Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Wang, Guang , Leclair, Steve , Roy, Luise-Andree , Motallebi, Shahrokh and Zhao, Yue(2005) 'Synthesis of a liquid crystalline azobenzene monomer for photoalignment of ferroelectric liquid crystals', Liquid Crystals, 32: 1, 125 — 131

To link to this Article: DOI: 10.1080/02678290412331329314

URL: http://dx.doi.org/10.1080/02678290412331329314

Liquid Crystals, Vol. 32, No. 1, January 2005, 125–131

Synthesis of a liquid crystalline azobenzene monomer for photoalignment of ferroelectric liquid crystals

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(*Received 14 August 2004; accepted 30 August 2004*)

A liquid crystalline dimethacrylate-based monomer containing an azobenzene group was synthesized. The miscibility of the azo monomer and its crosslinked polymer network with ferroelectric liquid crystals (FLCs) was improved by the liquid crystallinity of the monomer. By performing thermal polymerization of the azo monomer dissolved in a FLC host under linearly polarized visible light irradiation, following a pre-irradiation with unpolarized UV light at room temperature, bulk alignment of the FLC could be induced in the absence of surface orientation layers, as a result of the photo-orientation of azobenzene moieties related to the reversible *trans–cis* photoisomerization of the chromophore. The optical and rubbing-free alignment of a FLC could be achieved with as few as 0.5 wt% of the azo polymer network. This represents a step toward the preparation of uniform samples of photoaligned FLC by reducing the amount of the azo polymer network that may be phase-separated from the FLC host.

1. Introduction

In polymer-stabilized liquid crystals (PSLCs), a low concentration polymer network is used to stabilize the LC alignment or texture induced by surface orientation layers [1–4]. The polymer network is obtained by polymerizing a reactive monomer dissolved in the LC host. Our group previously demonstrated that a polymer network containing azobenzene moieties could impart new features and functions to PSLCs. In particular, the photoisomerization and photoalignment of azobenzene upon irradiation can induce a bulk alignment of LCs with no need for surface orientation layers [5–7]. Recently, our effort has been focused on the use of an azobenzene polymer network to optically align ferroelectric liquid crystals (FLCs). We have synthesized and investigated a variety of azobenzene-containing and network-forming monomers including achiral [8] and chiral diacrylates or dimethacrylates [9] as well as divinyl ethers and diepoxides [10]. The systematic study has confirmed that this optical method represents a general approach for aligning FLCs by light. In some cases, changing the polarization of the irradiating light can induce reorientation of azobenzene moieties on the polymer network, which brings reorientation of FLC molecules in the same direction [9]. Unlike the effect of 'commanding surfaces' [11], the photoalignment of a FLC by an azobenzene polymer network comes from a volume effect with the network dispersed in and phase-separated from the FLC host.

However, segregation of the azobenzene polymer network from the FLC host, which was observed to different degrees in all systems studied, creates an undesired inhomogeneity of the sample. A possible solution to this drawback is to diminish as much as possible the concentration of polymer network, whilst remaining sufficient to ensure the photoalignment. An increased miscibility of the azobenzene polymer with FLC obviously helps because this reduces the tendency for phase separation and thus maximizes the interaction between azobenzene moieties and the surrounding FLC molecules. Since all of our azobenzene monomers investigated so far are non-mesogenic and their solubility in FLCs is limited, in an effort to improve this optical alignment technique we have synthesized probably the first liquid crystalline azobenzene dimethacrylate monomer (hereafter referred to as LC-azomonomer). That is, the monomer is a liquid crystal before polymerization. We anticipated that the LC-azomonomer should have greater solubility in FLCs (and in LCs in general) and this could have a benefit for the miscibility of the azo polymer network with the FLC

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Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online © 2005 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290412331329314

host. In this paper, we report the synthesis and use of a LC-azomonomer for optical alignment of FLCs. Indeed, the photoalignment of a FLC could be achieved using as few as 0.5 wt% of LC-azomonomer due to improved miscibility of the azo polymer network with the FLC host.

2. Experimental

2.1. *Synthesis of the liquid crystalline azobenzene crosslinker*

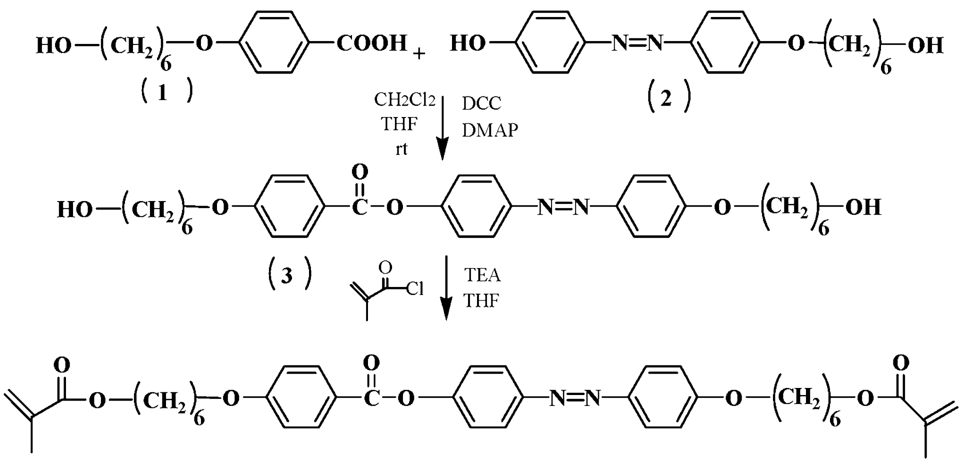
The scheme shows the synthetic route to the LC-azomonomer. As compared with the various non-mesogenic azobenzene monomers (or crosslinkers) we have studied, it seems clear that the liquid crystallinity of the LC-azomonomer is induced by the addition of the benzoate group on the azobenzene moiety, thus lengthening the rigid core. Details of the synthesis are given below. All reagents were purchased from Aldrich and used without further purification. Dry solvents were freshly distilled under anhydrous conditions.

Literature methods were utilized to synthesize the compounds **1** [12] and **2** [13], as shown in the scheme. For the synthesis of **3**, a solution of **1** (1.19 g, 5.0 mmol), **2** (1.57 g, 5.0 mmol) and 4-(dimethylamino)pyridine (DMAP) (0.06 g, 0.5 mmol) was prepared in dry tetrahydrofuran (THF) (20 ml) and methylene chloride (CH_2Cl_2) (5.0 ml). After stirring at 0°C for 1 h, *N,N′*-dicyclohexycarbodiimide (DCC) (1.03 g, 5.0 mmol) was added. The resulting mixture was stirred for another 2 h at 0°C, then at room temperature for 40 h. The precipitate was filtered off, and the filtrate dried under reduced pressure. The product was purified by column chromatography on silica gel (eluant: ethyl acetate/petroleum ether, 1.5/1); yield, 0.81 g (1.5 mmol, 30%), m.p. 136°C. MS (*m*/*e*): 534 (M^+). ^{1}H NMR (δ, $CDCl_3$): 8.20–8.10 (2H, d), 8.0–7.85 (4H, dd), 7.39–7.31 (2H, d), 7.04–6.91 (4H, dd), 4.10–3.98 (4H, m), 3.72–3.61 (4H, m), 1.92–1.68 (8H, m), 1.65–1.41 (8H, m), 1.25 (2H, s).

For the synthesis of the LC-azomonomer, a solution of compound **3** (0.75 g, 1.4 mmol), triethylamine (0.424 g, 4.2 mmol) and DMAP (0.034 g, 0.28 mmol) was prepared in dry THF (15 ml) and CH_2Cl_2 (5 ml). After stirring at 0°C for 30 min, a solution of methacryloyl chloride (0.32 ml, 3.36 mmol) in THF (5 ml) was added dropwise at 0°C. The reaction solution was then stirred at room temperature overnight. The precipitate was filtered off and the filtrate washed with dilute hydrochloric acid and water; the organic solution was then dried with anhydrous magnesium sulphate. The crude product was purified by column chromatography on silica gel (eluant: ethyl acetate/petroleum ether, 1/1.5); yield, 0.22 g (0.33 mmol, 23%). MS (*m*/*e*): 670 (M^+). ^{1}H NMR (δ, $CDCl_3$): 8.19–8.10 (2H, d), 7.99–7.84 (4H, dd), 7.39–7.30 (2H, d), 7.04–6.91 (4H, dd), 6.10 (2H, s), 5.55 (2H, s), 4.20–4.11 (4H, t), 4.10–3.99 (4H, t), 2.01–1.92 (6H, m), 1.79–1.87 (4H, m), 1.65–1.45 (4H, m), 1.42–1.17 (8H, m).

2.2. *Photoalignment of ferroelectric liquid crystals (FLCs)*

Two commercially available FLC mixtures purchased from Clariant, Felix017 and Felix-SCE8, were investigated in this study. They are denoted as FLC-1 and FLC-2, respectively, hereafter. FLC-1 has the following phase transitions: Cr–28°C SmC* 73°C SmA 77°C N* 84°C I; its spontaneous polarization ($\mathbf{P}_s$) measured at 25°C is +47 nC cm^{-2}. For FLC-2, the phase transition temperatures are: Cr–40°C SmC* 60°C SmA 80°C N* 102°C I, with $\mathbf{P}_s = -4.5$ nC cm^{-2}. Details of the procedure used to prepare an optically aligned FLC were reported in [9, 10]. In essence, a homogeneous mixture of the LC-azomonomer, the FLC and the initiator (AIBN) was first



Scheme. Synthetic route to the liquid crystalline azobenzene crosslinker.

prepared by dissolving all the compounds in THF. After the removal of solvent in vacuum, a drop of the mixture was compressed between two quartz plates to form a thin film, about 5 μm in thickness and 60 mm^2 in area. The film was then placed inside a microscope hot stage and heated at the polymerization temperature for 15 min (110°C in the isotropic phase of FLC) while being exposed to linearly polarized irradiation.

In the present study, a different procedure for the photoalignment of azobenzene, and thus for the FLC, was employed from that used in our previous studies [8–10]. As is shown later, on UV light irradiation, the *trans–cis* photoisomerization of the LC-azomonomer is near 100%, and azobenzene moieties in the *cis*-form are stable. In this case, the method utilized consisted of pre-irradiating the FLC/LC-azomonomer with unpolarized UV light (360 nm, ~15 mW cm^{-2}), at room temperature, to reach almost 100% *cis*-azobenzene dissolved in the FLC, and then applying linearly polarized visible light (440 nm, ~5 mW cm^{-2}), not only to convert *cis*-azobenzene to *trans*-azobenzene but also to induce efficiently the orientation of *trans*-azobenzene in the direction perpendicular to the polarization of the visible irradiation [14]. Afterward, the film was heated to polymerize the LC-azomonomer and cooled to room temperature with the polarized visible irradiation held. Only after the preparation procedure was completed was the irradiation light turned off and the sample characterized. Polarized and unpolarized irradiation lights were obtained using a UV-Vis spot curing system (Novacure) combined with filters and polarizers (Oriel).

2.3. *Characterization*

Various techniques were used to characterize the LC-azomonomer and the mixtures of FLC/LC-azomonomer or polymer. These included differential scanning calorimetry (Perkin-Elmer DSC-7), polarizing optical microscopy (POM) (Leitz DMR-P), ^{1}H nuclear magnetic resonance (Bruker, AC-300), mass spectroscopy (Micromass ZAB-1F), infrared spectroscopy (Bomem MB-200 FTIR), UV-Vis spectroscopy (HP-8452A) and scanning electron microscopy (SEM, JEOL JSC-840A). The molecular orientation of azobenzene groups on the polymer network was investigated through polarized UV-Vis measurements. The absorbance of trans azobenzene was measured as a function of the polarization of the spectrophotometer beam by placing a UV-Vis polarizer in front of the sample. In the case of SEM, the FLC/azo polymer film between quartz plates was dipped in hexane to slowly remove the FLC; the two plates were then carefully separated and the azo polymer network remaining on both substrates was dried before examination by SEM.

3. Results and discussion

The synthesized azobenzene monomer (LC-azomonomer) is indeed liquid crystalline. Figure 1 shows the DSC heating and cooling curves (10°C min^{-1}). On heating, two mesophase transitions are seen at 99 and 145°C after melting of the crystalline phase at 70°C. On cooling from the isotropic phase, these mesophase transitions display small supercoolings of 5°C, in contrast with the crystallization exothermic peak which shows a supercooling of 40°C. POM observations were carried out on cooling the LC-azomonomer from the isotropic phase. Figure 2 shows typical textures formed in the two mesophases and in the crystalline phase for comparison. The schlieren texture at 138°C is indicative of a nematic phase as the high temperature mesophase. The micrograph taken at 75°C shows the change in texture on cooling into the low temperature mesophase that is likely to be a smectic phase. The spherulite texture of the crystalline phase at 25°C is the result of transformation from the mesophase. The phase transition temperatures (°C) and enthalpies (J g^{-1}, in brackets) on heating as measured from DSC are Cr 70 (52) Sm 99 (0.8) N 145 (1.3) I.

The occurrence of *trans-cis* photiosmerization of the LC-azomonomer was investigated both in solution and in the mixture with the two FLCs. Figure 3 shows the UV-Vis spectra of LC-azomonomer dissolved in THF and in FLC-2 (5%, similar results for FLC-1). In solution, after 30 s of UV light irradiation, the absorption peak of azobenzene in the *trans*-form centred at 354 nm (π–π* transition) disappears, and is replaced by the absorption peak of azobenzene in the *cis*-conformation near 450 nm (n–π*). It can be seen that

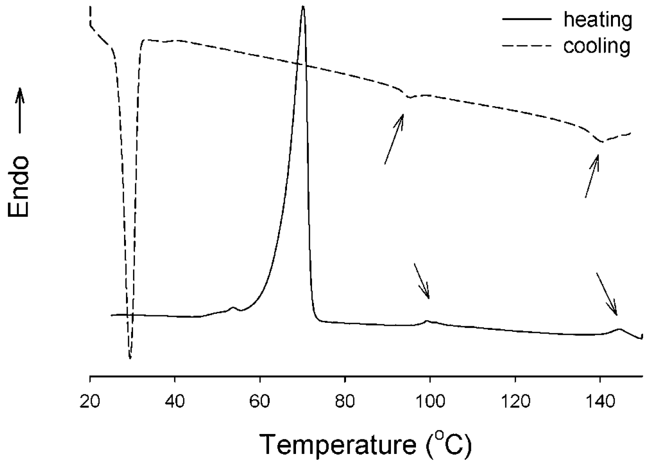


Figure 1. DSC heating and cooling curves (scan rate= 10°C min^{-1}) for the liquid crystalline azobenzene dimethacrylate monomer. The mesophase transition peaks are indicated by arrows.

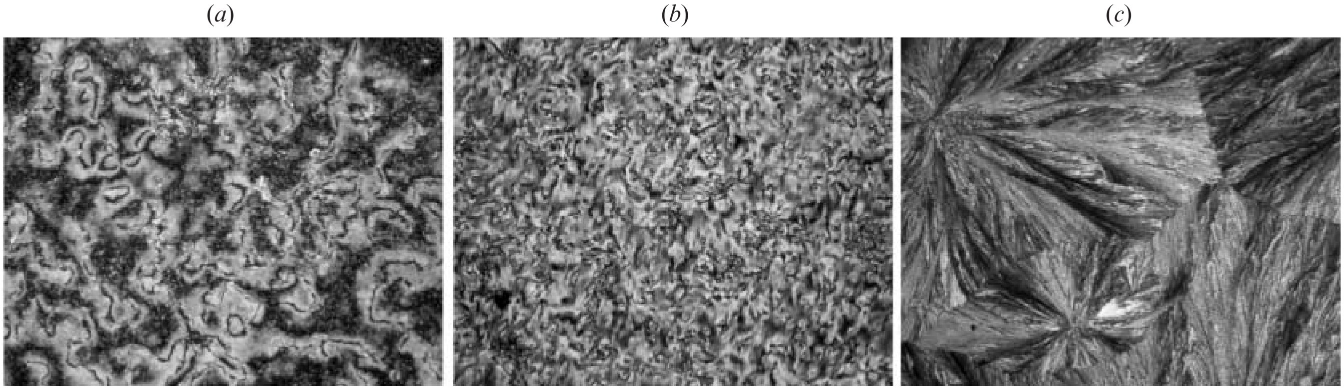


Figure 2. Polarizing optical micrographs of the liquid crystalline azobenzene monomer on cooling from the isotropic phase: (*a*) 138°C; (*b*) 75°C and (*c*) 25°C. Picture area: $760 \times 600\,\mu m^2$.

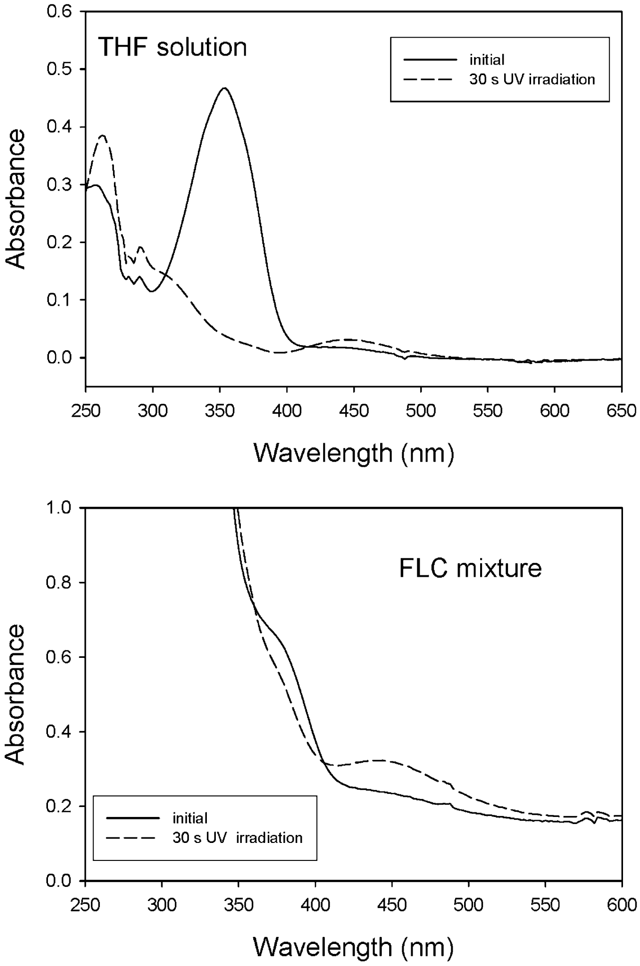


Figure 3. UV-Vis spectra of the liquid crystalline azobenzene monomer in THF solution and in a mixture with ferroelectric liquid crystal FLC-2 (5% monomer) before and after 30 s of UV light irradiation, showing a near 100% *trans-cis* photoisomerization.

the isomerization has an efficiency close to 100%. In the FLC host, the absorption peak of trans azobenzene is overlapped by the strong absorption of the FLC in the UV region. However, the absorption of *trans*-LC-azomonomer is till visible as a shoulder apparently shifted to longer wavelengths (~375 nm). After 30 s of exposure to UV light, the decrease in the shoulder is clear, which is accompanied by a rise in the absorption peak of *cis*-azobenzene near 450 nm. This indicates that a very efficient *trans–cis* photoisomerization also occurs in the FLC host. In both cases (spectra not shown), if a subsequent visible light irradiation (440 nm) is applied, the absorption peak of *trans*-azobenzene is recovered as a result of the *cis–trans* back isomerization. In the dark, the thermal relaxation of *cis*-azobenzene takes place slowly, needing hours to complete. In the case of a high concentration of *cis*-isomer in the photostationary state coupled with slow thermal relaxation, the application of linearly polarized visible light irradiation is effective for the photo-orientation of *trans*-azobenzene [14].

DSC was also used to check thermal polymerization of LC-azomonomer dissolved in FLCs and to gain information on the miscibility of the resulting azo polymer network with the FLC host. Figure 4 compares the DSC heating curve (second scan) of pure FLC-1 with those of the mixture of FLC-1 with 5% LC-azomonomer and 2% AIBN (first and second scans). The following observation can be made. During the first heating of the FLC/LC-azomonomer mixture, as expected, the mesophase transition endothermic peaks of FLC-1 are affected, mainly broadened, by the presence of 5% LC-azomonomer. However, the clearing temperature T_{ni}, is not reduced to lower temperatures as is always observed when non-mesogenic azo monomers are used [6–10]. This is clearly due to the liquid crystallinity of LC-azomonomer, leading to better miscibility or stronger affinity with the FLC host than

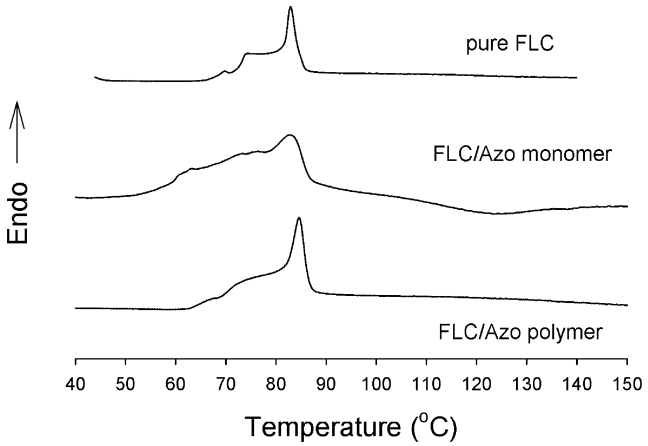


Figure 4. DSC heating curves (scan rate$=10^\circ$C min^{-1}) for pure ferroelectric liquid crystal FLC-1 (second scan) and the mixture of FLC-1 with 5% liquid crystalline azobenzene monomer (first and second scans). Thermal polymerization of the monomer occurred on the first heating scan.

with non-mesogenic azo monomers. On further heating of the mixture, thermal polymerization of LC-azomonomer in the FLC can be seen from the appearance of a broad exothermic reaction peak centred at about 122°C, leading to the formation of an azo polymer network. The consumption of LC-azomonomer is confirmed by the second heating curve of the mixture, which displays no exothermic peaks. Interestingly, in the presence of the resulting azo polymer network, the peak maximum $T_{\rm ni}$ is even increased by about 3°C. This is also significant because it confirms the expected improvement of the miscibility of the azo polymer with FLC, which originates from the use of the LC azo-monomer.

We used LC-azomonomer to optically align FLCs. Utilizing the polymerization and photoalignment procedure as described in § 2.2, bulk alignment of both FLCs could be obtained in the absence of surface orientation layers. With LC-azomonomer, FLC-1 could be photoaligned by as little as 0.5% of azo polymer. The lowest concentration of non-mesogenic azo monomers required for photoalignment of FLCs in our previous works is 1% [9, 10]. Presented in figure 5 are some representative polarizing optical micrographs showing the bulk alignment of FLCs at room temperature, i.e. in the SmC* phase. Between the two FLCs, the photoalignment of FLC-2 was more difficult to obtain, and a larger amount of azo polymer was needed. In the pictures, the alignment direction of smectic domains is perpendicular to the polarization of visible irradiation, which indicates that the photo-orientation of azobenzene moieties is responsible for the bulk alignment of FLC molecules. The photo-orientation of azobenzene moieties on the polymer network could be observed from polarized UV–Vis spectroscopic measurements. An example of the results is given in figure 6, where the angular dependence of the absorbance of *trans*-azobenzene moieties measured at 375 nm is shown for two photoaligned samples of FLC-1 with 0.5 and 3% of azo polymer. The angle is that between the polarizations of the spectrophotometer beam and the visible irradiation used for photoalignment. For the two samples, the highest absorbance was observed at 90°, confirming that azobenzene moieties on the polymer network are

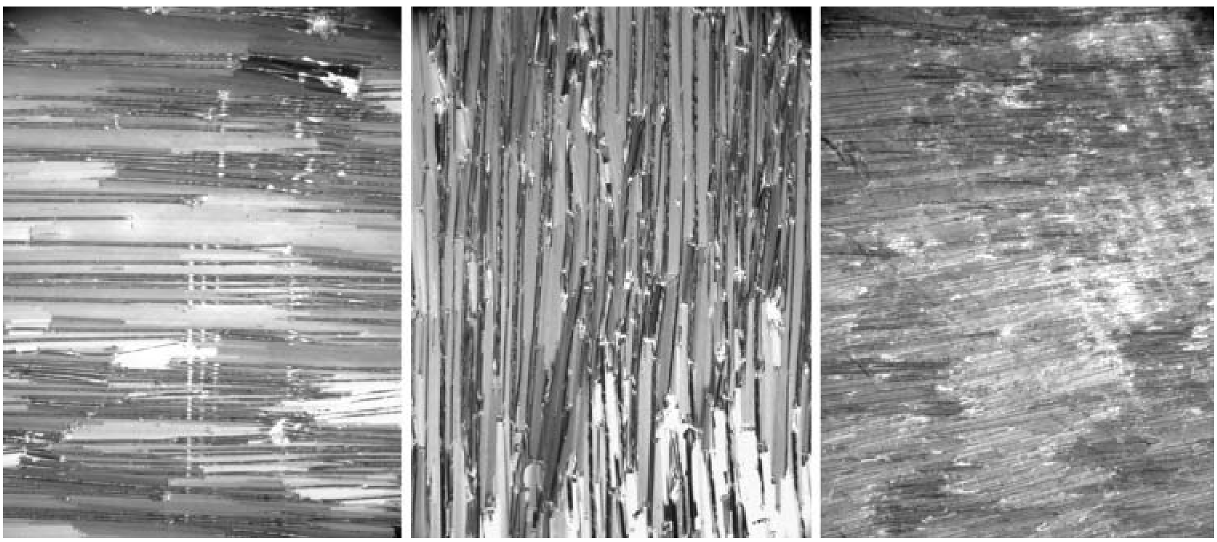

(*a*) (*b*) (*c*)

Figure 5. Polarizing optical micrographs showing the photoalignment of ferroelectric liquid crystals: (*a*) FLC-1 with 0.5%, (*b*) FLC-1 with 3% and (*c*) FLC-2 with 3% of the liquid crystalline azobenzene monomer. Picture area: $740 \times 1000\,\mu\mathrm{m}^2$.

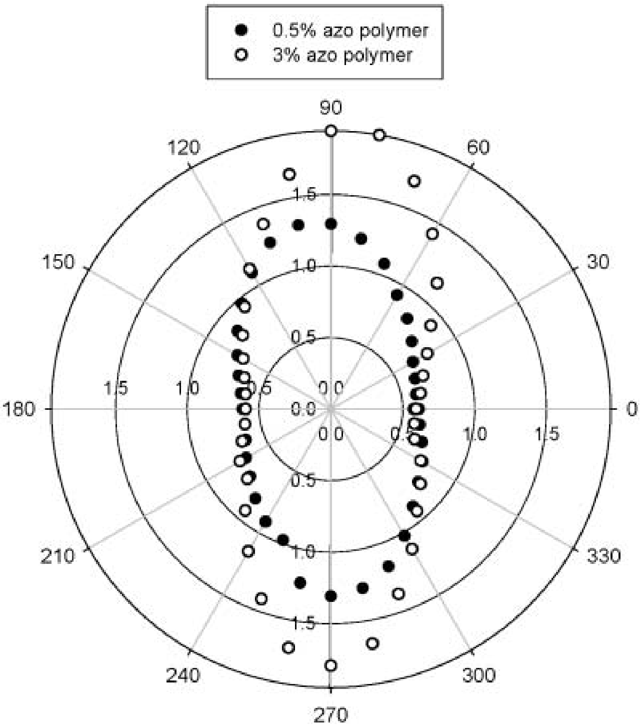


Figure 6. Angular dependence of the absorbance of azobenzene moieties on the polymer network measured at 375 nm for photoaligned ferroelectric liquid crystal FLC-1 with 0.5% and 3% of azobenzene polymer.

aligned in the same direction as FLC molecules; that is, perpendicular to the polarization of visible irradiation.

When using non-mesogenic azo monomers to prepare photoaligned FLCs, phase segregated, orange coloured azo polymer networks could often be observed in a bright field optical microscope, sometimes immediately after the preparation procedure [9] and sometimes several hours later as the segregation developed over time [15]. With LC-azomonomer, no such phase-separated polymer aggregates or strips were observed, which again suggested an improved dissolution of the azo polymer network. For samples with FLC-1, we were unable to observe azo polymer network by SEM after extraction of the FLC, which also suggests a solubilized polymer network in this FLC. In the case of FLC-2, azo polymer network could be found after removal of FLC, as shown by the SEM image in figure 7 for a sample containing 3% azo polymer. The network is formed by thin flake-like aggregates (thickness<100 nm). However, the network morphology may not reflect the actual network dispersed in the FLC host, since aggregation of the polymer could take place during the removal of FLC. On the whole, the SEM also revealed an enhanced miscibility of azo polymer network in FLCs as a result of the liquid crystallinity of the azo monomer.

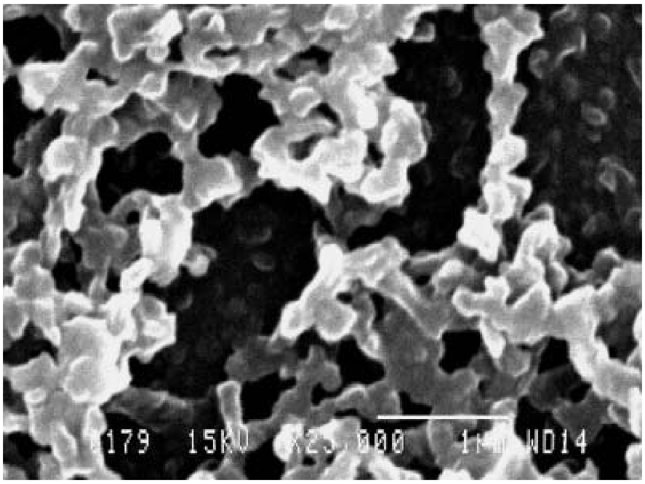


Figure 7. Scanning electron microscope image of the azobenzene polymer network remaining on quartz plates after extraction of ferroelectric liquid crystal FLC-2. The scale bar is 1 μm.

4. Conclusion

A liquid crystalline dimethacrylate monomer containing an azobenzene group was synthesized and characterized. Due to the liquid crystallinity, the azo polymer network formed by thermal polymerization of the LC azo monomer dissolved in FLCs has a greater miscibility with the FLC host than have polymer networks obtained using non-mesogenic azo monomers. As a result of the photo-orientation of azobenzene moieties on the polymer network, optical and rubbing-free alignment of a FLC was achieved by polymerizing as few as 0.5% of the LC azo monomer under linearly polarized visible light irradiation, which was preceded by unpolarized UV light irradiation. This study shows that improving the miscibility between the azo polymer network and FLC through the use of LC azo monomers is a way eventually to reach the minimum amount of azo polymer network needed for the photoalignment of FLC, and thus to reduce the inhomogeneity created by a phase-separated polymer network.

Acknowledgement

We would like to 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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