Induction of Liquid Crystal Orientation through Azobenzene-Containing Polymer Networks

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ABSTRACT: A diacrylate monomer containing a core of azobenzene groups was synthesized. Thermal polymerizations of mixtures of the monomer dissolved in a nematic liquid crystal, E7, resulted in liquid crystals stabilized by an azobenzene-containing polymer network. When their thin films were irradiated by linearly polarized UV light at room temperature, as a result of the alignment of azobenzene groups on the network, a macroscopic orientation of E7 molecules was induced perpendicular to the UV polarization direction. Infrared dichroism was used to measure the liquid crystal orientation in irradiated films. It was found that the achievable orientation, observed after minutes of irradiation, increases with increasing polymer network density and that a significant degree of the induced orientation remains stable after turning off the irradiation. This approach represents a new means to control the average liquid crystal orientation in materials such as polymer-stabilized liquid crystals.

Introduction

Among liquid crystal-based electrooptical materials, polymer-stabilized liquid crystals (PSLC) show great potential for a number of applications including display technologies.[1] Generally, PSLC is prepared by first dissolving a small amount of monomers in a low molecular weight liquid crystal and then performing thermally or photoinduced polymerization giving rise to a polymer network. If the polymerization proceeded while liquid crystal molecules are oriented by surface treatment or effects of other external fields, the formed polymer network can be anisotropic. The network in turn can stabilize the liquid crystal orientation or a specific texture. This is the basis for electrically controllable light scattering of these materials, which is necessary for display applications. Chien and co-workers[2,3] have made PSLC with an azo-containing network and used the dichroic azo dyes to measure the optical order parameter of the aligned network. Unlike polymer-dispersed liquid crystals (PDLC), which consist of liquid crystal droplets in a polymer matrix, PSLC needs no match of refractive indices because of the low polymer concentration. Many studies have already been devoted to PSLC containing cholesteric and ferroelectric liquid crystals.[1,4,5]

The purpose of this study is to investigate possibilities of using irradiation to control or promote liquid crystal orientation in this type of materials. The basic idea is to make a polymer network carrying azobenzene groups which not only can stabilize liquid crystal but also alter its orientation through irradiation. In recent years, azobenzene-containing polymers and liquid crystalline polymers have attracted a lot of attention.[6−10] They have the potential to be used as optical storage media. The basis of all the interests is the photoinduced isomerization of azobenzene. Among the many studies exploring the use of this phenomenon,[6−12] it has been shown that this photoisomerization can induce isothermal nematic to isotropic phase transition in liquid crystalline polymers[10] and can induce orientation of azobenzene moieties.[7] When linearly polarized light irradiates a thin film of azobenzene polymers, the azobenzene groups tend to be aligned perpendicular to the polarization direction. The orientation mechanism is now understood. Upon irradiation, each photoinduced trans−cis isomerization is followed by thermally activated cis−trans isomerization, which causes a small reorientation of the transition moment. After a large number of the trans−cis−trans cycles, the result is a preferential orientation of azobenzene groups normal to the polarization plane. The ability for azobenzene groups to induce orientation of nonreactive units has been well demonstrated.[13]

From the above, if a liquid crystal is stabilized by a polymer network carrying azobenzene groups, it is conceivable that any azobenzene orientation due to irradiation could alter the director fields of surrounding liquid crystal molecules, leading to their orientation. If this is true, the approach is of interest, considering the importance of controlling the average liquid crystal orientation over macroscopic length scales. The method can add an additional means to promote and manipulate liquid crystal orientation in PSLC. In contrast with surface alignment, a polymer network offers "volume" or "bulk" effects, which could have the advantage, for instance, to align liquid crystals in relatively thick films. Furthermore, aligning liquid crystals through irradiation of the polymer network gives selectivity for the orientation that surface treatment cannot. As azobenzene groups are aligned only in areas exposed to irradiation, the orientation of liquid crystal molecules should occur only in those areas. Combined with surface alignment, an irradiation-controllable orientation could give PSLC materials more possibilities for design of electrooptical properties. In addition to PSLC, the approach can be of general interest in the search of electrooptical materials, for which the basis of applications is often the induction and control of birefringence.

In this paper, we report our investigations on a system of liquid crystal/azobenzene−polymer network. A diacrylate monomer having an azobenzene moiety as the central core was synthesized for the purpose. It will

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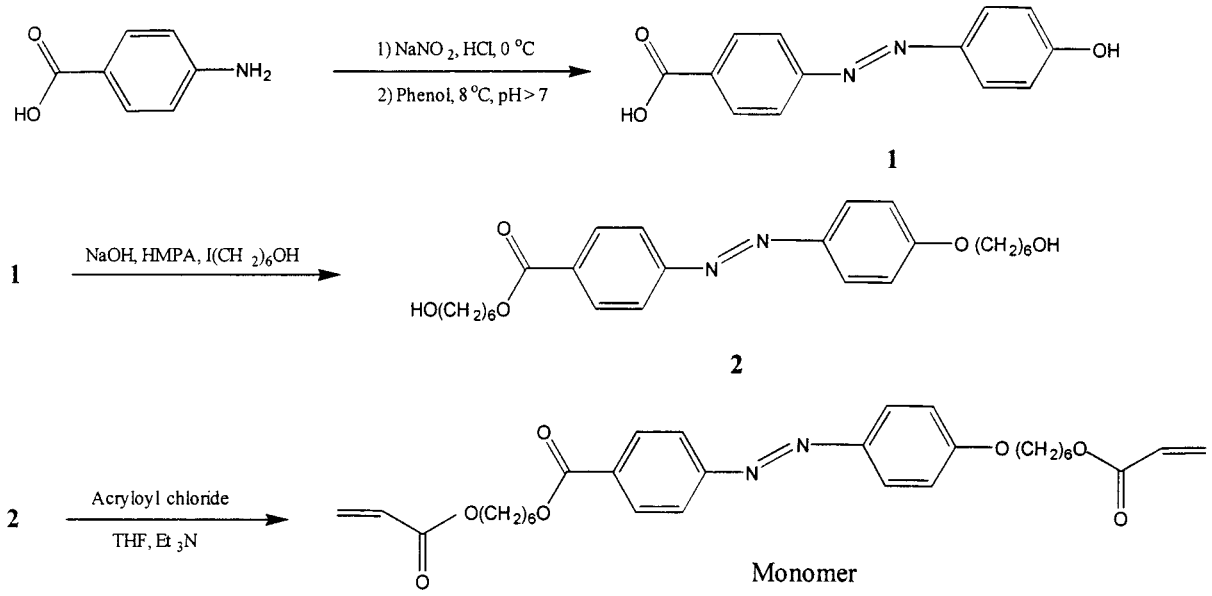
Scheme 1. Synthesis of Monomer



be shown that thermal polymerizations of mixtures of liquid crystal/monomer led to the formation of a homogeneous polymer network stabilizing the liquid crystal. Irradiation by a linearly polarized UV light could indeed induce orientation of liquid crystal molecules surrounding the network. The orientation was characterized using infrared dichroism.

Experimental Section

Synthesis of the Diacrylate Monomer. The synthetic route used to prepare the diacrylate monomer carrying an azobenzene group is shown in Scheme 1. It is interesting to notice that the monomer does not have a symmetrical chemical structure, possessing an ether group on one side and an ester group on the other side of the azobenzene core. The six methylene spacers on both sides are quite long, which should give the azobenzene group enough freedom for conformational changes and movement. Starting chemicals for the synthesis, such as 4-aminobenzoic acid, phenol, 6-chlorohexanol, and acryloyl chloride, were purchased from Aldrich and used as received. All compounds were characterized by differential scanning calorimeter (DSC) and a number of spectroscopic techniques including infrared (IR), ultraviolet (UV), proton nuclear magnetic resonance (^{1}H NMR), and mass spectroscopy. Details on the synthesis and characterization results are summarized below.

*4-(p-Hydroxyphenylazo)benzoic Acid (**1**).* Obtained through diazonium coupling between the diazonium salt of 4-aminobenzoic acid and phenol. After several recrystallizations from ethanol, **1** was obtained with good yield of about 66%. Mp: 276 °C. MS (*m*/*e*): 242 ($M^{\bullet+}$). UV λ/nm (methanol): 376 ($\pi \rightarrow \pi^*$, diazobenzene). IR ν/cm^{-1} (KBr): 3400−2500 (−CO_2H and −OH), 1683 (C═O), 1589 (phenyl), 1418, 1237, and 1289 (C−O, benzoic acid). ^{1}H NMR δ/ppm (acetone-d_6, *J*/Hz): 11.3 (br, 1H), 9.25 (br, 1H), 8.20 (d, *J* 8.5, 2H), 7.94 (d, *J* 8.5, 2H), 7.91 (d, *J* 8.9, 2H), 7.04 (d, *J* 8.9, 2H).

*6-Hydroxyhexyl 4-[p-(6-Hydroxyhexyloxy)phenylazo]benzoate (**2**).* Alkylation, with 6-iodohexanol, of both carboxylic acid and phenol functions of **1** occurred simultaneously in HMPA, using a NaOH solution as the deprotonating agent. Under these conditions, decarboxylation caused by NaOH was minimized. 6-Iodohexanol was preferred to the analogous chloro compound for improved yield and reduced reaction time. (6-Iodohexanol was prepared by reaction of 6-chlorohexanol with sodium iodide in acetone under reflux.) The typical procedure was as follows. To a solution of 1.0 g of **1** (4.1 mmol) in 13 mL of HMPA was added 1.1 mL of aqueous 33% NaOH solution (9.1 mmol). The solution was stirred for 0.5 h at 5 °C; then, 2.66 g of 6-iodohexanol (11.7 mmol) was added, and the solution was stirred for 4 days at room temperature (20−25 °C). The mixture was poured into 200 mL of water, and the precipitate formed was filtered, dried, and dissolved in chloroform. This solution was washed three times with water and then dried over anhydrous sodium sulfate overnight. Solvent was removed under reduced pressure. The product of **2** was purified by several recrystallizations from toluene, and the yield was 38%. Mp: 107 °C; clearing point: 123 °C (a smectic mesophase between 107 and 123 °C). MS (*m*/*e*): 442 ($M^{\bullet+}$). UV λ/nm (methanol): 360 ($\pi \rightarrow \pi^*$, diazobenzene), 442 (n $\rightarrow \pi^*$). IR ν/cm^{-1} (KBr): 3600−3100 (−OH), 1708 (C═O), 1599 (phenyl), 1277 and 1251 (C−O benzoate). ^{1}H NMR δ/ppm ($CDCl_3$, *J*/Hz): 8.17 (d, *J* 8.5, 2H), 7.94 (d, *J* 9.0, 2H), 7.90 (d, *J* 8.5, 2H), 7.01 (d, *J* 9.0, 2H), 4.35 (t, *J* 6.6, 2H), 4.06 (t, *J* 6.5, 2H), 3.68 (t, *J* 6.5, 2H), 3.67 (t, *J* 6.5, 2H), 1.79−1.85 (m, 4H), 1.53−1.65 (m, 4H), 1.35−1.49 (m, 8H).

*6-Acryloyloxyhexyl 4-[p-(6-Acryloyloxyhexyloxy)phenylazo]-benzoate (**3**).* Monomer **3** was obtained by esterification of **2** with acryloyl chloride. A stoichiometric amount of acryloyl chloride was added for reaction of the two alcohol functions carried by **2**. For a typical reaction, 0.27 g of acryloyl chloride (2.9 mmol) in 0.7 mL of anhydrous THF was added dropwise, under nitrogen and at 0 °C, to a stirred solution containing 0.5 g of **2** (1.1 mmol) and 0.24 g of triethylamine (2.9 mmol) in 7 mL of anhydrous THF. The stirring was continued for 6 h at 0 °C; then the solvent was removed and the residue dissolved in CH_2Cl_2. This solution was washed with water and aqueous 10% $NaHCO_3$ solution and dried over anhydrous sodium sulfate overnight. The crude product was dissolved in hexane, and the solution was washed with water and dried over anhydrous sodium sulfate before solvent was removed under reduced pressure. A yield of about 70% was obtained. Mp: 51 °C. MS (*m*/*e*): 550 ($M^{\bullet+}$). UV λ/nm (methanol): 358 ($\pi \rightarrow \pi^*$, diazobenzene), 442 (n $\rightarrow \pi^*$). IR ν/cm^{-1} (KBr): 1721 (C═O, acrylate), 1703 (C═O, benzoate), 1632 (C═C), 1601 and 1501 (phenyl), 1405 (C═CH2), 1286 and 1252 (C−O carboxylic esters), 1272 and 1199 (C═C). ^{1}H NMR δ/ppm (CDCl3, *J*/Hz): 8.16 (d, *J* 8.5, 2H), 7.94 (d, *J* 9.0, 2H), 7.90 (d, *J* 8.5, 2H), 7.00 (d, *J* 9.0, 2H), 6.40 (d, *J* 17.3, 2H), 6.07−6.17 (m, *J* 10.4 17.3, 2H), 5.82 (d, *J* 10.4, 2H), 4.35 (t, *J* 6.6, 2H), 4.18 (t, *J* 6.6, 4H), 4.06 (t, *J* 6.4, 2H), 1.78−1.89 (m, 4H), 1.68−1.77 (m, 4H), 1.44−1.59 (m, 8H).

Polymerization. A nematic liquid crystal, E7, was purchased from EM Industries and used in this study. E7 is a eutectic liquid crystal mixture of four cyanobiphenyl compounds containing an alkyl group.[14] E7 has a clearing tem-

Table 1. Characteristics of the Reacting Mixtures of Monomer and E7

mixture	E7 (wt %)	monomer (wt %)	AIBN (wt %)	azobenzene/ cyanobiphenyl (mole ratio)
1	93.8	4.9	1.3	2.6
2	88.1	10.7	1.2	6.0
3	78.9	19.1	2.0	11.9

perature $T_{ni} \sim 58$ °C. To prepare E7 stabilized by azobenzene-containing polymer network, a mixture was first obtained by dissolving, in E7, the desired amounts of the monomer as well as the initiator, azobis(isobutyronitrile) (AIBN). The mixture was warmed to about 45 °C, which allowed a complete dissolution of the monomer and AIBN in the liquid crystal without initiating the polymerization. Afterward, the polymerization proceeded by placing a drop of the E7/monomer mixture between two CaF_2 windows (transparent to IR and UV) and heating the whole to 80 °C. After 6 h of polymerization, the sample was cooled to room temperature. It was found that such a thermally induced polymerization of the monomer led to a homogeneous network stabilizing the liquid crystal. The resulting film lost the fluidity of the mixture before the reaction and became pasty. Listed in Table 1 are the compositions of the three mixtures used for polymerization. They resulted in E7/network samples of different densities of the azobenzene-containing network. Acronyms of E7/monomer-95/5, E7/monomer-90/10, and E7/monomer-80/20 are used in the paper because the actual concentrations of the monomer in the mixtures were close to 5, 10, and 20 wt %. For the same reason, similar acronyms are used for the E7/network samples. The approximate mole ratios of the groups of azobenzene (in the network) to cyanobiphenyl (liquid crystal molecules) are also indicated in Table 1. All the polymerizations resulted in thin films of a similar thickness of 5−6 μm, which was estimated by measuring the thickness of the two CaF_2 windows with and without the film using a digital micrometer.

A number of attempts were made to perform photoinduced polymerization, but they all failed to produce a homogeneous network. The failure was caused by the particular monomer synthesized for this study. The monomer has a strong UV absorption centered at 358 nm, which is close to the absorption of the photoinitiator (benzoin methyl ether) near 326 nm. As a combined result of the very high extinction coefficients and the large amount of the monomer as compared to the case of the photoinitiator, the latter could not absorb light efficiently and was unable to initiate the polymerization. Using an excess amount of the photoinitiator and prolonged reaction times, polymer networks were eventually obtained, but they were phase separated from E7 and could not stabilize the liquid crystal. Irradiation of those phase-separated azobenzene networks in E7 resulted in no molecular orientation, contrary to E7/network prepared from thermal polymerization.

Irradiation and Orientation Measurements. Using a 450 W xenon lamp and a polarizer, films of E7/network were irradiated, at preselected areas, by linearly polarized light at room temperature. The used irradiation wavelength, $\lambda = 358$ nm, was selected through the use of two monochromators. Intensity and width of irradiation were adjusted by using filters and two slits; the intensity was about 2 mW/cm^2. Typically, after a film was irradiated for a certain time, the irradiation was turned off. The film was then installed in the IR spectrometer for the dichroism measurements. The same film could be irradiated again at the same area. (The rest of the film was masked.) Irradiated areas became visibly transparent, while nonirradiated areas appeared translucent.

As mentioned above, polarized irradiation should align azobenzene groups on the network. This orientation, unfortunately, could not be measured directly from IR dichroism because of the low concentrations of the network (no suitable IR bands). UV dichroism could also not be employed because of too strong UV absorption. Instead, IR dichroism could monitor any macroscopic orientation of E7 molecules that surround the network, which was the main interest of this study. The absorption band of cyano end groups on liquid crystal molecules such as E7, near 2230 cm^{-1}, is often used to determine the order parameter S through[15]

$$S = (3\langle\cos^2\Theta\rangle - 1)/2 = (R - 1)/(R + 2)$$

where Θ is the angle between the long axes of liquid crystal molecules and a reference direction, e.g., the UV polarization direction; $R = A_{\parallel}/A_{\perp}$, $A_{\parallel}$ and $A_{\perp}$ being the absorbances of the 2230 cm^{-1} band with the infrared beam polarized parallel and perpendicular, respectively, to the reference direction. S measures the average molecular orientation and can have values between −0.5 and 1. $S = 1$ means a perfect orientation parallel to the reference direction, while a perfect perpendicular orientation gives $S = -0.5$. $S = 0$ indicates the absence of any macroscopic orientation, which is the case for liquid crystals having a polydomain texture.

Polarized IR spectra were recorded on a Bomem MB-102 FTIR spectrometer, with a wire-grid polarizer placed between the sample and the DTGS detector. Phase transition temperatures were determined using a Perkin-Elmer DSC-7 apparatus with a heating rate of 10 °C/min. Morphologies as well as changes in birefringence were examined on a Leitz DMR-P polarizing microscope, equipped with an Instec hot stage. Other apparatus used for characterizations were a Bruker AC-300 NMR spectrometer and a HP 8452A UV−vis spectrophotometer.

Results and Discussion

Figure 1 shows a series of photomicrographs taken under crossed polarizers at room temperature. Before polymerization, the reactive mixture of E7/monomer-90/10 displayed a typical schlieren texture, with some large defects developed. After 50 min of polymerization, the morphology of the mixture changed drastically. Even though the polymerization was incomplete, more defects appeared, and a sort of network could be seen. After 5 h of reaction, the polymerization was essentially completed. The texture of E7/network looked very much like a nematic side-chain liquid crystalline polymer, and no phase-separated polymer was observed. These results suggest the formation of a homogeneous polymer network throughout the sample. As the network structure developed with time, the director fields of E7 were continuously altered. In the end, defects could develop with the presence of a disordered polymer network, which led to an apparently fine texture. Similar results were obtained for other samples. An example of DSC results is also given to show the effects of the network formation. Figure 2 compares the DSC heating curves for pure E7, E7/monomer-80/20, and E7/network-80/20. Before the polymerization, T_{ni} of E7 in the mixture was reduced by about 20 °C below T_{ni} of pure E7, and the transition peak was much broadened. This indicates an extensive mixing and interaction between the two compounds. After the polymerization, without observable phase separation, T_{ni} of E7 raised to only 4 °C below that of pure E7. Such an effect is characteristic of a polymer solubilized in liquid crystals.

Indeed, a macroscopic orientation of E7 molecules can be induced in areas irradiated by a linearly polarized UV light. A qualitative analysis of polarized IR spectra can reveal interesting features of this orientation. Figure 3 shows the two IR spectra for a 6 μm film of E7/network-90/10, taken with IR beam polarized parallel and perpendicular to the UV polarization. The film was irradiated for 30 min. The strong perpendicular dichroism for the bands at 2227 (CN), 1606 , and 1494 cm^{-1} (phenyl) indicates orientation of E7 molecules perpendicular to the UV polarization. It is therefore

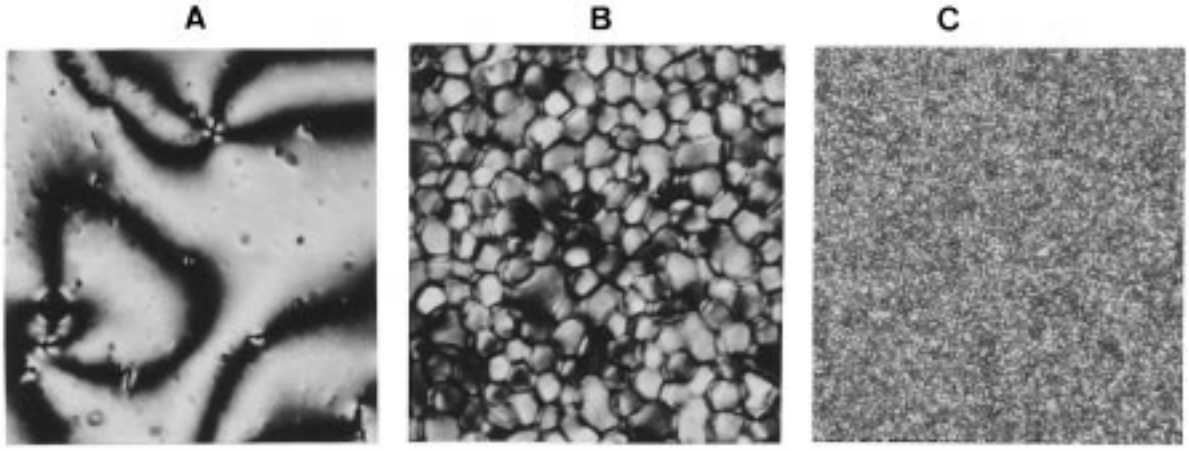


Figure 1. Polarized optical micrographs (250×) for E7/monomer-90/10 mixture at room temperature: before polymerization (A), 50 min after polymerization (B), and 5 h after polymerization (C).

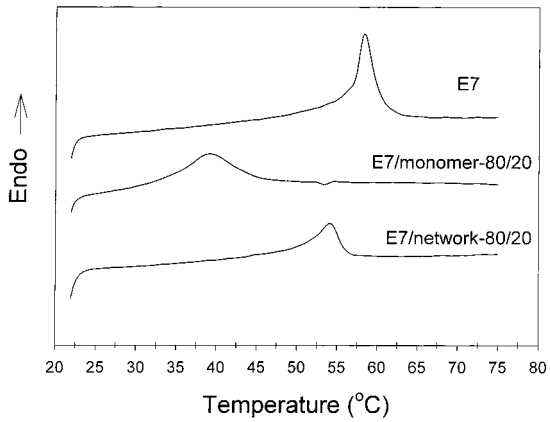


Figure 2. DSC heating curves for pure E7 and E7/monomer-80/20 mixture before and after polymerization.

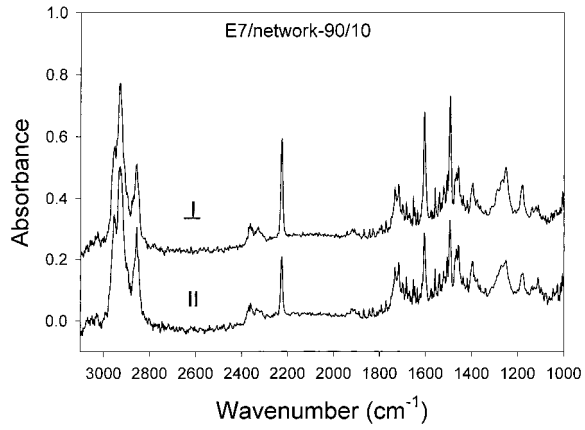


Figure 3. Polarized infrared spectra for an E7/network-90/10 film irradiated for 30 min at room temperature. The two spectra were recorded with the electric vector of the infrared beam parallel (||) and perpendicular (⊥) to the polarization direction of UV irradiation.

clear that alignment of azobenzene groups on the network alters the director fields of liquid crystal molecules and orients them along the same direction. Interestingly, this is true not only for the rigid biphenyl cores of E7, as probed by the CN and phenyl bands, but also for their flexible alkyl groups. Although less important, a parallel dichroism[16] can be noticed for the CH_2 bands at 2856 and 2929 cm^{-1}, which arise mostly from the alkyl spacers of E7 molecules because of the dominant concentration of E7 in the mixture. On the

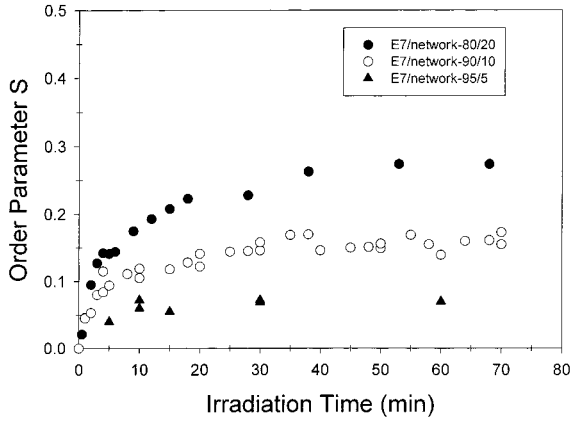


Figure 4. Order parameter of E7 vs irradiation time for samples having different azobenzene−polymer network densities.

other hand, the carbonyl bands at around 1723 cm^{-1}, which are only due to the network, show no noticeable dichroism. This suggests that although azobenzene groups are aligned by the irradiation, the rest of the polymer network remains essentially disordered.

The macroscopic orientation of E7 resulting from light irradiation was measured from the CN band for the three E7/network samples. The results are shown in Figure 4, where the order parameters, which were calculated with respect to the molecular orientation direction, are plotted as a function of irradiation time. The following observations can be made. First, in all cases, an orientation of E7 is induced after 1−2 min of irradiation, but the duration of irradiation does have an effect on the achieved orientation level, which increases with time. For irradiation longer than 10 min, only small improvement of orientation can be obtained. Second, the level of the achievable orientation is sensitive to the concentration of azobenzene groups on the polymer network. S increases from ∼0.07 to ∼0.28 when the network concentration raises from 5% to 20%. On one hand, the need of a finite time (in minutes) for liquid crystal molecules to reach an appreciable orientation is understandable. What is measured here is the reaction of E7 molecules to the orientation of azobenzene groups. The orientation of azobenzene upon irradiation can be fast (in seconds in ref 4, for example), but the reaction of E7 involves changes in the director fields and evolution of defects, and this can need more time. Actually, as compared with surface alignment, the orientation

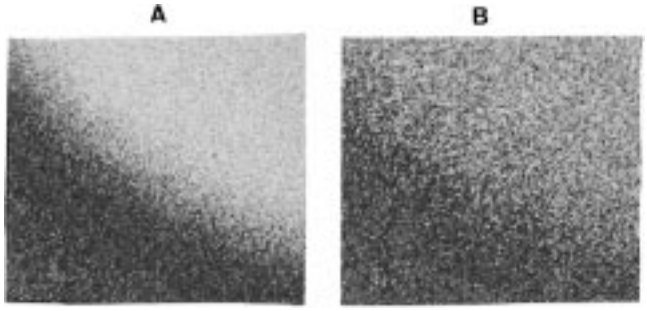


Figure 5. Polarized optical micrographs (125×) for an E7/network-90/10 film after 20 min irradiation at room temperature (A) and then heated to 53 °C (B). The film was placed with the UV polarization 45° to crossed-polarizers.

development in Figure 4 is fast. On the other hand, the effects of network concentration on the orientation of E7 can be explained by the mole ratio of azobenzene to E7 molecules (Table 1). Qualitatively speaking, when an azobenzene group is aligned, liquid crystal molecules immediately surrounding this azobenzene should react first. Those first reactions activate cooperatively the orientation of other liquid crystal molecules more distant from the azobenzene unit, but this propagating effect should diminish with distance. A higher network density means less liquid crystal molecules to be activated per azobenzene group, and the aligning ability should be greater.

The induction of a macroscopic orientation of liquid crystal molecules in films of E7/network leads to changes in birefringence. An example is given in Figure 5. The photomicrographs were taken on an E7/network-90/10 film irradiated for 20 min. When the film was placed with the UV polarization direction making an angle of 45° with respect to crossed-polarizers, the irradiated zone appeared bright as compared to the rest of the film, due to the orientation of E7 molecules. Heating the irradiated film, the birefringence was retained even at 53 °C, which was only 1 °C below T_{ni}. The lower birefringence in the vicinity of phase transition is indicative of a reduced macroscopic orientation of E7 due to thermal fluctuations. Not shown in Figure 5 is that when crossed-polarizers were rotated by 45°, the contrast was reversed: the irradiated zone became slightly darker than the rest of the film.

Choosing the polarization of UV irradiation can control the orientation direction of E7 molecules in the irradiated zone. To illustrate such an orientation control, a performed experiment is depicted in Figure 6. A film of E7/network-90/10 was first irradiated; the absorbance of the CN band of the film was measured with a polarized IR beam, as a function of the angle between the UV and IR polarization directions. As expected, because of the liquid crystal orientation perpendicular to the UV polarization, the absorbance has a maximum value at 90°. A second irradiation was then applied to the same film, rotating the UV polarization by 90°. Under this transversal irradiation, azobenzene groups on the network should undergo a reorientation of 90° and, as a result, reaction of E7 molecules should follow but, again, take a longer time. Indeed, as can be seen from Figure 6, after 5 min transversal irradiation, the macroscopic orientation of E7 disappeared, with the CN absorbance showing no angular dependence. As the transversal irradiation goes on, reorientation of E7 molecules develops. After 40 min, the CN absorbance shows a minimum value at 90, indicating that the

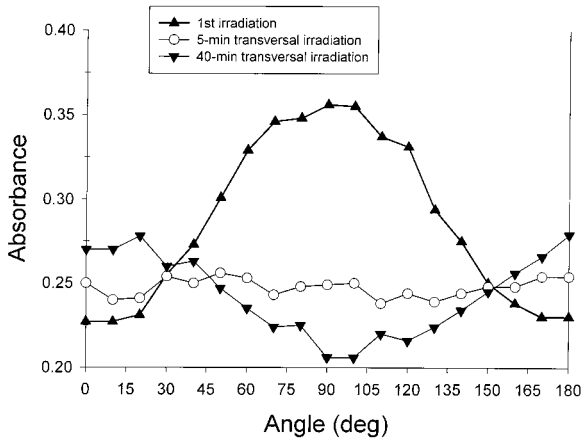


Figure 6. Angular dependence of infrared absorbance of cyano groups of E7 for an irradiated E7/network-90/10 film, the angle being that between the polarization of the infrared beam and the polarization of the first UV irradiation.

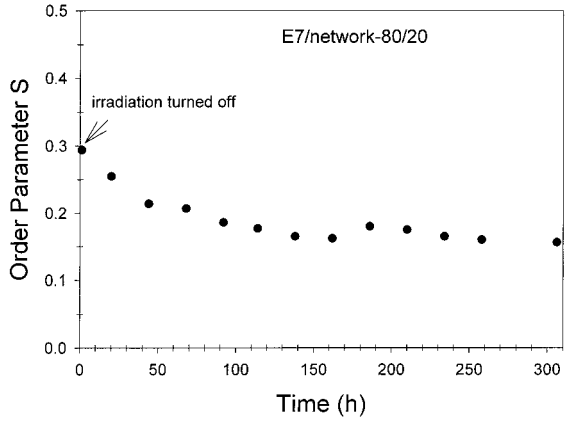


Figure 7. Order parameter of E7 at room temperature for an irradiated E7/network-80/20 film vs time after turning off the irradiation.

orientation of E7 molecules has changed direction by 90°.

After the irradiation was turned off, the stability of the induced liquid crystal orientation at room temperature was examined. Generally, the orientation decayed during the first days following the irradiation, and then the relaxation was slowed down and the orientation was retained at an almost constant level. An example of the measurements made on the E7/network-80/20 is given in Figure 7. The order parameter S decreased gradually from ∼0.3 to ∼0.17 after about 4 days, Then, the remaining orientation became stable, showing little change with time. What is important to emphasize is that this stable liquid crystal orientation can only be held by the azobenzene−polymer network. When mixtures of E7/monmer were irradiated before polymerization, similar alignment of azobenzene molecules should occur, but immediately after the irradiation was turned off, IR measurements at room temperature showed no macroscopic orientation of E7 induced in the materials. Therefore, in the absence of a polymer network structure, the orientation relaxation of the azobenzene monomer must be fast. In the case of the E7/network, as the alignment of azobenzene groups could not be monitored through IR or UV dichroism, we do not know whether aligned azobenzene groups on the network are relaxed after turning off the irradiation. But there are two possibilities that can explain the

remaining liquid crystal orientation. (1) The relaxation of aligned azobenzene groups on the network is not complete, and the retained network anisotropy holds the orientation of E7 molecules. (2) Aligned azobenzene groups relax completely, but as the relaxation goes slowly, oriented liquid crystal molecules and defects have time to evolve. In the end, elastic free energies related to macroscopic orientation are released due to, for example, elimination of defects, and the orientation becomes stable even without alignment of azobenzene groups.

Investigations were also made on thermal stability of the induced orientation of E7. When irradiated films were heated to temperatures above T_{ni} of E7 and cooled back slowly to ambient, a macroscopic orientation was recovered, but only partially. Typically, $S \sim 0.07$ was found following isotropization of E7 at $T_{ni} < T < 80$ °C. When films were heated to $T > 80$ °C, they showed no orientation at all at room temperature. It seems that some alignment of azobenzene groups on the network could be preserved for treatments at $T < 80$ °C and that the oriented azobenzene could still impose some orientation to E7 while entering the nematic phase. Actually, even if azobenzene alignment remained intact, this partial orientation recovery of E7 was no surprise because of a different aligning mechanism involved. When irradiated at room temperature, nematic E7 molecules respond to the aligning movement of the azobenzene groups, whereas when cooled from the isotropic state, E7 molecules form a nematic phase under the effects of existing aligned azobenzene groups. As revealed by IR dichroism (Figure 3), the azobenzene moieties are aligned upon irradiation, but the remainder of the network is essentially disordered. In other words, the anisotropy of the network is limited to rigid azobenzene cores. This oriented network is different from that induced by a mechanical stretching or even that resulting from polymerization in oriented liquid crystals.[1] This explains the limited orientation recovery of E7 after isotropization.

Conclusion

The synthesis of a diacrylate monomer containing an azobenzene group as its central core is shown. Thermal polymerization of the monomer dissolved in nematic liquid crystal E7 can result in a homogeneous azobenzene-containing polymer network that stabilizes the liquid crystal. When linearly polarized UV irradiation is applied on thin films of these materials, as a result of the alignment of azobenzene groups, a macroscopic molecular orientation of E7 can be induced perpendicular to the UV polarization direction. The liquid crystal orientation is achieved within minutes of irradiation at room temperature, and a significant degree of the induced orientation remains stable after turning off the irradiation. The orientation level increases with increasing the polymer network density. However, the relatively low liquid crystal orientation could be indicative of the absence of a true molecular azobenzene network in the samples due to the employed thermal polymerization. The method presented in this paper represents a new means to control and manipulate the average orientation of liquid crystal molecules in materials such as PSLC. Liquid crystal molecules can be oriented in selected areas, and their orientation direction can be controlled.

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References and Notes

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(16) The parallel dichroism of the CH_2 bands (symmetric and antisymmetric stretching) are due to their transition moments perpendicular to the axis of alkyl chain that can be defined as the line connecting two adjacent CH_2 units. The transition moment of the CN band (stretching) is parallel to the axis of the rigid biphenyl group.

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