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Liquid Crystals

Publication details, including instructions for authors and subscription information:

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To cite this Article Sévigny, Sonia , Bouchard, Luc , Motallebi, Shahrokh and Zhao, Yue(2005) 'Azobenzene polymer stabilized ferroelectric liquid crystals: simultaneous photopolymerization and photoalignment', *Liquid Crystals*, 32: 5, 599 – 607

To link to this Article: DOI: 10.1080/02678290500116813

URL: <http://dx.doi.org/10.1080/02678290500116813>

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Azobenzene polymer stabilized ferroelectric liquid crystals: simultaneous photopolymerization and photoalignment

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(Received 30 August 2004; in final form 10 January 2005; accepted 14 January 2005)

A single linearly polarized irradiation was used to initiate cationic photopolymerization of an azobenzene-containing diepoxide monomer dissolved in a ferroelectric liquid crystal (FLC) and, at the same time, to induce fast *trans-cis-trans* photoisomerization cycles for the azobenzene chromophore which leads to a bulk alignment of the FLC in the absence of surface orientation layers. The spectral output of the light source is required to have separate UV and visible wavelengths, which allow for simultaneous photopolymerization of the monomer and photoalignment of the chromophore. Photopolymerization was allowed to take place in different phases of the FLC to reveal the effects on the FLC photoalignment; the interaction between the anisotropic azobenzene polymer network and the FLC host was also investigated using polarizing UV-Vis spectroscopy.

1. Introduction

Polymer stabilized liquid crystals (PSLCs) are low molar mass liquid crystals containing a low concentration polymer network [1–4]. Generally, the purpose of introducing a polymer network is to stabilize either the bulk alignment or a specific texture of the LC host induced by rubbed surfaces or surface orientation layers. PSLCs of different LC types have been exploited, including nematic [2], cholesteric [1] and ferroelectric liquid crystals (FLCs) [3, 4]. In the case of FLCs, another benefit of having a polymer network is to improve the shock resistance of FLC cells [4]. In recent years, we have explored the use of azobenzene-containing polymer networks in PSLCs [5–9]. The *trans-cis* photoisomerization and the related photoalignment of the azobenzene chromophore can impart new features to these materials. In particular, we showed that the photo-orientation of azobenzene groups on the polymer network upon irradiation with linearly polarized light could be used to induce bulk alignment of a nematic LC [5, 6] and FLC [7–9] with no need for surface orientation layers. The alignment is a bulk effect given by a 3-dimensional azobenzene polymer network dispersed in the LC host, which differs from the so-called commanding surfaces coated with azobenzene polymers as developed by Ichimura and co-workers [10].

We have conducted a systematic investigation on FLC photoalignment using various synthesized

azobenzene-containing, network-forming monomers (diacrylates, dimethacrylates, divinyl ethers and diepoxides) and different commercially available FLC mixtures [7–9]. In all previous studies, polymerization of the azobenzene monomer dissolved in the FLC host was thermally initiated. The typical method employed was to heat the FLC/monomer/initiator mixture to the polymerization temperature while applying linearly polarized irradiation. Polymerization initiated by light, i.e. photopolymerization, has several advantages over thermal polymerization. It is faster, can be initiated in a chosen phase of the FLC host and allows the reactive mixture to be filled into the cell at higher temperatures (for greater fluidity) with no concern for polymerization occurring during the filling process. However, the use of photopolymerization to prepare azobenzene polymer stabilized FLCs is not trivial. Most photoinitiators absorb in the UV region, overlapping the absorption of most azobenzene monomers and the FLC host. Given the low concentration of the initiator, light is mostly absorbed by the FLC and azobenzene chromophore in the mixture, and this interference prevents the initiator from effectively initiating the polymerization reaction [11].

In this paper, we report a method that allowed us to overcome the problems. We have chosen (i) a photoinitiator that has significant absorptions in the visible region and (ii), more interestingly, a single light source whose spectral output has separate UV and visible wavelengths that not only excite the photoinitiator for polymerization but also promote fast *trans-cis-trans*

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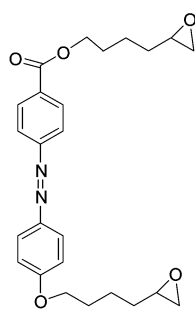
photoisomerization cycles for effective photo-orientation of azobenzene groups leading to bulk alignment of the FLC.

2. Experimental

2.1. Materials and preparation method

The synthesis of the azobenzene-containing diepoxide monomer used, whose chemical structure is shown below, has already been reported [9]. To perform photoinduced cationic polymerization of the monomer, the initiator system was composed of 50/50 (w/w) of diphenyliodonium hexafluorophosphate (DiPhIF₆P), which is a cationic initiator, and the photoinitiator Irgacure 784 (Ciba). The total concentration of initiators was 2 wt% with respect to the amount of the FLC/monomer/initiator mixture, i.e. 1% of each initiator component. Similarly to AIBN used in thermal cationic polymerization [9], photoinduced radicals of Irgacure 784 act as electron donors to the iodonium salt to generate cationic reactive centres that initiate the polymerization [12].

In addition to the major absorption in the UV region, Irgacure 784 has significant absorption in the 400–500 nm region (spectrum not shown), which is some distance from the absorption maximum of the azobenzene monomer in the UV region, centred at about 375 nm. The FLC host used in this work was different from those tested in the previous studies [7–9]. It was Felix017 (Clariant) which has the following phase transitions: Cr–28°C SmC* 73°C SmA 77°C N* 84–87°C I; and a spontaneous polarization of +47 nC cm⁻² at 25°C. It has negligible absorptions at wavelengths above 380 nm. Therefore, using visible wavelengths to initiate the photopolymerization should minimize the interference problem.



Azobenzene monomer

Typically, the homogeneous mixture of FLC/monomer/initiator was prepared by dissolving all compounds in a small amount of acetone, followed by evaporation of most of the solvent under ambient conditions and further drying in vacuum oven at 40°C. The mixtures

were stored in the dark before use. Unless otherwise stated, the concentration of azobenzene monomer was 1 wt%. To obtain simultaneous photopolymerization and photoalignment, a freshly prepared mixture was first compressed between two quartz plates to form a thin film (*c.* 60 mm² area and 5 μm thick) and then placed in a microscope hot stage. Before applying the irradiation light, the sample was heated quickly into the isotropic phase of the FLC for equilibrium (100°C, 5 min), and then cooled to a predetermined temperature at which the linearly polarized irradiation light was turned on. The polymerization under irradiation generally lasted 30 min before cooling the sample to room temperature and turning off the irradiation light.

2.2. Characterization

Samples were characterized by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-7 apparatus, polarizing optical microscopy (POM) on a Leitz DMR-P microscope, UV-Vis spectroscopy with a HP-8452A spectrophotometer and scanning electron microscopy (SEM) using a JEOL JSC-840A system. SEM observations of the azobenzene polymer network were performed after slow extraction of the FLC by dipping the sample in hexane; the two quartz plates were carefully separated and the polymer network remaining on both substrates was dried before SEM experiments. Samples used to measure the electro-optical effects were prepared between glass plates coated with transparent indium tin oxide (ITO) electrodes. For pure FLC, parallel rubbed cells with a gap of 5 μm (E.H.C. Japan) were used. The measurements were conducted using a photodetector (Displaytech) mounted on the optical microscope with collection to a digital oscilloscope (Tektronix, TDS 210).

2.3. Light source

The single light source, which played a central role, needs to be explained. A UV-visible spot curing system (Exfo Lite) was used with a 320–480 nm bandpass filter whose spectral output is shown in figure 1(a). The peak at about 367 nm is suited to the *trans*–*cis* photoisomerization of azobenzene monomer, while the intense peak at 438 nm and other higher wavelengths emission should ensure the excitation of the photoinitiator that absorbs in this region, as mentioned earlier. In this way, both photopolymerization and photoisomerization of the azobenzene monomer (or azobenzene groups on the polymer) can be achieved. Another important feature can be explained with figure 1(b) showing the UV-Vis spectra of pure FLC and an FLC/azobenzene monomer (10%) mixture, containing no initiators, before and after

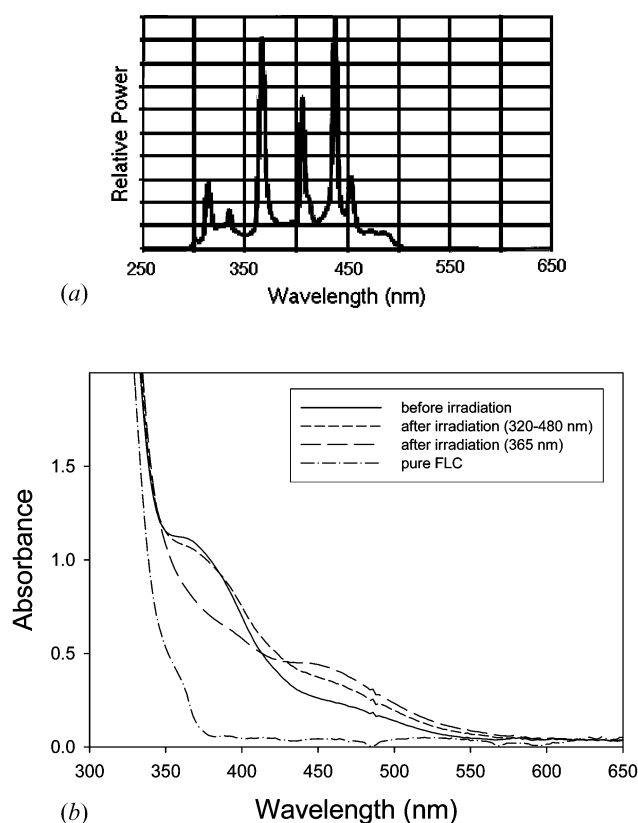


Figure 1. (a) Spectral output of the light source with the 320–480 nm bandpass filter; (b) UV-vis spectra for pure FLC and an FLC/monomer (10%) mixture before and after 2 min irradiation with the light source using both the 320–480 nm and 365 nm bandpass filters.

irradiation with this light source (the use of a high monomer concentration is aimed better to observe the absorption and photoisomerization of azobenzene in the FLC host). It is seen that after 2 min irradiation with the 320–480 nm bandpass filter, there is only a slight decrease in the absorption of azobenzene in the *trans*-form at about 375 nm (π – π^* transition) and that the absorption peak of the *cis*-isomer near 450 nm (n – π^* transition) is not clear, considering the change in baseline due to an increased light scattering. This, however, is not indicative of the absence of effective *trans*–*cis* isomerization of the azobenzene monomer in the FLC, but instead is caused by the spectral output of the light source. Indeed, in addition to initiating photopolymerization, the intense 438 nm peak also activates the *cis*–*trans* back-isomerization of azobenzene. In other words, despite the well separated absorptions of the *trans*- and *cis*-isomers of the azobenzene monomer, this light source optically creates fast *trans*–*cis*–*trans* isomerization cycles that (as with azobenzene derivatives bearing strong electron-donor

and electron-acceptor groups, and having almost superimposed absorptions for *trans*- and *cis*-isomers) favour the photo-orientation of azobenzene groups in a direction perpendicular to the polarization of the irradiating light [13]. This analysis was confirmed by the UV-Vis spectrum of the same mixture after 2 min irradiation with a 365 nm bandpass filter that has only one peak centred at 365 nm for the *trans*–*cis* isomerization (spectral output not shown). The drop of the absorption at 375 nm and the rise of the absorption band around 450 nm become much more prominent, indicating highly efficient photoisomerization of the azobenzene monomer in the FLC host. In this study, the actual intensities of linearly polarized irradiation measured at 365 and 440 nm were about 2.5 and 2.1 mW cm⁻², respectively.

3. Results and discussion

3.1. Photopolymerization

A number of experiments have been carried out in order to confirm the occurrence of photopolymerization of the azobenzene monomer in the FLC host under the linearly polarized irradiation. We first prepared an FLC/monomer/initiator mixture containing 1% AIBN (thermal initiator) in addition to 1% of DiPhIF₆P (cationic initiator) and 1% of Irgacure 784 (photoinitiator). Figure 2 compares the DSC heating curve of the pure FLC with those of the mixture being subjected or not to 30 min irradiation at room temperature before starting the thermal scanning. When the mixture was

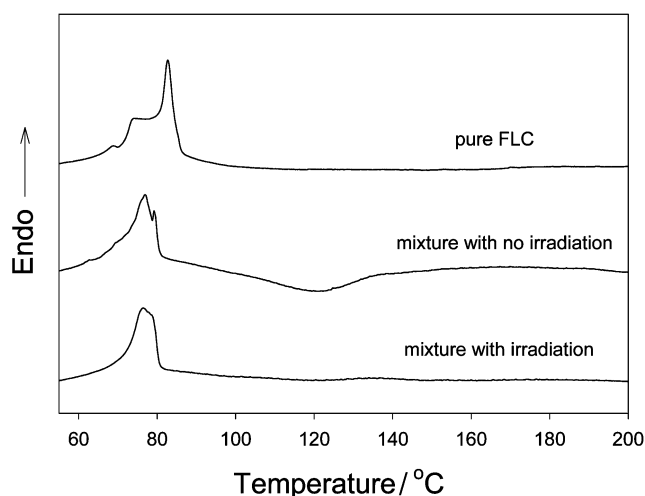


Figure 2. DSC heating curves for pure FLC and an FLC/monomer (10%) mixture containing both a thermal initiator and a photoinitiator. No thermally induced polymerization is observable for the mixture subjected to irradiation at room temperature before the scanning.

not exposed to irradiation, the curve displays FLC mesophase transition peaks shifting to lower temperatures (by *c.* 3°C) due to interaction with the monomer, as well as a broad exothermic peak at higher temperatures indicating the occurrence of thermal cationic polymerization triggered by AIBN [9]. By contrast, for the mixture exposed to irradiation prior to scanning, the broad exothermic peak almost totally disappeared, which implies the occurrence of photopolymerization at room temperature, triggered by Irgacure 784, before the thermal scanning. The presence of the resulting polymer network also reduces slightly the FLC mesophase transition temperatures. Note that this experiment could only indicate qualitatively the occurrence of photopolymerization, since the results using 10% of monomer may not be the same as with 1% of monomer, and it is not excluded that a fraction of monomer was unreacted in the mixture, which could not be revealed by this experiment.

To ensure further the occurrence of photopolymerization in the FLC/monomer/initiator mixtures actually used for photopolymerization and photoalignment, which contained 1% of azobenzene monomer and no AIBN, after polymerization under irradiation from the light source described above, the FLC host was extracted in hexane and the residue on the substrates was examined by SEM. Figure 3 shows an example of SEM images for two mixtures polymerized in the isotropic phase (at 100°C) and the chiral smectic C (SmC*) phase of the FLC (at 65°C). In both cases, the polymer network is visible, confirming the occurrence of photopolymerization under the conditions used. Interestingly, even though the pictures may not reveal the actual structure or morphology of the polymer network, because coalescence or condensation processes could take place

during the removal of FLC, some differences are noticeable. The polymer network formed in the SmC* phase is composed of very thin sheets, whereas the polymer aggregates appear thicker and more irregular, with the polymerization taking place in the isotropic phase of the FLC. We speculate that when the mixture was cooled to the SmC* phase before polymerization, part of monomer could segregate from the FLC and be located in the space between smectic layers, which would account for the formation of the thin sheet-like aggregates after polymerization.

3.2. Photoalignment

One advantage of using photopolymerization is that the polymerization temperature can readily be chosen; this makes it possible to investigate the effect of the phase in which polymerization takes place on the FLC photoalignment. To perform these experiments, typically, a freshly prepared FLC/monomer/initiator mixture was first heated to the isotropic phase for 5 min and then cooled to a predetermined temperature in a specific phase for another 5 min; the phase transition was confirmed by observation of texture changes by POM. Linearly polarized light was then applied to the mixture and the reaction was continued for 30 min before cooling to room temperature, where the FLC alignment in the SmC* phase was observed by POM. Figure 4 shows some representative polarizing optical micrographs of samples polymerized in the various FLC phases. A bulk alignment of the FLC was achieved in samples polymerized in either the isotropic phase (at 100°C) or the chiral nematic (N*) phase (80°C), as can be seen in figures 4(a) and 4(b), respectively. The alignment of smectic domains was developed in the

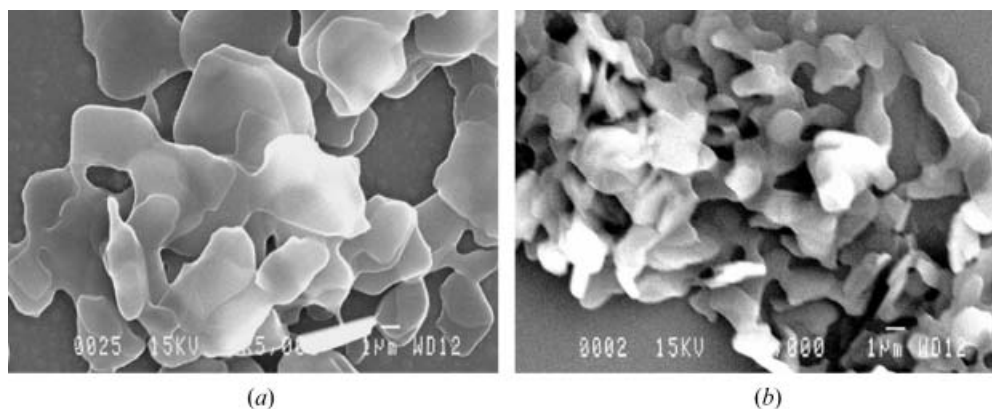


Figure 3. SEM pictures of the azobenzene polymer network remaining on the substrate after removal of the FLC host in hexane. Photopolymerization was performed in (a) the chiral smectic C phase and (b) the isotropic phase of the FLC. The scale bars are 1 μ m.

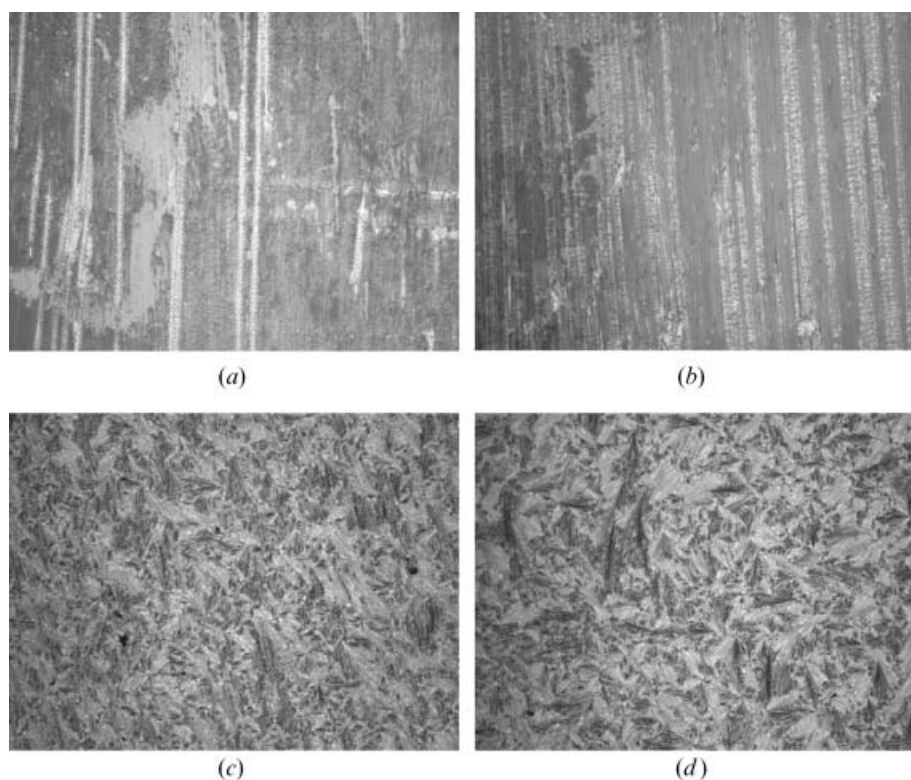


Figure 4. Polarizing optical micrographs showing the FLC bulk alignment developed at room temperature (chiral smectic C phase) for samples polymerized in (a) the isotropic phase at 100°C and (b) the chiral nematic phase at 80°C; but the absence of bulk alignment for samples polymerized in (c) the smectic A phase at 75°C and (d) the chiral smectic C phase at 65°C. Picture area: 940 × 700 μm².

expected direction, i.e. perpendicular to the polarization of the irradiation light. This clearly indicates that the photo-orientation of azobenzene is at the origin of the observed FLC alignment with no use of surface orientation layers. By contrast, as shown by figures 4(c) and 4(d), no bulk alignment of the FLC was observed in samples polymerized in either the smectic A (SmA) phase (75°C) or the SmC phase (65°C).

It should be emphasized that the single light source, with the matching UV and visible wavelengths for simultaneous photopolymerization of the monomer and fast *trans*–*cis*–*trans* isomerization cycles for the photo-orientation of azobenzene, is crucial for the FLC photoalignment. Test experiments found that when the two events of photoisomerization and photopolymerization were allowed to take place sequentially, no FLC photoalignment could be obtained. In one experiment, using the 365 nm bandpass filter (only UV light), the photoisomerization of azobenzene monomer in the mixture was first induced. Afterward, quickly changing the bandpass filter to the one with 400–500 nm visible wavelengths (spectral output not shown), linearly polarized visible light was applied to initiate photopolymerization and the *cis*–*trans* back-isomerization.

However, no bulk FLC alignment was obtained. Similarly, performing photopolymerization using visible wavelengths followed by linearly polarized UV irradiation also failed to produce photoaligned FLC.

Interaction between the azobenzene polymer network and the FLC host can be investigated by means of polarizing UV-Vis spectroscopy. Figure 5 shows the polarizing optical micrograph of an aligned sample polymerized in the isotropic phase (left photo) as well as the angular dependence of the absorbance of azobenzene groups in this sample; the angle in the polar figure is that between the polarization of the irradiation light used for photopolymerization and photoalignment and that of the spectrophotometer beam. The results indicate high orientation of azobenzene groups in the same direction as the smectic domains. Note that the absorbance was calculated at $\lambda=378$ nm where aligned FLC showed negligible contribution to the polarization-dependent absorbance of azobenzene. When the aligned sample was heated to the isotropic phase (110°C) with no irradiation, the bulk alignment could not be retained after cooling back to room temperature, with the whole sample displaying polydomain morphology (right photo). Quite surprisingly, a significant amount of

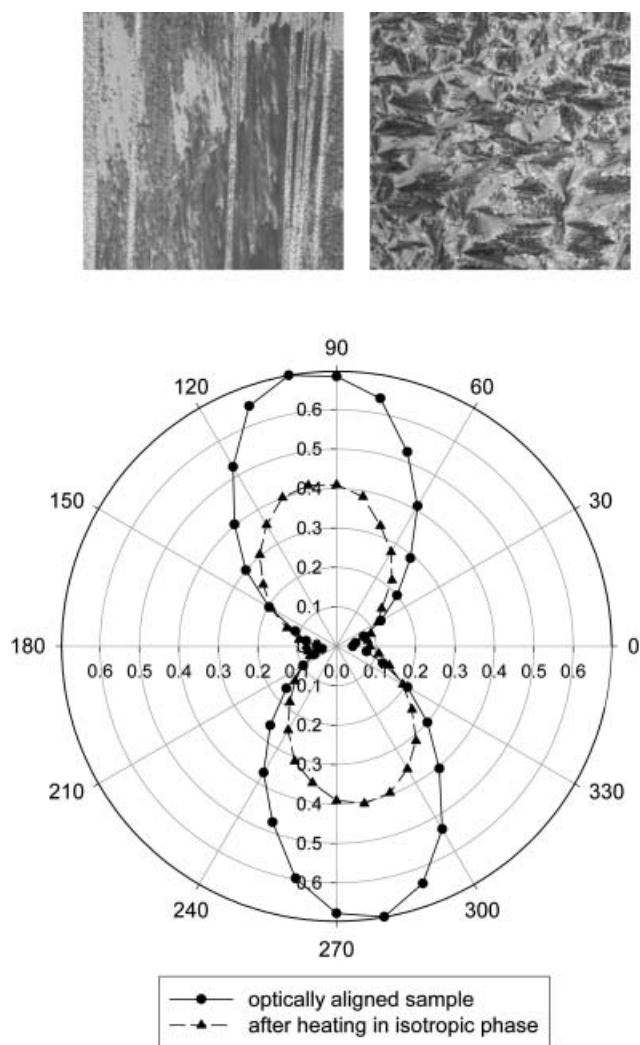


Figure 5. Angular dependence of the absorbance of azobenzene groups at 378 nm for an optically aligned sample at room temperature, before and after heating into the isotropic phase of FLC under no irradiation. The polarizing optical micrographs show the corresponding alignment state of the FLC in the sample (left: before; right: after). Picture area: $470 \times 470 \mu\text{m}^2$.

orientated azobenzene groups apparently remained in the sample.

More experiments have been conducted to probe the interaction and to investigate the possibility of FLC reorientation by light. In figure 6, an optically aligned sample (left photo) was heated to the N^* phase (80°C) while a second irradiation was applied for 30 min in this phase with its polarization rotated by 90° with respect to the first irradiation. After cooling to room temperature under irradiation, the initially aligned domains were partly disturbed, showing an increased disorder (right photo). The polar figures of the absorbance indicate a partial rotation of the preferential orientation

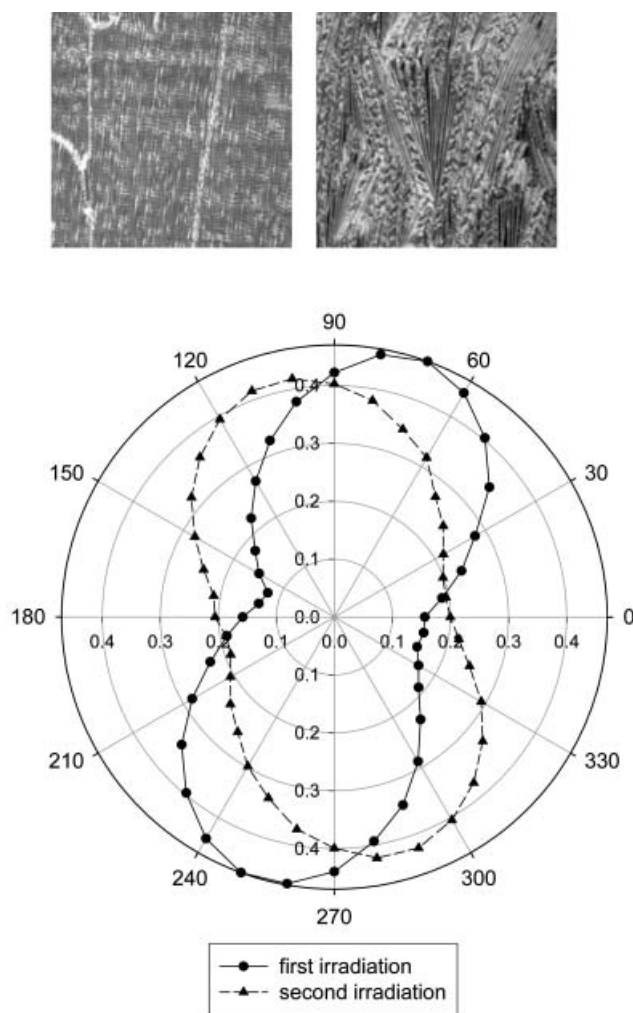


Figure 6. Angular dependence of the absorbance of azobenzene groups at 378 nm for an optically aligned sample at room temperature, before and after exposure to a second irradiation in the chiral nematic phase of the FLC with the polarization changed by 90° . The polarizing optical micrographs show the corresponding FLC alignment state in the sample (left: before; right: after). Picture area: $470 \times 470 \mu\text{m}^2$.

direction of azobenzene groups in the sample after the second irradiation. This result reveals the strong interaction between, and the mutual influence of, the two components in the N^* phase. On the second irradiation, azobenzene groups would tend to reorient by 90° , but they were unable to rotate already aligned FLC molecules in the N^* phase by that angle; this partial FLC reorientation might in turn impose a constraint on the reorientation of azobenzene groups, giving rise to the observed results.

As shown in figure 7, a complete reorientation of the FLC could be achieved by heating an aligned sample to the isotropic phase (100°C) while applying the second irradiation with the polarization rotated by 90° . The

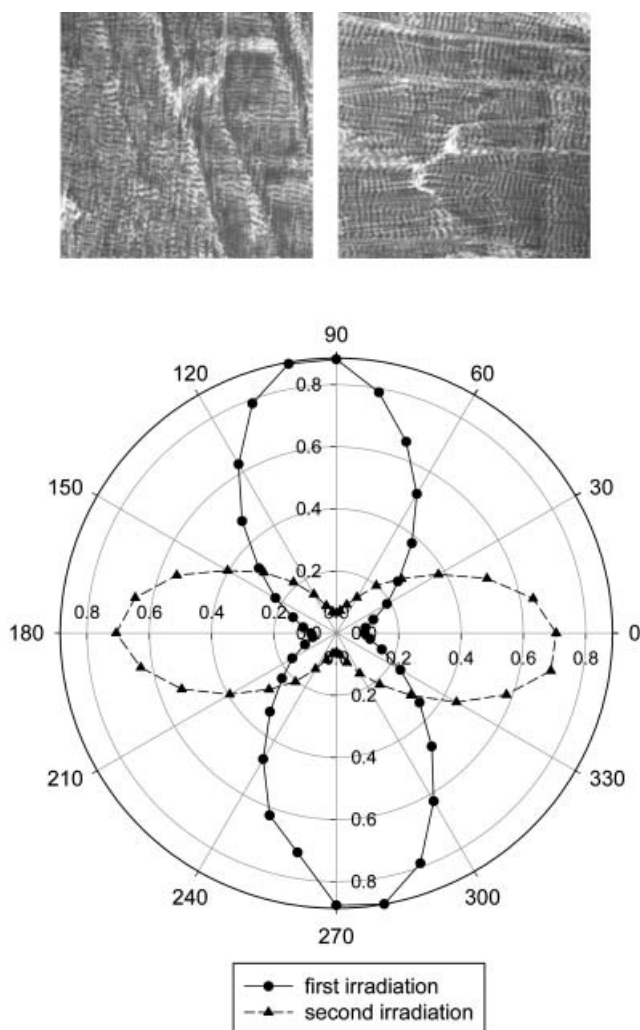


Figure 7. Angular dependence of the absorbance of azobenzene groups at 378 nm for an optically aligned sample at room temperature, before and after exposure to a second irradiation in the isotropic phase of the FLC with the polarization changed by 90° . The polarizing optical micrographs show the corresponding FLC alignment state in the sample (left: before; right: after). Picture area: $470 \times 470 \mu\text{m}^2$.

reorientation of the SmC^* domains at room temperature (from left to right photo) is accompanied by a complete reorientation of azobenzene groups. This result suggests that a 90° reorientation of azobenzene groups on the polymer network could be obtained by subsequent irradiation in the FLC isotropic phase, which is responsible for the FLC reorientation on cooling. Note that in figures 5–7, before the isotropization treatment or the second irradiation, the apparent discrepancy between the maximum absorbance and the 90° angle was caused mainly by experimental errors in positioning the sample in the spectrophotometer with respect to the polarizations.

We now discuss the possible mechanisms for the photoinduced alignment of FLCs. As with previous studies using different systems and thermal polymerization [7–9], the best alignment was obtained by polymerization of the azobenzene monomer in the isotropic phase followed by cooling under irradiation. There was no evidence that the photo-orientation of azobenzene monomer occurring during polymerization in the isotropic phase, which is weak due to thermal relaxation, could lead to the formation of an anisotropic polymer network that then serves as a frame to induce the alignment of the FLC on cooling into the LC phases. However, the isotropic network formed by microphase separated azobenzene polymer can contain a number of photo-oriented azobenzene moieties on the surface of the aggregates and, importantly, has maximized interfacial interaction of FLC molecules due to greater solubility in the isotropic phase. On cooling under irradiation, which preserves the presence of photo-oriented azobenzene moieties on the surface of polymer aggregates, the extensive interface between the microphase separated 3D polymer network and the FLC can act similarly to the planar commanding surface coated with an azobenzene polymer containing oriented azobenzene moieties [10]. It will induce orientation of FLC molecules, once entering the N^* phase, in the same direction as photo-oriented azobenzene moieties. As suggested earlier, in the fluid N^* phase, aligned FLC molecules could, in turn, exert constraints on the well dispersed polymer network that could become anisotropic by adapting the oriented FLC environment.

The situation of polymerization in the N^* phase, which also gave rise to appreciable FLC alignment on cooling under irradiation, may be different. In this case, there was no polymer network with photo-oriented azobenzene moieties before entering the N^* phase. Instead, the polymer network was formed inside the N^* phase. On the basis of the results, it seems that in the course of polymerization the photo-orientation of azobenzene monomer or moieties on the polymer could act to bring the surrounding FLC molecules to align in the same direction due to the co-operative effect, which is also helped by the remaining fluidity in the N^* phase. The failure to induce FLC alignment by photopolymerization in the two smectic phases could be explained by two factors. First, before polymerization, the azobenzene monomer may be expelled by layers of FLC in the smectic phases, and segregated into the inter-layer spacing as well as in the defect regions. Upon irradiation, polymerization and photoisomerization of azobenzene take place, but the segregation considerably reduces the required interaction between azobenzene

and the FLC molecules. Second, although the photo-orientation of azobenzene moieties in the smectic phases should be greater due to the less important thermal relaxation, the high viscosity in these phases may prevent the orientation of FLC molecules forming smectic domains.

Finally, the use of 1% of azobenzene polymer network seems to be effective for inducing FLC photoalignment. Such a low concentration should minimize the undesired heterogeneity of the sample due to the presence of polymer. However, the quality of photoalignment achieved under the current conditions is limited and needs to be improved in order to produce electro-optical effects comparable to pure FLC aligned by rubbed surfaces. An example is given in figure 8, where the contrast of optical transmission of a photoaligned sample is compared with that of pure FLC aligned by rubbed surfaces (triangular wave, 100 Hz, 20 V peak-to-peak). The lower contrast for the photoaligned sample is caused mainly by its less well developed alignment observable by POM. Similar results were obtained when comparing spontaneous polarization (P_S) as a function of temperature for the two samples. The photoalignment of a FLC on ITO-coated surfaces is more difficult to develop than on quartz plates, and an ozone treatment was used to increase the surface tension of the electrode [9]. More studies are needed to optimize the method using a single light source for simultaneous photopolymerization of azobenzene monomers and uniform photoalignment of FLC in an azobenzene polymer stabilized FLC.

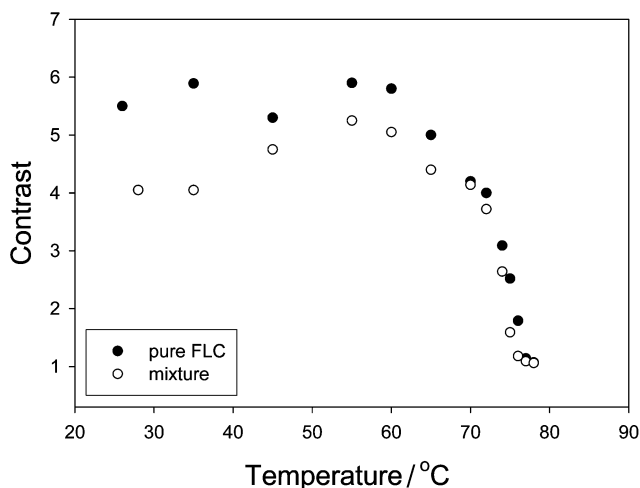


Figure 8. Optical contrast vs. temperature for pure FLC aligned by rubbed surfaces and an optically aligned sample. Applied a.c. field: triangular wave, 100 Hz, 20 V (peak-to-peak).

4. Conclusions

This study shows that a single linearly polarized light can be used to initiate photopolymerization of an azobenzene-containing diepoxide monomer dissolved in a FLC host and, at the same time, to induce the photoisomerization of azobenzene groups on the polymer network, which results in a bulk alignment of the FLC with no need for surface orientation layers. An appropriate spectral output of the light source requires separate UV and visible wavelengths which not only activate the photoinitiator in the visible region, but also create fast *trans-cis-trans* isomerization cycles for the azobenzene chromophore, which favour the photo-orientation of azobenzene groups and, consequently, the photoalignment of the FLC. While a low concentration (1%) of the azobenzene polymer may be effective for the FLC photoalignment, the phase in which polymerization is carried out affects the result. Polymerization in the isotropic and chiral nematic phases of the FLC results in bulk alignment on cooling into the smectic phases. By contrast, polymerization in neither the smectic A nor chiral smectic C phases leads to FLC alignment. The results of this study suggest that a well dispersed azobenzene polymer network with photoaligned azobenzene groups in the high temperature phases of the FLC (N^* and isotropic) is necessary for inducing bulk alignment of the FLC on cooling into the low temperature smectic phases.

Acknowledgment

We thank the Natural Sciences and Engineering Research Council of Canada and le Fonds québécois de la recherche sur la nature et les technologies (Québec) for financial support.

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