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# Photoinduced Alignment of Ferroelectric Liquid Crystals Using Azobenzene Polymer Networks of Polyethers and Polyepoxides

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ABSTRACT: Several divinyl ether and diepoxide monomers bearing an azobenzene moiety were synthesized and used to investigate the photoalignment of a ferroelectric liquid crystal (FLC) with no use of surface orientation layers. Azobenzene polymer networks, obtained by cationic polymerization of the monomers dissolved in the FLC host and exposed to linearly polarized irradiation, were found to be able to induce and stabilize a bulk alignment of FLC. Photoinduced reorientation of the FLC can also be achieved by changing the polarization of irradiation light, but in contrast with the use of chiral azobenzene poly(meth)acrylates,[1] the results suggest a mechanism based on the formation of an anisotropic azobenzene polyether or polyepoxide network for the commanding effect on the FLC alignment.

## Introduction

In polymer-stabilized liquid crystals (PSLC), a polymer network of low concentration exerts the effect of stabilizing the LC alignment or textures induced by surface orientation layers or an electric field.[2,3] In the case of ferroelectric liquid crystals (FLC), the use of a polymer network is also aimed at improving the shock resistance of the FLC cell whose bulk alignment is induced by rubbed surfaces.[4] Alignment has always been an important issue for LC in general and for FLC technologies in particular. Development of novel methodology, different from the established surface-stabilized FLC,[5] is of interest from both fundamental and applied points of view.[6−9]

In a previous study,[1] we reported on and discussed the use of some chiral azobenzene-containing polyacrylate and polymethacrylate networks to optically align FLC with no need for surface orientation layers. The photoisomerization and the related photoalignment of azobenzene moieties under linearly polarized irradiation[10] are the basis of this optical and rubbing-free approach.[11] This method is different from the photoalignment of LC by coating the substrate surfaces with photochromic molecules such as azobenzene polymers, i.e., the so-called commanding surfaces developed by Ichimura and co-workers.[12] The azobenzene polymer network, which is dispersed in the FLC host, provides a volume effect on the latter, even though the azobenzene moieties on the surface of the network may play a central role in some systems.[1]

All the azobenzene polymer networks studied so far were either polyacrylates or polymethacrylates prepared from free radical polymerization.[1,11] In pursuit of our efforts aimed at understanding the photoalignment mechanisms and fully assessing the effectiveness of this optical approach, we have synthesized a series of new azobenzene divinyl ether and diepoxide monomers and investigated the use of their polymer networks, prepared through cationic polymerization, to optically align FLC. The results reported in this paper show that the photoalignment of FLC could also be achieved by using azobenzene polyether or polyepoxide networks, but the mechanism of action may be different from the chiral polyacrylates or polymethacrylates.[1]

## Experimental Section

**1. Materials.** Mercury(II) acetate (98+%), aminobenzonitrile (98%), isoamyl nitrite (97%), resorcinol (98%), and bromohexene (95%) were used as received from Aldrich. 3-Chloroperoxybenzoic acid (MCPBA, Alfa Aesar, 70−77%), diphenyliodonium hexafluorophosphate (TCI America, 97%), potassium carbonate (BDH, 99%), potassium iodide (BDH, 99%), acetic acid (Fisher, 99%), and hydrochloric acid (EMD, 36−38%) were used as received. Prior to use, 2,2′-azobis(isobutyronitrile) (AIBN, Polysciences) was recrystallized from ethanol, 6-chlorohexanol (Aldrich, 96%) mixed with dichloromethane was neutralized by washing with 10% $NaHCO_3$, and ethyl vinyl ether (Aldrich, 99%) was distilled to remove the peroxides (bp 35−36 °C). 4-(4-Hydroxyphenylazo)benzoic acid was prepared using the method reported elsewhere.[1] All solvents were commercially available and used as received.

The ferroelectric liquid crystal (FLC) mixture used was Felix-015 (Clariant) that has the following phase transitions: Cr −12 °C $S_C$* 72 °C $S_A$ 83 °C N* 85 °C Iso. Its spontaneous polarization and rotational viscosity measured at 25 °C are +33 nC/cm$^2$ and 80 mPa, respectively (date provided by Clariant). As compared with the FLC used in the study with methacrylate- and acrylate-based chiral azobenzene polymers,[1] this FLC has a very narrow temperature range for the N* phase and a strong spontaneous polarization. In the case of surface-stabilized FLC, the absence of an N* phase is known to make the alignment more difficult to achieve. The choice of a different commercially available FLC aimed at investigating the general validity of this optical alignment approach for FLC.

**2. Synthesis of Azobenzene Monomers.** Two divinyl ethers and two diepoxides were synthesized. Their chemical structures are shown in Figure 1. Basically, ether1 is similar to epoxide1 in structure, differing only in the reactive group and the number of methylene units in the spacer. The same can be noted between ether2 and epoxide2, which have the two reactive groups linked to the same aromatic ring. Their synthetic schemes and details are given below.

**2.1. Preparation of Ether1. (6-Chlorohexyloxy)ethene (2):** Ethyl vinyl ether (249.24 g, 3.45 mol) was reacted with neutralized 6-chorohexanol (79.43 g, 0.58 mol) and mercury acetate (3.46 g, 0.01 mol). The reaction was performed at reflux for 6 h. Then 10 g (0.07 mol) of anhydrous potassium carbonate was added to the solution. The product was first separated

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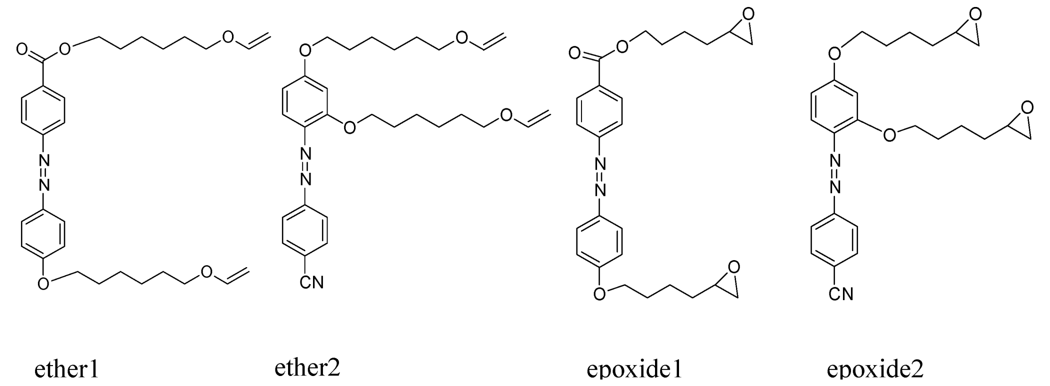
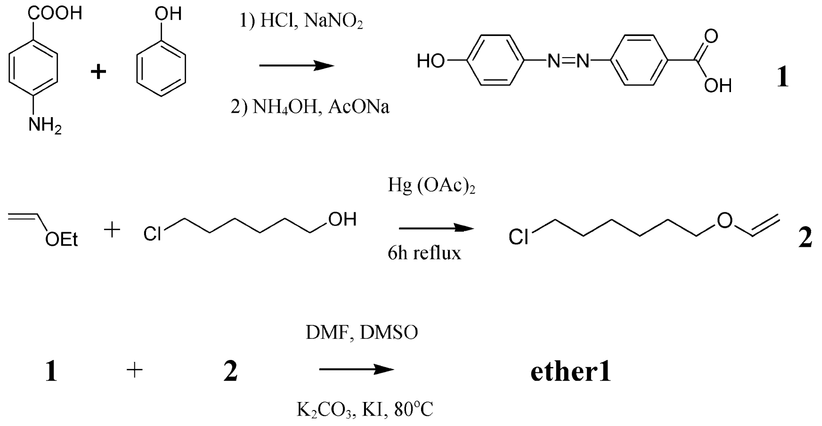


**Figure 1.** Chemical structures of azobenzene divinyl ether and diepoxide monomers.

**Scheme 1. Synthetic Route to 4-(4-Vinyloxymethoxyphenylazo)benzoic Acid 6-Vinyloxyhexyl Ester (Ether1)**



from remaining ethyl vinyl ether through distillation under reduced pressure (bp 85−87 °C, 8 mmHg) and then purified by silica gel column chromatography using AcOEt/hexane (1:9) as eluent. A yellow oily liquid was obtained; yield 30% (22.3 g, 0.14 mol); mp −21 °C. MS (*m*/*e*): 162 ($M^+$). $\lambda_{\mathrm{max}}$ (THF): 256 nm. $^1$H NMR ($\delta$, acetone): 1.30−1.41 (4H, m, $\mathrm{Cl{-}CH_2{-}CH_2{-}C}H_2{-}\mathrm{C}H_2$), 1.53−1.62 (2H, m, $\mathrm{O{-}CH_2{-}C}H_2$), 1.65−1.74 (2H, m, $\mathrm{Cl{-}CH_2{-}C}H_2$), 3.59−3.65 (2H, m, $\mathrm{Cl{-}C}H_2$), 3.92−3.94 (2H, m, $\mathrm{O{-}C}H_2$), 4.12−4.17 (4H, m, $\mathrm{O{-}CH{=}C}H_2$), 6.44−6.51 (1H, m, $\mathrm{O{-}C}H$).

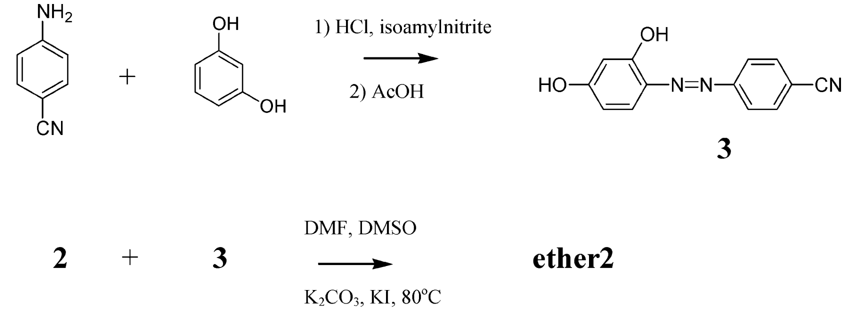
**4-(4-Vinyloxymethoxyphenylazo)benzoic Acid 6-Vinyloxyhexyl Ester (Ether1)**: 4-(4-Hydroxyphenylazo)benzoic acid (370 mg, 1.54 mmol) (**1**) and (6-chlorohexyloxy)ethene (750 mg, 4.63 mmol) (**2**) were added to a mixture of 5 mL of DMSO and 25 mL of DMF containing $K_2CO_3$ (640 mg, 4.63 mmol) and KI (770 mg, 4.63 mmol). The reaction was performed at 80 °C for 14 h. The solution was cooled, and chloroform was added prior to extraction of the product with water. The organic phase was collected and dried over anhydrous magnesium sulfate. After removing the solvent, an orange powder was obtained with a yield of 34% (150 mg, 0.3 mmol); mp 77 °C. MS (*m*/*e*): 494 ($M^+$). $^1$H NMR ($\delta$, DMSO): 1.44−1.56 (8H, m, $\mathrm{C(O){-}O{-}CH_2{-}CH_2{-}C}H_2{-}\mathrm{C}H_2$ and $\mathrm{C{-}O{-}CH_2{-}CH_2{-}C}H_2{-}\mathrm{C}H_2$), 1.65−1.86 (8H, m, $\mathrm{C(O){-}O{-}CH_2{-}C}H_2\mathrm{{-}CH_2{-}CH_2{-}C}H_2$ and $\mathrm{C{-}O{-}CH_2{-}C}H_2\mathrm{{-}CH_2{-}CH_2{-}C}H_2$), 3.58−3.70 (4H, m, $\mathrm{CH{-}O{-}C}H_2$), 3.87−3.92 (2H, m, $\mathrm{C{-}O{-}C}H_2$), 4.07−4.14 (4H, m, $\mathrm{O{-}CH{=}C}H_2$), 4.26−4.35 (2H, t, *J* = 6.6 Hz, $\mathrm{C(O){-}O{-}C}H_2$), 6.42−6.49 (2H, m, $\mathrm{O{-}C}H\mathrm{{=}CH_2}$), 7.06−7.08 (2H, m, aromatic H ortho to C−O), 7.90−7.95 (4H, m, aromatic H ortho to C−N=N), 8.14−8.17 (2H,m, aromatic H ortho to C(O)−O).

**2.2. Preparation of Ether. 2. 4-(2,4-Dihydroxyphenylazo)benzonitrile (3):** Aminobenzonitrile (10.0 g, 84.8 mmol) was dissolved in ethanol (25.0 g) cooled in an ice−acetone bath, to which a cold solution of HCl (10.02 g, 101.7 mmol) was added drop-by-drop to keep the temperature under 5 °C, followed by addition of isoamyl nitrite (10.42 g, 88.98 mmol). Afterward, a solution of resorcinol (9.33 g, 84.8 mmol) dissolved in ethanol (40.0 g) was mixed with the first solution, and the reaction lasted 14 h at room temperature. To collect the product, the reaction mixture was added to a mixture of acetic acid (3.75 g) and water (500 g), the solution was filtered, and the product, a red powder, was rinsed with water and dried. Yield: 81% (16.4 g, 68.6 mmol); mp: decomposed at 210 °C prior to melting. MS (*m*/*e*): 239 ($M^+$). $\lambda_{\mathrm{max}}$(THF): 400 nm. $^1$H NMR ($\delta$, acetone): 6.26 (1H, s, aromatic H ortho to both C−OH), 6.49−6.52 (1H, m, aromatic H ortho to C−OH and para to the other), 7.62−7.64 (1H, m, aromatic H meta to C−OH), 7.77−7.80 (2H, m, aromatic H ortho to C−CN), 7.85−7.88 (2H, m, aromatic H meta to C−CN), 9.60 (2H, OH).

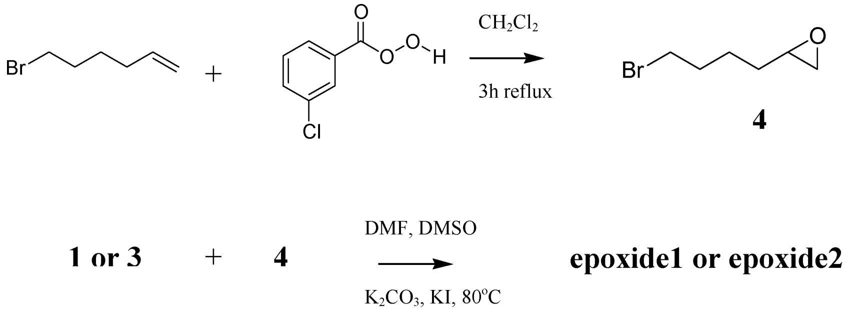
**4-[2,4-Bis(6-vinyloxyhexyloxy)phenylazo]benzonitrile (Ether2):** The reaction procedure was similar to ether1, except that 4-(2,4-dihydroxyphenylazo)benzonitrile (**3**), instead of 4-(4-hydroxyphenylazo)benzoic acid (**1**), was used to react with **2**. For purification, the monomer, a red powder, was washed several times with 2-propanol. Yield: 50%; mp: 52°C. MS (*m*/*e*): 438 ($M^+$). $^1$H NMR ($\delta$, DMSO): 1.34−1.49 (8H, m, $\mathrm{C{-}O{-}CH_2{-}CH_2{-}C}H_2{-}\mathrm{C}H_2$), 1.55−1.63 (4H, m, $\mathrm{CH_2{=}CH{-}O{-}CH_2{-}C}H_2$), 1.72−1.82 (4H, m, $\mathrm{C{-}O{-}CH_2{-}C}H_2$), 3.60−3.67 (4H, m, $\mathrm{C{-}O{-}C}H_2$), 3.82−3.95 (4H, m, $\mathrm{CH_2{=}CH{-}O{-}C}H_2$), 4.06−4.21 (4H, m, $\mathrm{C}H_2\mathrm{{=}CH{-}O}$), 6.41−6.48 (2H, m, $\mathrm{CH_2{=}C}H\mathrm{{-}O}$), 6.75−6.76 (1H, d, *J* = 2.3 Hz, aromatic H ortho to both $\mathrm{C{-}O{-}CH_2}$), 6.96−6.99 (1H, d, *J* = 8.4 Hz, aromatic H ortho to one C−O and para to the other), 7.64−7.67 (1H, d, *J* = 9.1 Hz, aromatic H meta to C−O), 7.86−7.89 (2H, d, *J* = 8.5 Hz, aromatic H ortho to CN), 7.99−8.02 (2H, d, *J* = 8.5 Hz, aromatic H meta to CN).

**2.3. Preparation of Epoxide1 and Epoxide. 2. 2-(4-Bromobutyl)oxirane (4):** Bromohexene (50 mg, 0.3 mmol) was reacted with 3-chloroperoxybenzoic acid (70−77% pure, 165 mg, 0.71 mmol) in dichloromethane (5 mL) at reflux for 3 h. Then dichloromethane (30 mL) was added prior to washing with aqueous solution of $K_2CO_3$ (1 N) and then with water. The organic phase was collected and dried over anhydrous magnesium sulfate. The product obtained was a yellow oily liquid. Yield: 95% (52 mg, 0.28 mmol). Mp: −22 °C. MS (*m*/*e*): 179 ($M^+$). $\lambda_{\mathrm{max}}$(THF): 240 and 290 nm. $^1$H NMR ($\delta$, acetone):

**Scheme 2. Synthetic Route to 4-[2,4-Bis(6-vinyloxyhexyloxy)phenylazo]benzonitrile (Ether2)**



**Scheme 3. Synthetic Route to 4-[4-(4-Oxiranylbutoxy)phenylazo]benzoic Acid 4-Oxiranylbutyl Ester (Epoxide1) and 4-[2,4-Bis(4-oxiranylbutoxy)phenylazo]benzonitrile (Epoxide2)**



1.77−1.85 (2H, m, $\mathrm{Br{-}CH_2{-}CH_2{-}C}H_2$), 1.90−2.03 (2H, m, $\mathrm{Br{-}CH_2{-}CH_2{-}CH_2{-}C}H_2$), 2.22−2.28 (2H, m, $\mathrm{Br{-}CH_2{-}C}H_2$), 2.96−3.01 (2H, m, $\mathrm{O{-}C}H_2$ from epoxide), 3.12−3.22 (1H, m, $\mathrm{O{-}C}H$ from epoxide), 3.83−3.91 (2H, m, $\mathrm{Br{-}C}H_2$).

**4-[4-(4-Oxiranylbutoxy)phenylazo]benzoic Acid 4-Oxiranylbutyl Ester (Epoxide1):** The reaction procedure was similar to ether1, except that 2-(4-bromobutyl)oxirane (**4**), instead of (6-chlorohexyloxy)ethene (**2**), was reacted with **1**. The monomer, an orange powder, was recrystallized in methanol and dried under vacuum. Yield: 30%; mp: 62 °C. MS (*m/e*): 491 (M$^+$). $^1$H NMR ($\delta$, DMSO): 1.46−1.59 (8H, m, $\mathrm{C(O){-}O{-}CH_2{-}CH_2{-}C}H_2\mathrm{{-}C}H_2$ and $\mathrm{C{-}O{-}CH_2{-}CH_2{-}C}H_2\mathrm{{-}C}H_2$) 1.73−1.81 (4H, m, $\mathrm{C(O){-}O{-}CH_2{-}C}H_2$ and $\mathrm{C{-}O{-}CH_2{-}C}H_2$) 2.43−2.50 (4H, m, $\mathrm{O{-}C}H_2$ from epoxide), 2.65−2.68 (2H, m, $\mathrm{O{-}C}H$ from epoxide), 4.08−4.12 (2H, t, $J = 6.4$ Hz, $\mathrm{C{-}O{-}C}H_2$), 4.23−4.33 (2H, t, $J = 6.4$ Hz, $\mathrm{C(O){-}O{-}C}H_2$), 7.13−7.16 (2H, d, $J = 7.0$ Hz, aromatic H ortho to C−O), 7.88−7.96 (4H, m, aromatic H ortho to N=N), 8.11−8.14 (2H, d, $J = 8.5$ Hz, aromatic H meta to N=N).

**4-[2,4-Bis(4-oxiranylbutoxy)phenylazo]benzonitrile (Epoxide2):** A similar reaction procedure was employed as for epoxide1, except that 4-(2,4-dihydroxyphenylazo)benzonitrile (**3**), instead of **1**, was reacted with 2-(4-bromobutyl)oxirane (**4**). The monomer was purified by washing with hexane. A red powder was obtained with a yield of 28%; mp 66 °C. MS (*m/e*): 435 (M$^+$). $^1$H NMR ($\delta$, DMSO): 1.44−1.63 (8H, m, $\mathrm{C{-}O{-}CH_2{-}CH_2{-}C}H_2\mathrm{{-}C}H_2$), 1.75−1.86 (4H, m, $\mathrm{C{-}O{-}CH_2{-}C}H_2$), 2.41−2.50 (4H, m, $\mathrm{C{-}O{-}C}H_2$), 2.64−2.70 (2H, m, $\mathrm{O{-}C}H$ from epoxide), 4.08−4.23 (4H, m, $\mathrm{C{-}O{-}C}H_2$), 6.61−6.65 (1H, m, aromatic H ortho to both C−O), 6.78 (1H, s, aromatic H ortho to one C−O and para to the other), 7.65−7.68 (1H, d, $J = 2.7$ Hz, aromatic H meta to CN), 7.84−7.89 (2H, d, $J = 8.5$ Hz, aromatic H ortho to CN), 7.99−8.02 (2H, d, $J = 8.3$ Hz, aromatic H meta to CN).

**3. Preparation of Optically Aligned FLC.** Photoaligned FLC was prepared by polymerizing azobenzene monomers dissolved in the FLC host while exposing the mixture to linearly polarized UV or visible light. Unlike the free radical polymerization used for acrylate and methacrylate monomers,[1] cationic polymerization was required for divinyl ether and diepoxide monomers.[13,14] The thermal initiator used in this study was composed of 50/50 (w/w) of diphenyliodonium hexafluorophosphate (DiPhIF$_6$P) and AIBN, and its concentration was 2 wt % with respect to the total amount of the mixture. AIBN was used to diminish the cationic polymerization temperature through AIBN radicals acting as electron donors to the iodonium salt.[13] The typical procedure is described in the following example.

In a small flask, ether1 (2.5 mg, 0.005 mmol), FLC (47.5 mg), AIBN (0.5 mg), and DiPhIF$_6$P (0.5 mg) were dissolved in acetone (about 0.1 mL) at room temperature to obtain a homogeneous solution. The solvent was allowed to evaporate at room temperature first under the atmosphere pressure for 3−5 h and then in a vacuum oven for 1 h. A drop of the freshly dried mixture was then placed between two quartz plates, warmed to 50 °C, and finally compressed manually to produce a film of about 60 mm$^2$ large and with a thickness around 5 $\mu$m. Afterward, the sample was moved into a microscope hot stage and, without delay, exposed to linearly polarized light (normal incidence) while being heated, at a rate of about 20 °C/min, to 110 °C for 10 min. Finally, under irradiation the mixture was cooled, at a rate of about 5 °C/min, to 83 °C for 10 min before being cooled to room temperature. After the preparation procedure was completed, the irradiation light was turned off. All samples prepared under these conditions were first examined on a polarizing optical microscope to observe the photoalignment of FLC and then used in different experiments as shown in the paper.

The concentration of azobenzene monomer in the FLC was between 1 and 10 wt %. Linearly polarized irradiation light was obtained by using an UV−vis curing system (Novacure) combined with an UV or visible interference filter (10 nm bandwidth, Oriel) and an UV linear dichroic polarizer (Oriel). Both polarized UV irradiation at 360 nm (~10 mW/cm$^2$) and polarized visible exposure at 400 nm (~5 mW/cm$^2$) were produced. In all experiments, samples with ether1 and epoxide1 were irradiated at 360 nm while those with ether2 and epoxide2 were irradiated at 400 nm.

**4. Characterizations. Monomers:** The four azobenzene monomers and the compounds used for their synthesis were characterized using several techniques. Their $^1$H NMR spectra, in either acetone or DMSO, were recorded on a Bruker-AC300 (300 MHz) or a Bruker DMX-600 (600 MHz) spectrometer. Mass spectra were recorded on a gas chromatography−mass spectrometer (GC-MS), an Agilent GC6890 system coupled to a detector Agilent MSD5973 with a HP-5 column using helium as carrier gas. The thermal behavior was investigated by means of a differential scanning calorimeter (Perkin-Elmer DSC-7), using indium as the calibration standard and a heating or cooling rate of 10 °C/min. All compounds were found

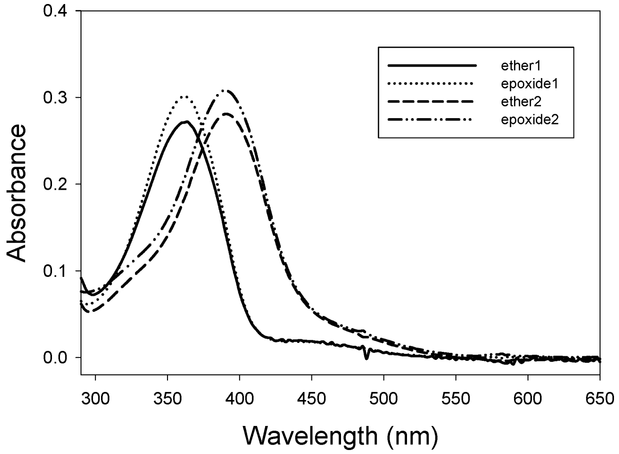


**Figure 2.** UV−vis spectra of the monomers in tetrahydrofuran solution.

to display only a crystalline phase before melting. Their reported melting temperature was determined as the maximum of the endothermic peak during the second heating scan. UV−vis spectra in THF solution were recorded on a Hewlett-Packard 8452A diode array spectrophotometer.

**Mixtures of Monomer/FLC and Polymerized Samples:** The cationic polymerization of azobenzene monomers dissolved in the FLC was examined by means of DSC. Typically, a freshly dried mixture (about 15 mg) was inserted into a DSC pan, and the first heating scan was recorded up to 200 °C to complete the polymerization. Then the sample was cooled to room temperature, and a second heating scan was conducted to observe the changes. A polarizing optical microscope (Leitz DMR-P, magnification 100×) equipped with an Instec hot stage was used to examine the photoalignment of FLC after the irradiation light was turned off at room temperature (see the conditions described above for the preparation of optically aligned samples). Optical micrographs were taken using a Leica DC-300 digital camera. The photoisomerization of azobenzene monomers (before polymerization) and polymers (after polymerization) in the FLC was also investigated using the UV−vis spectrophotometer. UV−vis spectra of thin films (about 5 $\mu$m thick) cast between two quartz plates were recorded immediately following the UV or visible irradiation. For polarized UV−vis spectra, a polarizer (Oriel) was placed in front of the optically aligned sample. Scanning electron microscopy (SEM) was used to observe the azobenzene polymer networks. For these experiments, samples between quartz plates were dipped in hexane to slowly remove the FLC; the two plates were then carefully separated, and the polymer network remaining on both substrates was dried before being examined on a scanning electron microscope (JEOL JSC-840A). Finally, photoaligned samples for the electrooptic effects measurements were prepared between glass plates coated with conducting indium−tin oxide (ITO) using the procedure described above. The measurements were conducted using a photodetector (Displaytech) mounted on the optical microscope and collected to a digital oscilloscope (Tektronix, TDS 210), and a high-voltage waveform generator (WFG500, FLC Electronics) was used to apply the ac field.

## Results and Discussion

### 1. Monomers, Polymers, and Photoisomerization.

Before studying the photoalignment of FLC, the photochromic properties of the azobenzene monomers and their cationic polymerization in the FLC host were investigated. Shown in Figure 2 are the UV−vis spectra of the monomers in THF solution. The absorptions of *trans*-azobenzene ($\pi-\pi^*$ transition) of ether2 and epoxide2 appear at higher wavelengths than ether1 and epoxide1 because of stronger electron donor, electron acceptor, and the 2,4,4′ substitution on the azobenzene moiety. Reversible trans−cis photoisomerization was observed in solution for all monomers. In the FLC, the situation is a little bit complicated for ether1 and epoxide1 due to the overlapping of the absorption band of the FLC. Figure 3a shows an example with a mixture containing 5% ether1. The absorption maximum of azobenzene moieties is noticeable as a shoulder over the strong absorption of the FLC host. Nevertheless, the trans-to-cis photoisomerization takes place in the mixture, since the absorption around 450 nm, which is mostly contributed by the n−$\pi^*$ transition of cis isomer, increases on UV irradiation. By contrast, as is noted in Figure 3b, the photoisomerization of azobenzene in epoxide2, likewise for ether2, can easily be seen since their absorption peak is well separated from that of FLC. Table 1 collects the absorption maxima of all monomers in THF and in the FLC before and after polymerization as well as their melting temperature. It is noted that the absorption of all monomers shift to higher wavelengths in the FLC and that a further red shift seems to occur after polymerization for ether1 and epoxide1. Without ruling out possible effects from light scattering and interaction of the chromophore with the FLC, the increase in absorption wavelength is probably caused by aggregation of azobenzene moieties in the FLC, considering the high azobenzene monomer concentrations used.[15]

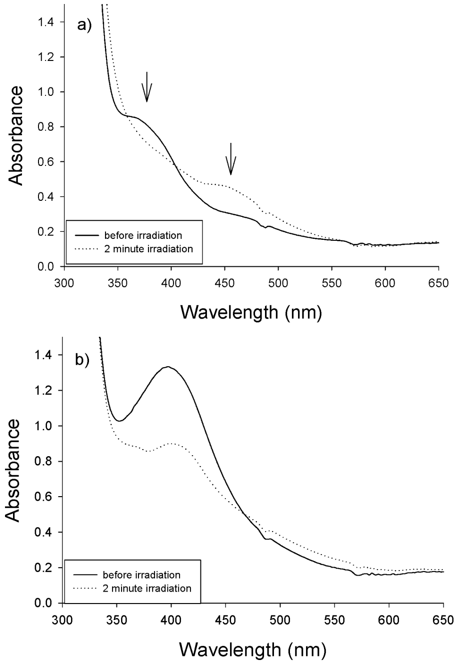


**Figure 3.** UV−vis spectra of 5% azobenzene monomers in the ferroelectric liquid crystal host before and after irradiation: (a) 4-(4-vinyloxymethoxyphenylazo)benzoic acid 6-vinyloxyhexyl ester (ether1) and (b) 4-[2,4-bis(4-oxiranylbutoxy)phenylazo]benzonitrile (epoxide2).

The occurrence of cationic polymerization of all monomers in the FLC, with the used DiPhIF$_6$P/AIBN (50/50) initiator, was confirmed by DSC measurements. Figure 4 shows the heating curves (first scan, 10 °C/min) of the pure FLC and the mixtures with 10% of azobenzene monomers. Several observations can be made. First, polymerization of all monomers is revealed by the exotherms around 115 °C, and for the two ethers, a second exotherm appears at higher temperature. The diminution of polymerization temperature by AIBN is clear because with pure DiPhIF$_6$P, the polymerization exotherm was observed at about 200 °C. Second, prior

**Table 1. Characteristics of the Azobenzene Monomers**

| monomer | $\lambda_{THF}$ (nm) | $\lambda_{FLC}{}^{a}$ (nm) | $\lambda_{FLC}{}^{b}$ (nm) | $T_m$ (°C) |
|---|---|---|---|---|
| 4-(4-vinyloxymethoxyphenylazo)benzoic acid 6-vinyloxyhexyl ester (ether1) | 363 | ~378 | ~386 | 77 |
| 4-[2,4-bis(6-vinyloxyhexyloxy)phenylazo]benzonitrile (ether2) | 391 | 399 | 399 | 52 |
| 4-[4-(4-oxiranylbutoxy)phenylazo]benzoic acid 4-oxiranylbutyl ester (epoxide1) | 362 | ~374 | ~385 | 62 |
| 4-[2,4-bis(4-oxiranylbutoxy)phenylazo]benzonitrile (epoxide2) | 390 | 398 | 398 | 66 |

[a] Before polymerization. [b] After polymerization.

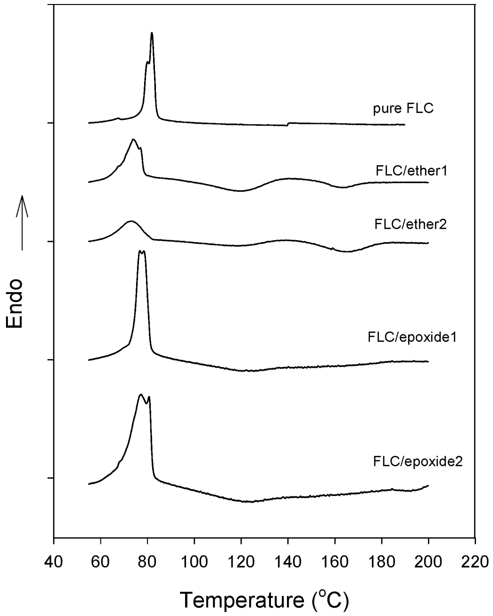


**Figure 4.** DSC curves (first heating scan, 10 °C/min) for the pure ferroelectric liquid crystal and its mixtures with 10% azobenzene monomers.

to polymerization of the monomer, the shift to lower temperatures for the phase transitions of the FLC, as compared with the pure FLC, reflects the interaction between the two components. It is apparent that the disruption effect of the two ethers was greater than the two epoxides. Third, after polymerization (the second-scan curves are not shown), interactions between the azobenzene polymers and the FLC can still be noticed from changes in the transition peaks. On the basis of the above results, in the preparation of optically aligned FLC, the mixture exposed to linearly polarized irradiation was heated to 110 °C, in the isotropic phase, for 10−15 min to complete the polymerization process. We have no explanation for the second exothermic peak observed for the two ethers in Figure 4, but what matters for the present study is that under the used experimental conditions subsequent DSC scans showed no reaction exotherm, implying the depletion of the monomer during the polymerization.

**2. Photoalignment of FLC.** Similar to acrylate- and methacrylate-based polymers,[1,11] azobenzene-containing polyether and polyepoxide networks are able to induce photoalignment of FLC without the use of surface orientation layers. Polarizing optical micrographs are presented in Figure 5 for the mixture with 3% ether2. Prior to heating, the film prepared by compressing a freshly prepared homogeneous mixture between two quartz plates appears birefringent, displaying no phase separation or developed smectic texture (Figure 5a). In the absence of irradiation, polymerization in the isotropic phase followed by cooling to room temperature results in no bulk alignment of smectic domains, but the smectic texture is now visible (Figure 5b). By contrast, the same polymerization process under irradiation leads to a bulk alignment of smectic domains in the direction perpendicular to the polarization of irradiation light (Figure 5c). Again, the action of azobenzene moieties is clearly at the origin of the photoalignment of FLC. Among the four monomers, and with the FLC used, ether1 and epoxide1 were found to be most effective in inducing the photoalignment. The typical results of photoalignment of FLC achieved using various concentrations of ether1 and epoxide1 are presented in Figures 6 and 7, respectively. In both cases, good bulk alignment was obtained with 1−5% azobenzene network, but the number of defects increases with the polymer concentration. The quality of photoalignment with 1% epoxide1 is actually close to that obtained by surface orientation layers of a 5 $\mu$m cell. We also used 0.5% ether1 and epoxide1, but this concentration seemed to be too low to sustain a bulk alignment of FLC; only partial alignment was observed. No bulk alignment could be induced with 10% exther1 or epoxide1 because of phase separation, which is consistent with the result obtained with chiral azobenzene polyacrylates and polymethacrylates.[1] On the other hand, ether2 and epoxide2 were less efficient for photoalignment of FLC than ether1 and epoxide1, with the alignment observed only at low monomer concentrations (1−3%). This difficulty may be related to their molecular structures (Figure 1), as both have the two reactive groups linked to the same phenyl unit which may sterically hinder the movement of the azobenzene moiety.

Similar to chiral diacrylate or dimethacrylate monomers,[1] using azobenzene divinyl ethers and diepoxides, no enhanced phase separation of the polymer network from FLC was observed in the aligned $S_C$* phase. Moreover, exposing an optically aligned sample to irradiation light with its polarization changed by 90° could also rotate the bulk alignment of FLC by 90°. A marked difference, however, is that the orientational memory effect was observed with azobenzene polyethers and polyepoxides, contrary to chiral polyacrylates or polymethacrylates.[1] That is, after isotropization of an aligned sample in the isotropic phase, the bulk alignment of FLC can be recovered on cooling to the LC phases in the absence of irradiation. Such orientational memory effect is the signature of the formation of an anisotropic polymer network.[2,3,16] Unfortunately, polyether and polyepoxide networks were very difficult to observe by a scanning electron microscope (SEM) after extraction of the FLC in hexane; most of the polymer seemed to be washed out during the process. This suggests that these polymer networks may be extremely fine and well dispersed in the FLC host, which is indeed supported by the observation that, unlike samples with chiral polyacrylates or polymethacrylates,[1] no azobenzene polyether or polyepoxide networks were discernible on bright field optical microscope. The networks found on the substrates after removal of FLC do display a very different morphology, as is seen from the SEM pictures in Figure 8. Instead of polymer threads or beads,[1,16] the

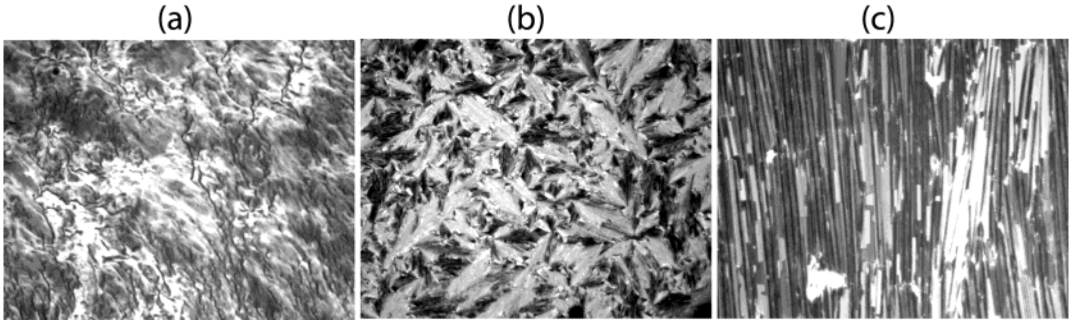


**Figure 5.** Polarizing optical micrographs for a film of ferroelectric liquid crystal with 3% 4-[2,4-bis(6-vinyloxyhexyloxy)phenylazo]-benzonitrile (ether2): (a) before polymerization and irradiation, (b) after polymerization without irradiation, and (c) after polymerization under linearly polarized irradiation. Picture area: 780 $\mu$m × 625 $\mu$m.

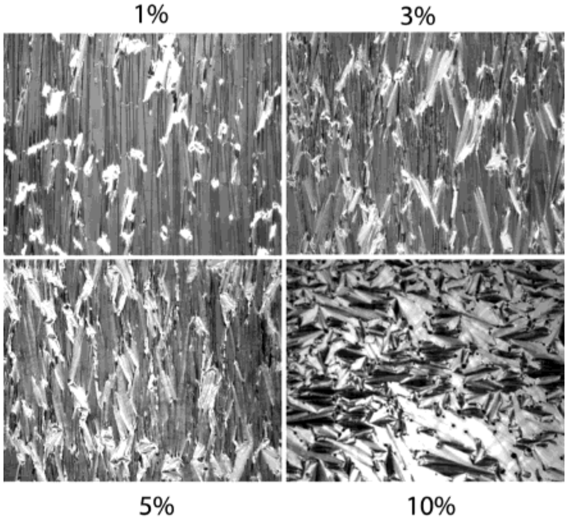


**Figure 6.** Photoalignment of ferroelectric liquid crystal achieved using various concentrations of 4-(4-vinyloxymethoxyphenylazo)benzoic acid 6-vinyloxyhexyl ester (ether1). Picture area: 780 $\mu$m × 625 $\mu$m.

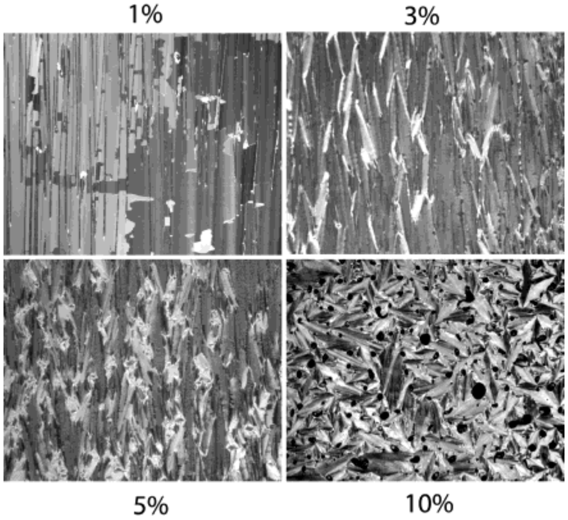


**Figure 7.** Photoalignment of ferroelectric liquid crystal achieved using various concentrations of 4-[4-(4-oxiranylbutoxy)phenylazo]benzoic acid 4-oxiranylbutyl ester (epoxide1). Picture area: 780 $\mu$m × 625 $\mu$m.

networks from 3% ether1 andepoxide2 are apparently formed by connection of thin leaves (~200 nm thick).

Another note regarding the previous study using chiral azobenzene polyacrylates and polymethacrylates[1] needs to be made. One dimethacrylate monomer having a similar chemical structure to ether1 and epoxide1 was found to be unable to induce the photoalignment of FLC. Some factors may be responsible for the different behavior. First, the FLC hosts used in the two studies are different for the reason explained earlier. The different FLC with a different monomer may well develop different intermolecular interactions that affect the interaction and compatibility between the azobenzene polymer and FLC. Second, the diacrylate and dimethacrylate monomers were polymerized through free radical polymerization,[1] while cationic polymerization was used for the ether and epoxide monomers. The rate of chain growth through ionic reactive species is generally faster than that via free radicals.[17] This difference, together with the effect of different polymer and FLC interactions, would result in different polymer network morphologies, which is indeed the case as revealed by SEM. Third, ether1 and epoxide1 have longer flexible spacers than the dimethacrylate monomer whose short spacer also contains the chiral center. This structural difference may provide the azobenzene moiety in ethre1 and epoxide1 with greater freedom of movement, which is important for photoinduced orientation.

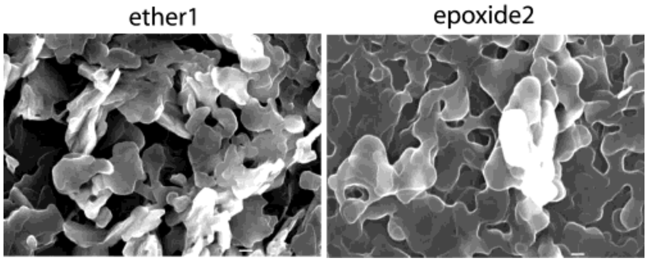


**Figure 8.** Scanning electron microscope (SEM) images of azobenzene polyether and polyepoxide networks remained on the substrate after extraction of the ferroelectric liquid crystal in hexane. The scale bar is 1 $\mu$m.

Now we discuss the commanding effect observed with networks of polyethers and polyepoxides. Even though the orientational memory effect suggests the formation of an anisotropic azobenzene polymer network in the FLC, the photoinduced reorientation of FLC upon subsequent irradiation must be the consequence of a reorientation of azobenzene moieties on the polymer network. More experiments on photoinduced reorientation of FLC were performed in order to get clues about the commanding effect provided by azobenzene moieties or an anisotropic network. A couple of examples are discussed below. In the experiment shown in Figure 9, part of an optically aligned sample with 5% ether1 was subjected to a second irradiation whose polarization was rotated by 90° (the other part was covered by an

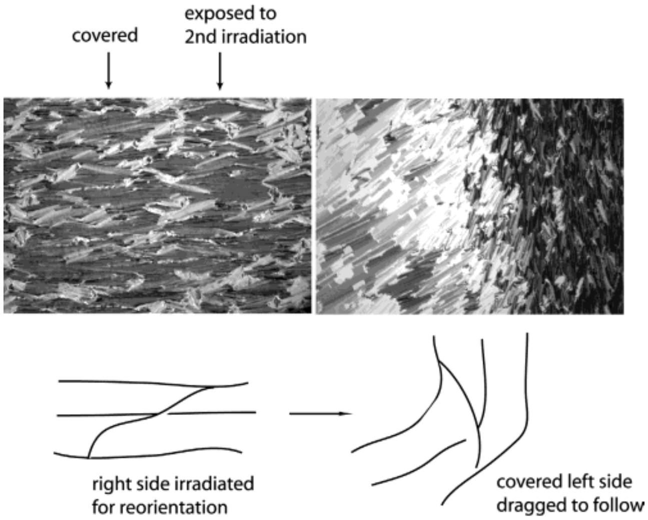


**Figure 9.** Polarizing optical micrographs showing the photoinduced reorientation of ferroelectric liquid crystal for a sample with 5% 4-(4-vinyloxymethoxyphenylazo)benzoic acid 6-vinyloxyhexyl ester (ether1). The sketch depicts the reorientation of smectic domains and the possible change in the azobenzene polymer network (see text for details). Picture area: 940 $\mu$m × 780 $\mu$m.

aluminum sheet), while the sample being heated to and cooled from the isotropic phase. A 90° reorientation of smectic domains was achieved in the irradiated area, with the reoriented domains appearing dark under crossed polarizers. Interestingly, smectic domains in the nonirradiated area were severely altered by the reorientation in the irradiated area in such way that they changed the alignment direction gradually across the boundary. The photoinduced 90° reorientation of azobenzene moieties in the irradiated area is responsible for the reorientation of FLC in the irradiated area and may lead to the observed changes in the nonirradiated area through two possible ways. First, the photoinduced reorientation of azobenzene moieties changes the anisotropy of the polymer network; that is, the network is “stretched” in the same direction as the azobenzene groups and reoriented by 90° during the second irradiation. As a result of this, the left side of the network in the covered area would be dragged to follow, creating a curvature that dictates the gradual change in alignment of the smectic domains through the boundary. The second possible mechanism is that the 90° reorientation of azobenzene moieties in the irradiated area induces a reorientation of the surrounding FLC molecules, which results in the 90° reorientation of smectic domains in this area. Because of the strong cooperative movement that characterizes liquid crystals, the propagation of this reorientation effect leads to the gradual changes in domain alignment direction through the boundary. In the latter case, the sketch in Figure 9 simply illustrates the alignment and interaction of smectic domains arising from the reorientation of azobenzene moieties in the irradiated area. As mentioned earlier, SEM could not confirm the formation of an anisotropic network for the reason explained, but the orientational memory effect suggests its existence. What actually happened may well be a combination of the two mechanisms that both find the origin in the photoinduced reorientation of azobenzene moieties on the polymer network.

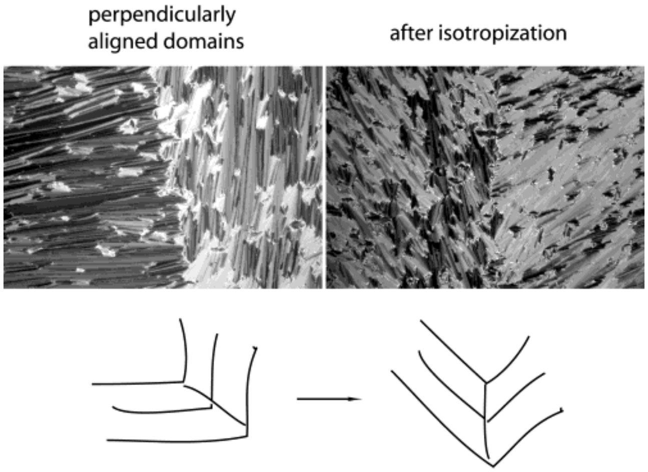


**Figure 10.** Polarizing optical micrographs showing changes after isotropization of a sample with 1% 4-[4-(4-oxiranylbutoxy)phenylazo]benzoic acid 4-oxiranylbutyl ester (epoxide1) containing two areas with perpendicularly aligned domains. The sketch depicts the reorientation of smectic domains and the possible relaxation of the azobenzene polymer network (see text for details). Picture area: 940 $\mu$m × 780 $\mu$m.

Another experiment (Figure 10) is also worth being presented. A 90° reorientation was first achieved for part of a sample containing 1% epoxide1, using the same procedure as in Figure 9. Again, the photoinduced reorientation of azobenzene moieties is responsible for the result. Nevertheless, the apparently sharper boundary between the two areas with perpendicularly aligned domains is in contrast with the result in Figure 9 and hints at the effect of an anisotropic network. This is because at this low polymer network concentration, a change in network anisotropy in the area subjected to the second irradiation would be expected to affect less the covered area due to the low network density. For the experiment, the film was then heated to the isotropic phase (10 min at 100 °C) and cooled back to room temperature. While the perpendicular bulk alignment was recovered in the two areas, with the boundary remained visible, the smectic domains in both areas changed their orientation direction to about 45° with respect to the boundary. This phenomenon may be the manifestation of evolution of the whole anisotropic polymer network crossing the boundary, which determined the recovered alignment of FLC. A plausible option for the relaxation of the anisotropic network during the isotropization process is schematically illustrated in the figure, being a compromise for the different anisotropies in the two areas initially imposed by the two irradiations. On the other hand, without invoking a dominant effect by an anisotropic network, the result may come from relaxation of aligned smectic domains in the presence of a polymer network. In this case, the sketch simply presents the changes in domain alignment direction.

Polarized UV–vis spectroscopic measurements confirmed that the photoinduced reorientation of FLC is accompanied by reorientation of azobenzene moieties on the polymer network. Plotted in Figure 11 is an example of the angular dependence of the absorbance of azobenzene, measured at 398 nm for a sample with 1% epoxide2 subjected to two irradiations with the polarization changed by 90°, the angle being that between the polarization of the beam of spectrophotometer and the polarization of irradiation light used for the first irradiation. It is seen that the orientation of azobenzene moieties is in the same direction as FLC domains, i.e., perpendicular to the polarization of irradiation light, and that the reorientation of azobenzene after the

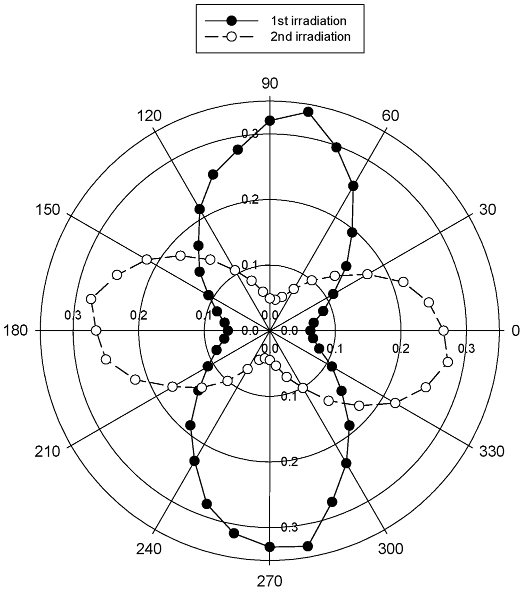


**Figure 11.** Angular dependence of the absorbance of azobenzene moieties on the network at 398 nm for a sample with 1% 4-[2,4-bis(4-oxiranylbutoxy)phenylazo]benzonitrile (epoxide2) after two irradiations with the polarization changed by 90°.

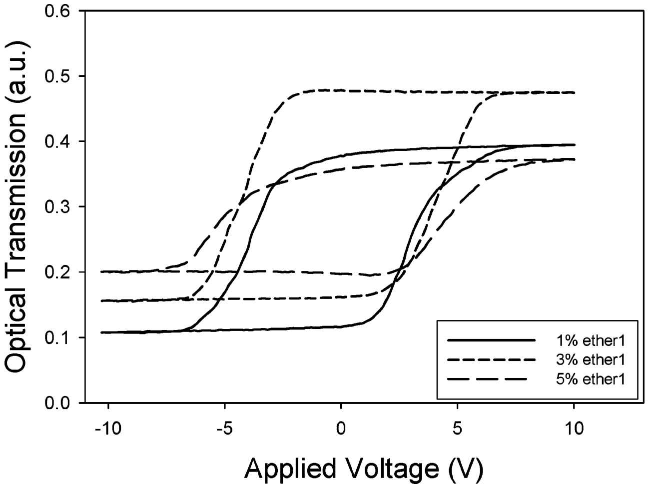


**Figure 12.** Electrooptical effects for photoaligned ferroelectric liquid crystal with different network concentrations of 4-(4-vinyloxymethoxyphenylazo)benzoic acid 6-vinyloxyhexyl ester (ether1). Applied ac field: triangular wave, 100 Hz, 20 V (peak-to-peak).

second irradiation is obvious. A slight decrease in absorbance of azobenzene is noted after the second irradiation. This may be explained by the fact that data in Figure 11 were obtained from two separate sets of measurements. After the second irradiation, during which the sample was placed inside the hot stage for heating and cooling, the sampling area for the recording of polarized spectra may not be exactly at the same position as in the first series of measurements after the first irradiation. No noticeable development of azobenzene moieties aligned perpendicular to the film plane, which may also decrease the absorption of azobenzene, was observed in separate test experiments by exposing samples to different irradiations.

Similar to the use of chiral azobenzene polyacrylates and polymethacrylates,[1] photoinduced alignment of FLC with polyether and polyepoxide networks was difficult to achieve on indium−tin oxide (ITO)-coated glass plates. However, when the ITO surface was treated with ozone, which increases the surface tension, reasonably good bulk alignment could be obtained. Figure 12 shows an example of the electrooptical effects of the photoaligned FLC with 1−5% ether1. Even though the exact data may vary from one series of samples to another due to a varying quality of bulk alignment, the results are representative and some trends can be noticed. Generally, the optical contrast increases with decreasing the network concentration because of reduced light scattering. The hysteresis loop also becomes larger for a higher concentration of network. As compared with surface-aligned pure FLC with a comparable quality of alignment, the presence of a polymer network slightly diminishes the optical contrast and enlarges the hysteresis loop.

## Conclusions

In this paper, azobenzene-containing divinyl ether and diepoxide monomers were synthesized and used for optically aligned FLC in the absence of surface orientation layers. Together with the previous studies,[1,11] we have performed a systematic investigation on various types of azobenzene polymer networks. The results demonstrate unambiguously that using the photoalignment of an azobenzene polymer network to induce bulk alignment of FLC represents a generic approach, even though different mechanisms of action may be involved. In the case of azobenzene polyethers and polyepoxides, and achiral polyacrylates as well,[11] the results suggest the formation of an anisotropic polymer network that induces the alignment of FLC and provides the characteristic orientational memory effect. By contrast, an isotropic polymer network of colloidal particles may be formed with a chiral dimethacrylate.[1] In that case, the photoalignment of azobenzene moieties on the surface of the network commands the alignment of FLC, and the orientational memory effect is absent. Using some azobenzene monomers, good-quality bulk alignment of FLC could be achieved with as low as 1% of monomer, which points out the potential of discovering new azobenzene systems that may satisfy the requirements for practical uses of photoaligned FLC.

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