Macromolecules **2000,** *33,* 1049−1053

Liquid Crystalline Anisotropic Gels Based on Azobenzene-Containing Networks

Yue Zhao,* Yanick Chénard, and Nadine Paiement

Département de chimie, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1, and Centre de recherche en science et ingénierie des macromolécules (CERSIM), Université Laval, Québec, Canada G1K 7P4

Received July 22, 1999; Revised Manuscript Received November 2, 1999

ABSTRACT: A method is described using optical alignment of azobenzene groups to prepare liquid crystalline anisotropic gels. We demonstrate that anisotropic gels with uniform liquid crystal orientation can be obtained by performing thermal polymerization of a homogeneous mixture composed of a nonreactive nematic liquid crystal BL006 and a reactive nonmesogenic diacrylate monomer bearing azobenzene groups while the mixture is exposed to linearly polarized light. Infrared dichroism measurements show that this liquid crystal orientation is recoverable upon repeated cycles of heating the sample into the isotropic phase followed by cooling it to the nematic phase. In this method, the optical alignment of azobenzene monomer and, as a result, of liquid crystal molecules before and during the polymerization replaces the surface alignment or electric and magnetic fields, which are usually used to prepare anisotropic gels. Anisotropic gels were obtained from two diacrylate monomers that lead to networks having azobenzene groups as part of main chain and side groups.

Introduction

Anisotropic gels refer to oriented liquid crystals (LC) stabilized by a polymer network. Generally they are prepared by photopolymerization of mixtures composed of a reactive mesogenic monomer and a liquid crystal compound.[1,2] While the molecules of both components are aligned by rubbed surfaces or effects of an electric or magnetic filed, photopolymerization occurring in the oriented environment results in an anisotropic network that, in turn, can maintain permanently the LC orientation. The signature of anisotropic gels is that the LC orientation lost in the isotropic phase is recovered once the sample is cooled into LC phases. A number of applications of anisotropic gels have been proposed and studied.[1,2] Another development from anisotropic gels is the polymer-stabilized liquid crystals (PSLC),[3,4] which has the particular feature of a low network concentration (usually <10%). The formation of anisotropic networks in PSLC can stabilize orientation or specific director configurations of LC, generating useful electrooptical properties for applications. An example is the polymer-stabilized cholesteric LC, whose uses for LC displays have been demonstrated.[3,4]

In a previous study,[5,6] a nematic LC stabilized by a polymer network bearing azobenzene moieties was prepared in our laboratory. The sample was obtained through thermal polymerization of a homogeneous mixture containing a nematic LC, E7, and a reactive diacrylate monomer, in the absence of surface alignment or any other aligning effects. Using infrared dichroism, it was demonstrated that the azobenzene network could be used to promote LC orientation on the basis of the optical alignment of azobenzene when exposed to linearly polarized light.[7] This orientation results from the reaction of the E7 molecules to the alignment of the azobenzene groups on the network. Interestingly, a significant degree of the LC orientation remains stable at room temperature after turning off the irradiation. However, if the sample is heated into the isotropic phase, no noticeable orientation can be recovered by cooling the sample back to the nematic phase. This behavior is understandable for this type of material. Unlike in anisotropic gels, as the polymerization is carried out in a nonoriented environment, the formed azobenzene network is isotropic. In this paper, we present a study on the preparation of anisotropic gels through the use of azobenzene alignment induced by irradiation, without surface alignment or application of an electric filed. We show that anisotropic gels can be obtained by proceeding thermal polymerization on a mixture composed of a nonreactive LC compound and a reactive nonmesogenic diacrylate monomer (5−10 wt %) that bears azobenzene groups, while the mixture is exposed to linearly polarized light. The LC orientation lost in the isotropic phase is recoverable upon cooling into the nematic phase. Two diacrylate monomers were used to prepare anisotropic gels, which lead to polymer networks having respectively azobenzene moieties incorporated in the main chain and grafted as side groups.

Experimental Section

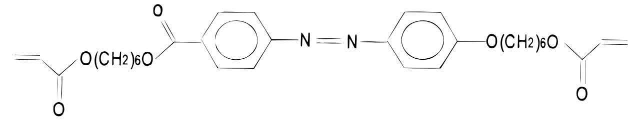
The used LC is BL006 obtained from EM Industries. Similar to E7, BL006 is a nematic mixture mainly composed of cyanobiphenyl compounds. It has, however, a higher clearing temperature T_{ni} (nematic-to-isotropic transition) around 115 °C as compared to ~58 °C for E7. The interest of using BL006 is that polymerization of diacrylate monomer can be carried out while BL006 is in both the nematic and isotropic phase. The two diacrylate monomers prepared and investigated in this study have the chemical structures shown below.

It is clear that after polymerization azobenzene moieties are parts of main chain for the network resulted from monomer 1, but side groups for the network from monomer 2. The synthesis of monomer 1 was reported elsewhere.[5] Monomer 2 was obtained by esterification of Disperse red 19 (from Aldrich) with acryloyl chloride. For a typical reaction, 3 equiv of triethylamine was first added to a solution of Disperse red 19 in anhydrous dichloromethane. Then, the solution was cooled to 0 °C, and 3 equiv of acryloyl chloride, also dissolved in dichloromethane, was added dropwise under a nitrogen at-

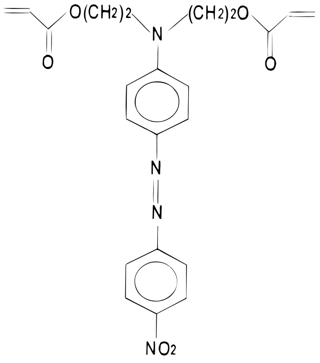
---

* To whom correspondence should be addressed.

10.1021/ma9912103 CCC: $19.00



monomer 1



monomer 2

mosphere. After the reaction overnight with the solution under stirring, the solution was extracted with $NaHCO_3$, washed with water, and dried with $MgSO_4$. The product was collected after filtration of the solution, evaporation of the solvent, and purification through recrystallization. Like monomer 1, monomer 2 is nonmesogenic. DSC measurements show only a crystal melting endotherm at 80 °C, as compared to 51 °C for monomer 1. The two monomers absorb light at different regions because of different chemical structures. The maximum absorption of monomer 2 is centered on 442 nm, which is much longer than 360 nm for monomer 1.

Typically, anisotropic gels were obtained using the following procedure. A mixture of BL006 and monomer 1 or monomer 2 was first prepared. It contained 2 wt % of initiator, azobis(isobutyronitrile) (AIBN) for BL006/monomer 1, and benzyl peroxide in the case of BL006/monomer 2. Heating the mixture to 40−45 °C without initiating the polymerization ensured the solubility and homogeneity of the mixture. A drop of warmed mixture was then cast between two CaF_2 windows (transparent to UV and infrared); the whole was placed inside a temperature-controlled hot stage. Using a 450 W xenon lamp and a combination of polarizer and monochromators, the mixture was exposed to linearly polarized light. The used irradiation wavelength was 358 nm for BL006/monomer 1 and 442 nm for BL006/monomer 2, corresponding to the absorption maxima of the two monomers. The intensity of the irradiation beam was about 2 mW/cm^2. Prior to polymerization, the mixture was first irradiated for 30 min at room temperature, where BL006 is nematic. Afterward, the mixture was heated to a predetermined temperature for thermally induced polymerization, which lasts 3−4 h. The irradiation was maintained during the entire polymerization. After polymerization, the irradiation was turned off, and the sample was cooled slowly to room temperature. By adjusting the amount of the mixture, the obtained films had a thickness around 4−5 μm, which was estimated by measuring the thickness of the two CaF_2 windows with and without the film. The area subjected to irradiation was about 10 mm^2. The used monomer concentration was 5 or 10 wt %. Acronyms are used in the text for studied samples. For instance, BL006/monomer1-90/10 indicates that the used monomer was monomer 1 and the weight ratio of LC to monomer was 9:1 in the mixture before polymerization, while BL006/network1-90/10 denotes the resultant film after polymerization.

To characterize the molecular orientation of BL006, its order parameter was determined by means of infrared dichroism. Details about the use of this technique have already been reported.[5] In this study, a homemade thermostat sample holder (±2 °C) was used to record polarized infrared spectra as a function of temperature. The FTIR spectrometer is a Bomem MB-200 equipped with a wire-grid polarizer and a DTGS detector. In addition, a Perkin-Elmer DSC-7 differential scanning calorimeter and a Leitz MP polarizing microscope were used for characterization of the samples.

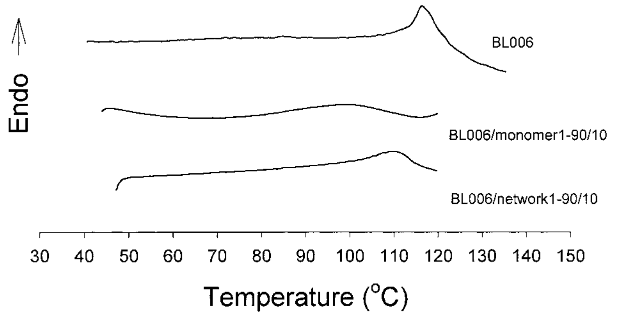


Figure 1. DSC heating curves for pure BL006 and its mixture with 10% of monomer 1 before and after polymerization.

Results and Discussion

DSC measurements were performed for all mixtures before and after polymerization. Although polymerization inside a DSC pan does not correspond exactly to polymerization under irradiation, which could align molecules, the measurements reveal some general features. Figure 1 shows an example of the results by comparing the heating curve of pure BL006 with those of BL006/monomer1-90/10 and BL006/network1-90/10. Before polymerization, the presence of monomer 1 lowers the clearing temperature T_{ni} of BL006 by about 15 °C and broadens the transition peak, which confirms the solubility of the monomer in the LC. After polymerization, T_{ni} shifts to higher temperatures but remains ~5 °C below that of pure BL006. A certain degree of phase separation is expected to occur during the polymerization, which explains the reincrease in T_{ni}. The results of DSC were also served to choose the temperatures for polymerization with BL006 in the nematic and isotropic phase. In the case of BL006/monomer1-90/10, the mixture was polymerized under irradiation at 80 and 100 °C in the nematic phase and at 120 °C in the isotropic phase.

As mentioned earlier, anisotropic gels are characterized by a uniform LC orientation that is permanently held in LC phases by the polymer network. This feature indeed was found for BL006/network1-90/10 polymerized at 100 °C. Figure 2 shows the polarized infrared spectra taken at room temperature after the sample was cooled from 140 °C, in the isotropic phase. The two spectra were recorded with the infrared beam polarized parallel and perpendicular to the polarization of the irradiation light. The 2227 cm^{-1} band is characteristic of the −CN groups that only the BL006 molecules contain; its strong dichroism is the result of a uniform molecular orientation of BL006. The phenyl bands around 1605 and 1493 cm^{-1} also indicate this orientation, even though those two bands arise from both BL006 and the network. Unfortunately for the azobenzene-network, no infrared band could be used to quantify its alignment because of its low concentration. On inspection of the spectra, the bands in the region of 2800−3000 cm^{-1}, which are assigned to the CH_2 and CH_3 units of both BL006 and the network, also display some degree of dichroism. Qualitatively, it appears that the alkyl tails of the BL006 molecules are oriented, too, but to a lesser degree than the rigid biphenyl cores. Figure 3 is a plot of the absorbance of the −CN band as a function of the angle between the infrared and light

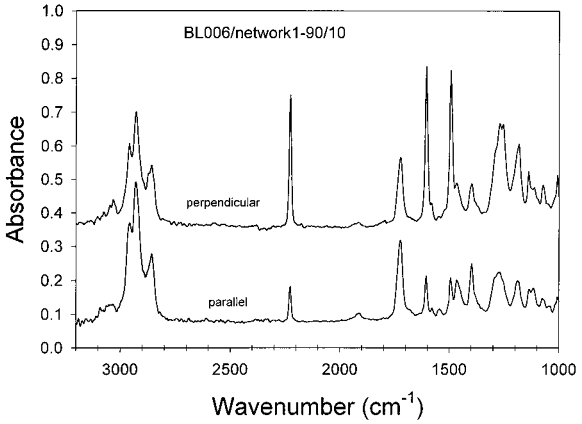


Figure 2. Polarized infrared spectra for a film of BL006/network1-90/10 polymerized in the nematic phase. The two spectra were taken at room temperature after the film was cooled from the isotropic phase, the infrared beam being polarized parallel and perpendicular to the polarization direction of the irradiation.

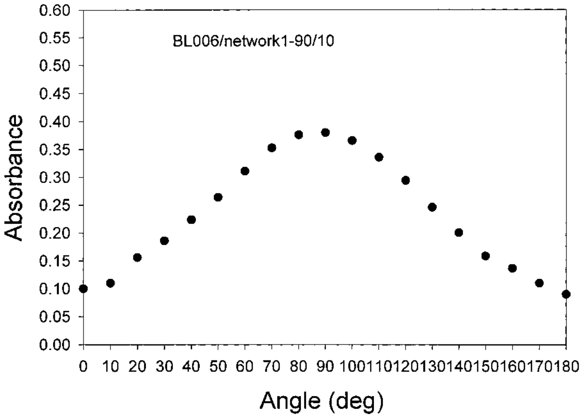


Figure 3. Angular dependence of infrared absorbance of cyano groups of BL006 for a film of BL006/network1-90/10 polymerized in the nematic phase, the angle being that between the infrared polarization and that of the irradiation.

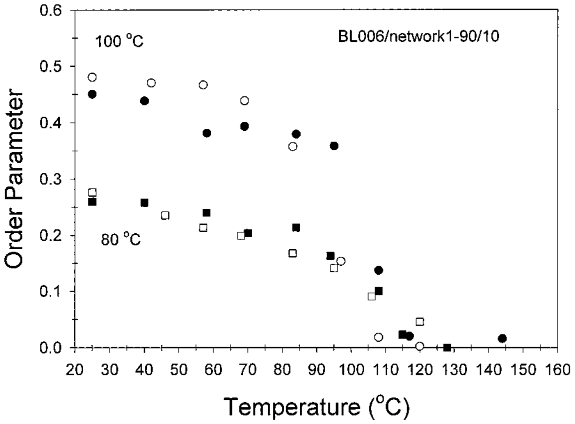


Figure 4. Order parameter of BL006 vs temperature for BL006/network1–90/10 subjected to heating (closed symbols) and cooling (open symbols). The samples were polymerized in the nematic phase at the two temperatures indicated in the figure.

polarization, showing the anisotropy that arises from the orientation of BL006. The maximum absorbance at 90° indicates that the long axes of biphenyl cores are oriented perpendicular to the polarization of irradiation. This is expected because polarized light is known to align azobenzene moieties in the direction normal to the polarization,[7] which should induce the orientation of the BL006 molecules in the same direction.

For all polymerized samples, the LC orientation in the direction normal to the polarization was determined by measuring the order parameter of BL006 as a function of temperature. Each sample was first heated into the isotropic phase ($T > T_{ni}$) and then cooled to the nematic phase ($T < T_{ni}$). Shown in Figure 4 are the results for BL006/network1-90/10 polymerized under irradiation at two temperatures in the nematic phase. The following observations can be made. First, the effect of polymerization temperature is evident. The sample polymerized at 100 °C, where BL006 is just below the nematic-to-isotropic phase transition, shows much greater LC orientation than the sample polymerized at 80 °C. Not shown in the figure are data obtained for the sample polymerized at 120 °C, with BL006 in the isotropic phase. It was found that polymerization in the isotropic phase could not produce anisotropic gels; no orientation of BL006 was observed (order parameter ~ 0). Second, when the sample is heated within the nematic phase, the LC orientation decreases only slightly, reflecting increased thermal fluctuations while approaching the nematic-to-isotropic phase transition. Once into the isotropic phase, the LC orientation disappears as expected. The lost orientation, however, is totally recovered when BL006 re-enters into the nematic phase during the cooling. Repeated heating–cooling cycles resulted in no changes in the LC orientation. This recoverable LC orientation is indicative of the formation of anisotropic gels during thermal polymerization under irradiation. In the present system, an oriented azobenzene network must be formed from irradiation-aligned diacrylate monomer. This anisotropic network remains stable at $T > T_{ni}$ of BL006, leading to the memory effect for the LC orientation.

The above results indicate that polymerization in the nematic phase is necessary for the preparation of anisotropic gels. This characteristic is similar to anisotropic gels obtained by photopolymerization under surface alignment.[1] As a matter of fact, in the present method, the mixture is irradiated in the nematic phase before polymerization. This ensures the alignment of azobenzene monomer and, in the same time, the orientation of the LC molecules as a result of their collective response to the alignment of the monomer. This period prior to thermal polymerization has the same effect as the surface alignment before photopolymerization.[1] When the mixture is then heated for polymerization in the nematic phase, the polymer network is emerged from oriented azobenzene monomer surrounded by oriented LC molecules. The anisotropic network formed this way is intrinsically adaptable to the LC orientation and stabilizes it. It is hence no surprise to observe the complete LC orientational recovery (Figure 4). The situation is different if the mixture is heated into the isotropic phase for polymerization. In principle, azobenzene monomer can still be aligned by the irradiation, but the monomer is no longer surrounded by oriented LC molecules. As the resulting network is formed in an isotropic medium, once the irradiation is turned off, it may lose the anisotropy and cannot impose LC orientation when the sample is cooled into the nematic phase. On the other hand, studies on polymer-stabilized ferroelectric liquid crystals[8] found that the rate of polymerization may depend on the order of the LC medium in which the polymerization takes place. Therefore, it is possible that polymerization occurring in the nematic

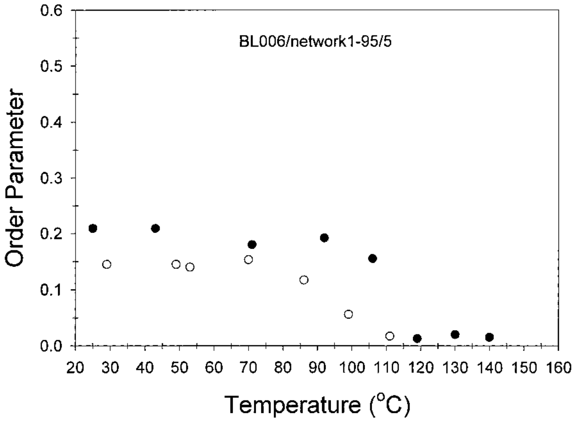


Figure 5. Order parameter of BL006 vs temperature for BL006/network1-95/5 subjected to heating (closed symbols) and cooling (open symbols). The sample was polymerized in the nematic phase at 80 °C.

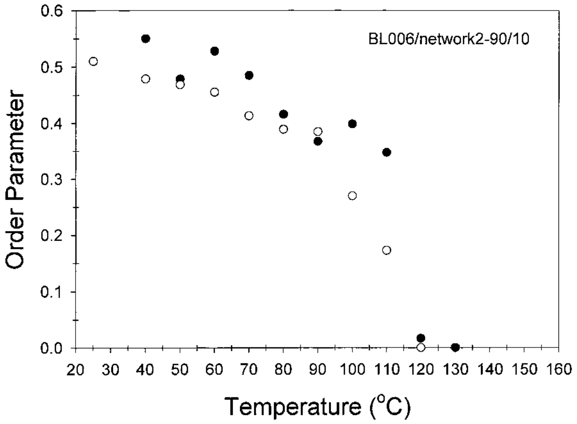


Figure 6. Order parameter of BL006 vs temperature for BL006/network2-90/10subjected to heating (closed symbols) and cooling (open symbols). The sample was polymerized in the nematic phase at 90 °C.

and isotropic phase may have different kinetics. To explain the difference in LC orientation for samples polymerized in the nematic phase at 80 and 100 °C, the rate of polymerization may be the main factor. Understandably, the stabilizing effect of the network on the LC orientation should increase with the interaction between both components. As the rate of thermal polymerization initiated by AIBN is controlled by the rate of producing primary radicals from the initiator, it is much faster at 100 °C than at 80 °C. A faster polymerization means a more effective gelation and, consequently, a lesser degree of segregation of the network from the LC.

The concentration of azobenzene monomer should influence the irradiation-induced LC orientation before and during polymerization and determines the network density after polymerization, which is important for the orientation stabilization. For the reasons of phase separation, anisotropic gels with high concentrations of azobenzene network could not be made using those nonmesogenic monomers. Actually, with 20 wt % of monomer in the mixture, T_{ni} of BL006 is depressed to about 80 °C, meaning that polymerization in the nematic phase cannot be performed at higher temperatures in order to have a fast polymerization limiting phase separation. Some attempts have failed to produce homogeneous anisotropic gels containing 20 wt % of azobenzene network because of phase separation. The use of mesogenic monomers could be a solution for this problem. Studies are underway in our laboratory. Samples with 5 wt % of azobenzene network could be prepared. Figure 5 shows the results obtained for BL006/network1-95/5 polymerized in the nematic phase at 80 °C. (T_{ni} of BL006 in the mixture before polymerization is about 106 °C.) Despite the low concentration of azobenzene monomer, LC orientation is induced in the polymerized sample and is recoverable upon cooling from the isotropic phase. However, the recovered orientation is slightly lower than that found during the first heating of the sample. Also, the orientation in this sample is lower than that for BL006/network1-90/10 (Figure 4), which should be related to different orientations induced by the irradiation before polymerization.

Discussed so far are the results for BL006/network1, in which azobenzene moieties are parts of main chain of the network. The question that can be raised is whether anisotropic gels can also be prepared through optical alignment and thermal polymerization with azobenzene moieties as side groups of the network, which is the case for samples obtained from monomer 2. The answer is yes as can be seen from Figure 6 showing the results for BL006/network2-90/10 polymerized in the nematic phase at 90 °C. (T_{ni} of BL006 in the mixture before polymerization is about 104 °C.) Similar to BL006/network1, a uniform molecular ori-

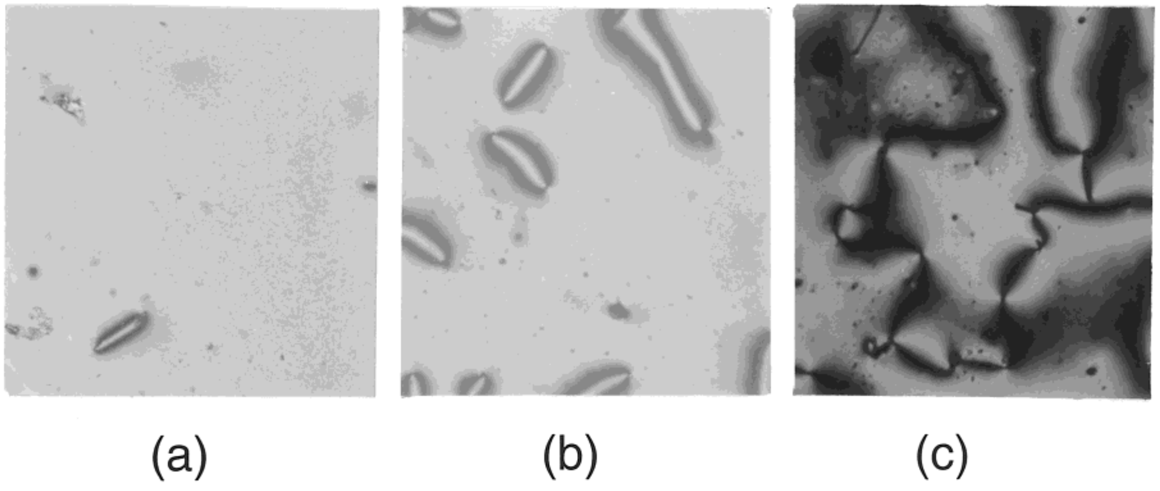


Figure 7. Polarized optical micrographs (150×) taken at room temperature for BL006/network2-90/10 polymerized in the nematic phase at 90 °C: (a) and (b) irradiated area, and (c) nonirradiated area.

entation of BL006 is obtained. This orientation decreases slightly upon heating, drops to zero in the isotropic phase, but recovers when the sample is cooled into the nematic phase. Again, no noticeable changes were found after repeated cycles of heating and cooling. No orientation was obtained for BL006/network2-90/10 polymerized in the isotropic phase at 120 °C. These results suggest that the network anisotropy, which stabilizes LC orientation, be determined by the alignment of the azobenzene groups regardless of their positions on the network. In other words, the polymer network would be formed in a way that complies with oriented azobenzene groups and ensures the stability of this alignment.

Some general properties were observed for anisotropic gels displaying a uniform LC orientation. First, the LC orientation is stable at room temperature, the order parameter showing no diminution with time. Second, re-exposing the sample to linearly polarized light with the polarization rotated by 90° induces no change in the LC orientation. We speculate that during the reirradiation some changes in the alignment of azobenzene moieties on the network and of surrounding LC molecules could occur. But once the irradiation is turned off, the azobenzene moieties are back to their initial positions determined by the anisotropic network, and so are the LC molecules. Third, the films of anisotropic gels appear transparent. When viewed under crossed polarizers, they show strong birefringence due to the LC orientation and a mainly uniform background. An example of optical micrographs is shown in Figure 7 for a film of BL006/network2-90/10 with areas under and without irradiation during polymerization in the nematic phase at 90 °C. Most of the area exposed to irradiation (Figure 7a), in which a uniform LC orientation like that shown in Figure 6 is present, appears homogeneous and is almost defect-free. It is noticed, however, that some parts of the irradiated area contain more defects (Figure 7b) even though the induced LC orientation is similar. This may be caused by some nonuniformity of the intensity of the UV beam. By contrast, the area polymerized without irradiation (Figure 7c) displays numerous defects and polydomain texture, and no LC orientation is induced.

Conclusion

Anisotropic gels can be prepared using optical alignment of azobenzene groups. When a homogeneous mixture composed of a nonreactive nematic LC compound and a reactive azobenzene-containing diacrylate monomer (5−10 wt %) is exposed to linearly polarized light, orientation of LC molecules is induced by the alignment of azobenzene monomer in the direction normal to the polarization. If subsequent thermal polymerization is initiated under irradiation in the nematic phase, an anisotropic azobenzene network can be formed in the oriented LC medium. Similar to anisotropic gels obtained through photopolymerization and alignment by rubbed surfaces or external electric and magnetic fields, the anisotropic azobenzene network stabilizes the LC orientation in LC phases, which is characterized by the recovery of LC orientation for samples cooled from the isotropic phase. Using this method, anisotropic gels can be obtained from nonmesogenic diacrylate monomers that result in networks having azobenzene moieties as part of main chain or as side groups of the network.

Acknowledgment. The authors thank Ms. Corvazier for the synthesis of one of the monomers. Financial support from the Natural Sciences and Engineering Research Council of Canada and the Fonds pour la Formation de Chercheurs et l'Aide à la Recherche of Québec is also acknowledged.

References and Notes

(1) Hikmet, R. A. M. In *Liquid Crystals in Complex Geometries Formed by Polymer and Networks*; Crawford, G. P., Zumer, S., Eds.; Taylor & Francis: London, 1996; p 53.

(2) Hikmet, R. A. M.; Michielsen, M. *Adv. Mater.* **1995**, *7*, 300.

(3) Yang, D.-K.; Chien, L.-C.; Fung, Y. K. In *Liquid Crystals in Complex Geometries Formed by Polymer and Networks*; Crawford, G. P., Zumer, S., Eds.; Taylor & Francis: London, 1996; p 103.

(4) Yang, D.-K.; Doane, J. W. *SID Dig. Technol. Pap.* **1992**, 759.

(5) Corvazier, L.; Zhao, Y. *Macromolecules* **1999**, *32*, 3195.

(6) Galstian, T.; Chenad, Y.; Zhao, Y. *Opt. Lett.* **1999**, *24*, 1865.

(7) Natansohn, A.; Rochon, P.; Gosselin, J.; Xie, S. *Macromolecules* **1992**, *25*, 2268.

(8) Guymon, C. A.; Dougan, L. A.; Martens, P. J.; Clark, N. A.; Walba, D. M.; Bowman, C. N. *Chem. Mater.* **1998**, *10*, 2378.

MA9912103