalent network is to improve the shock resistance of surface-stabilized FLCs. It would be of interest to see if a non-covalent network formed by nanofibres of the gelator could also improve the mechanical strength of the aligned FLC host.

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