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Azobenzene-Assisted Alignment of Ferroelectric Liquid Crystals in the Chiral Smectic C Phase with an Alternating Current Field

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Since the discovery of ferroelectricity in liquid crystals[1] and the description of the surface-stabilized ferroelectric liquid crystal devices,[2] a large number of theoretical and experimental studies have been carried out[3] because of their potential electrooptical applications as displays and light devices.[3−5] One very important factor in building a switching or display device is the alignment quality of the liquid crystal within the cell. It is difficult to obtain a uniform alignment of the molecules of the liquid crystals by merely injecting the liquid crystal between the upper and lower substrates. Therefore, alignment layers, such as rubbed polyimides,[6] polyamides,[7] organic silane,[8] and side chain ferroelectric liquid crystal polymers,[9] have been used to achieve uniform alignment. An alignment is usually achieved by slowly cooling from the isotropic liquid into the respective smectic phase at a rate of 0.1−0.2 °C/min.[6,10] While cooling occurs, an electric field has to be applied in order to produce a well-aligned sample in most cases, especially for samples which do not exhibit a chiral nematic (N*) phase between the isotropic and the smectic phases.[11−13] In this paper, we describe the unexpected observation of achieving alignment relatively rapidly in the chiral smectic C (SmC*) phase under an ac field simply by addition of small quantities of azobenzene compounds.

Chart 1. Molecular Structures of FLCs and Dopants

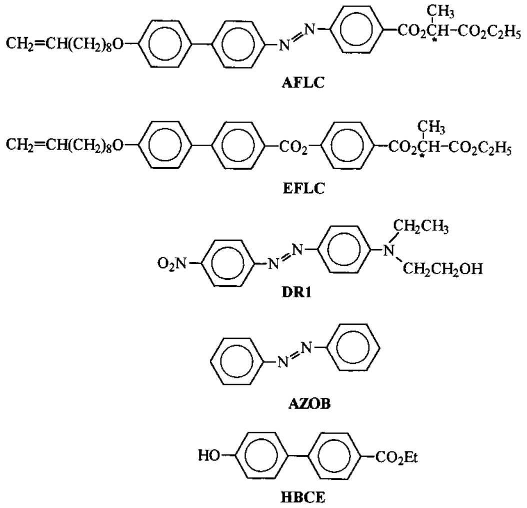

Table 1. Physical Properties of AFLC and EFLC

name	phase transitions (°C)	spontaneous polarization P_s (nC/cm^2)	tilt angle θ_t, deg
AFLC	K 38.6 Sm(I or F)* 96 SmC* 145 SmA* 172 Iso	141 (120 °C)	30 (120 °C)
EFLC	K 4.5 Sm(I or F)* 39.2 SmC* 119.6 SmA* 152.4 Iso	107 (80 °C)	29 (80 °C)

Two ferroelectric liquid crystals (FLC), AFLC and EFLC, were used in this study. Their chemical structures together with the structures of some azo and nonazo dopants used are shown in Chart 1. Table 1 summarizes some of their physical properties. The thermal transition temperatures were measured by differential scanning calorimetry (DSC) with a Mettler TA 3000 thermal analysis system equipped with a TC10A TA processor and a DSC30 head at a rate of 5 °C/min in all cases. Optical observations were made on a Nikon Labophot-2 microscope under cross-polarized light (magnification 200×) with an RTC-1 temperature controller (Instec Inc., Broomfield, CO). P_s was measured by the triangular wave method using a Displaytech Automated Polarization Testbed III (6 V/μm, 100 Hz) in conjunction with the RTC-1 temperature controller. The Displaytech Automated Polarization Testbed III (6 V/μm) was also used as ac frequency generator. Tilt angles (θ_t) were measured between crossed polarizers using a red cutoff filter (λ > 650 nm), as half the rotation between two extinction positions corresponding to opposite polarization orientations. Full synthetic details and characterization data are available elsewhere.[14] Both AFLC and EFLC exhibit an isotropic →

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[1] Meyer, R. B.; Liebert, L.; Strzelecki, L.; Keller, P. *J. Phys. Lett., Paris* **1975**, *36,* 69.

[2] Clark, N. A.; Larerwall, S. T. *Appl. Phys. Lett.* **1980**, *36,* 899.

[3] Goodby, J. W.; Blinc, R.; Clark, N. A.; Lagerwall, S. T.; Osipov, M. A.; Sakurai, T.; Yoshino, K.; Zeks, B. *Ferroelectric liquid crystals: principles, properties and applications;*Gordon & Breach: Philadelphia, 1991.

[4] Walba, D. M. *Science* **1995**, *270,* 250.

[5] Dijon, J., In *Liquid crystals: applications and uses*; Bahadur, B., Ed., World Scientific: Singapore, 1990; Vol. 1, Chapter 13.

[6] Myrvold, B. *Ferroelectrics* **1988**, *85,* 25.

[7] Patel, J. S.; Leslie, T. M.; Goodby, J. W. *Ferroelectrics* **1984**, *59,* 137.

[8] Doroski, D.; Perlmutter, S. H.; Moddel, G. *Appl. Opt.* **1994**, *33,* 2608.

[9] Jin, S. H.; Lee, J. C.; Park, D. K. *Polym. Bull.* **1996**, *37,* 799.

[10] Booth, C. J.; Dunmur, D. A.; Goodby, J. W.; Toyne, K. J.; Waston, M. J. *J. Mater. Chem.* **1996**, *6,* 919.

[11] Patel, J. S.; Goodby, J. W. *J. Appl. Phys.* **1986**, *59,* 2355.

[12] Naciri, J.; Ruth, J.; Crawford, G.; Shashidhar, R.; Ratnu, B. R. *Chem. Mater.* **1995**, *7,* 1397.

[13] Cooray, N. F.; Fujimoto, H.; Kakimoto, M.; Imai, Y. *Macromolecules* **1997**, *30,* 3169.

[14] Xu, Z.-s.; Lemieux, R. P.; Natansohn, A.; Rochon, P.; Shashidhar, R. *Liq. Cryst.* Submitted.

10.1021/cm980336w CCC: $15.00

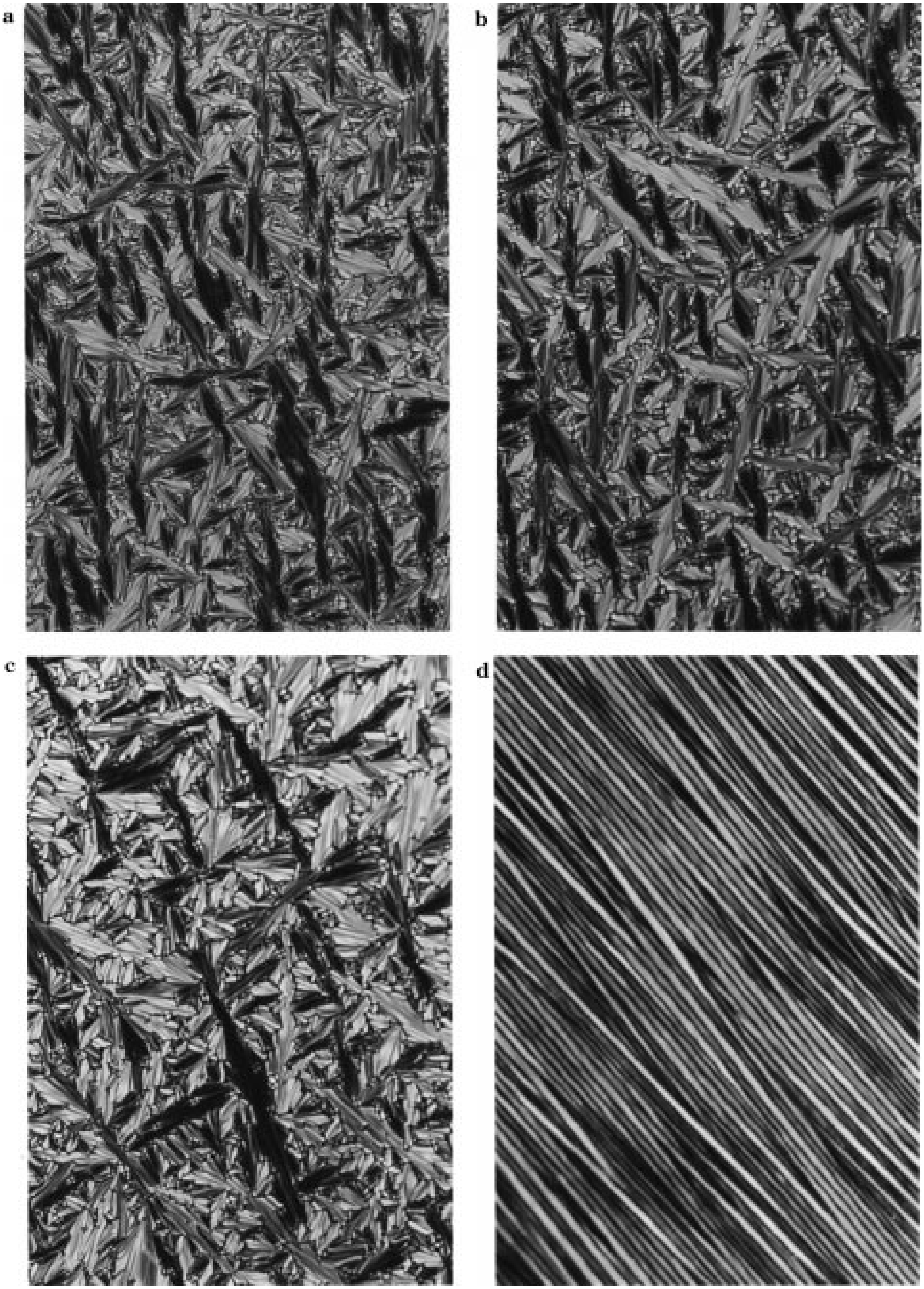

Figure 1. Polarizing optical micrographs of samples A and E confined in the cell at $T - T_{ac} = -2.5$ °C: (a) sample E formed by cooling rapidly from the isotropic phase, (b) after applying an ac field for 2 h, and (c) sample A formed by cooling rapidly from isotropic phase, (d) after applying an ac field for 5−10 min.

Table 2. LC Phase Transitions of the Mixtures

no.	% dopant in EFLC	Sm(I or F)*− SmC*(°C)	SmC*− SmA* (°C)	SmA*− isotropic (°C)
1	75% AFLC	77.5	134.5	166.4
2	50% AFLC	63.0	128.0	161.1
3	25% AFLC	47.8	122.7	156.4
4	2.8% AFLC	39.6	119.9	152.8
5	2.0% DR19	39.4	108.8	149.5
6	2.0% AZOB	39.9	105.3	147.5
7	2.0% HBCE	40.2	109.3	151.3

SmA* → SmC* → Sm(I or F)* phase sequence on cooling; their SmC* phases exist over a broad temperature range and have large spontaneous polarization. The structural difference is that AFLC has an azo bond and EFLC has an ester bond. Cells filled with 100% AFLC and EFLC are thereafter denoted sample A and sample E, respectively. Polyimide-coated ITO glass cells (4 μm × 0.25 cm^2, both surfaces rubbed in a parallel direction), supplied by Displaytech Inc. (Longmont, CO), were used for all measurements. The materials were heated into the isotropic phase and flow-filled into the glass cells. The mixtures of FLC and dopant with different weight ratios were obtained by dissolving the compounds in dichloromethane. The solution of the mixture was left in the fumehood overnight and then kept in a vacuum oven at 50−60 °C to completely remove the solvent. The thermal transition temperatures of all the mixtures (samples **1**−**7**) are shown in Table 2. All of them exhibit the same phase sequence. No phase separation was observed for these guest−host samples. The effect of adding a small amount of non-FLC dopant to EFLC on the transition temperatures was slight (samples **5**−**7**).

Figure 1 shows polarizing optical micrographs of samples A and E at $T - T_{ac} = -2.5$ °C (T_{ac} is the SmA* to SmC* transition temperature). The samples were prepared by cooling rapidly from the isotropic phase without electric field. Before applying an ac field, multidomain textures were observed in both samples A and E, as shown in parts c and a of Figure 1, respectively. Upon applying an ac field (100 Hz, 6 V/μm), the domains in sample A began to coalesce, resulting in the formation of a monodomain (uniform alignment) within 5−10 min, as shown in Figure 1d. This process is repeatable. The multidomain sample A formed by heating the monodomain sample to the isotropic phase and then cooling rapidly to the SmC* phase can be changed to a monodomain again by applying an ac field. However, the domains in sample E remained unchanged, even after several hours under the same conditions, as shown in Figure 1b. The same field-induced alignment effect was observed in samples **1**−**4**, which are formed by mixing EFLC with AFLC in various compositions. The time needed to achieve the uniform alignment in samples **1**−**4** was found to increase with decreasing AFLC content: 15 min (**1**), 25 min (**2**), 35 min (**3**), and 50 min (**4**).

Further experiments with samples **5** and **6** showed that other non-FLC azobenzene derivatives also produce the same field-induced alignment effect. Sample **5** contains 2% DR1, which has a strong longitudinal dipole moment, while sample **6** contains 2% azobenzene (AZOB), which has no longitudinal dipole moment, as dopants in EFLC. There is no obvious difference between the alignment of these two samples. Both samples produce a uniform alignment from similar multidomain states in about 50 min under an ac field, which suggests that any kind of azobenzene derivative can be used to assist in the alignment of a FLC in the SmC* phase under the influence of an ac field. The fact that the multidomains in sample **7**, which contains the non-azo compound hydroxybiphenylcarboxylic acid ethyl ester (HBCE), cannot be changed to a monodomain under the same conditions, confirms that this process requires an azobenzene structure. This field-induced alignment can be achieved in the dark, which means that photoisomerization of the azo dye is not necessary.

In conclusion, we have observed the unexpected phenomenon of aligning FLC directly in the SmC* phase, relatively rapidly, in the presence of an ac field, by doping a small amount of an azobenzene derivative into it. In this process there may be some interactions between the azo compound and the FLC molecules under the ac field. Interactions with the rubbed polyimide surface layer may also play a role. The mechanism is unclear at present and any explanation at this point is clearly speculative. Our preliminary results show that the kinetics of this azobenzene-assisted alignment depends on the concentration of azobenzene derivative. The structure of azo compound does not appear to be important. The possibility of aligning FLC molecules in the SmC* phase relatively rapidly by doping with small amounts of azo compounds and by applying an ac field may have some useful applications, and it provides a fairly simple method for aligning FLCs.

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