Liquid Crystalline Anisotropic Gels Prepared from Optical Alignment: Polymer Network Formed in the Isotropic Phase

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Received March 7, 2000; Revised Manuscript Received May 30, 2000

ABSTRACT: Anisotropic gels were prepared through the induction of a long-range liquid crystal (LC) orientation by the action of an anisotropic polymer network formed in the isotropic phase. The method uses a mixture composed of a nonreactive nematic liquid crystal and a reactive diacrylate monomer bearing azobenzene groups. When thermal polymerization is carried out in the isotropic phase while the mixture is exposed to linearly polarized light, an anisotropic polymer network can be obtained as a result of the optical alignment of either the azobenzene monomer or the azobenzene moieties on the network. By holding the irradiation, the anisotropy of the network is preserved in the isotropic phase, and upon cooling, the network is able to induce a long-range LC orientation in the nematic phase. Subsequent heating of the sample into the isotropic phase, with irradiation turned off, can no longer randomize the azobenzene network, which leads to the LC orientation recovery once the sample is cooled to the nematic phase. The orientation recovery is complete or partial depending on the concentration of azobenzene monomer, the nematic LC used, and the polymerization temperature.

Introduction

The presence of a polymer network in liquid crystals (LCs) can result in interesting materials. In cholesteric LCs, the network can stabilize different textures, giving rise to the bistability required for display applications.[1,2] In ferroelectric liquid crystals (FLCs), a small amount of network can improve shock resistance of the surface-stabilized FLCs.[3] LC anisotropic gels are another system useful for many applications.[4,5] They basically are oriented LCs whose long-range molecular orientation is permanently held by the network. One important feature of the anisotropic gels is that the LC orientation, absent in the isotropic phase, is recovered once the sample is cooled into the LC phases. The orientational memory effect provided by the network is also the basis for the design of attractive applications such as electrically switchable mirrors made from cholesteric anisotropic gels.[6] To prepare anisotropic gels or the other mentioned systems of polymer-stabilized LCs, the well-known procedure is as follows. A reactive monomer is dissolved in a nonreactive LC, together with a photoinitiator; the homogeneous mixture is aligned using surface orientation layers in the LC phases, generally in the nematic phase; and photopolymerization is carried out to produce the network. As the network is formed inside oriented LC molecules, it is anisotropic and, in turn, has the capability of retaining the LC orientation. Using this method, it is clear that anisotropic gels can only be obtained with polymerization performed in the LC phases because the LC molecules need to be aligned by surface effect. As a matter of fact, when polymerization takes place in the isotropic phase of the LC, only an isotropic network is formed, and the resulting materials are not anisotropic gels, even though they can also display some interesting electrooptic properties.[7]

In recent studies[8−11] we have used optical alignment to prepare anisotropic gels in the absence of surface orientation layers. Reactive diacrylate monomers bearing azobenzene groups were synthesized.[8,10] Being dissolved in the LC, such an azobenzene monomer has a dual function of inducing the long-range LC orientation through its alignment under irradiation of linearly polarized light and fixing the LC orientation through its network formed upon subsequent polymerization. We previously reported that,[10] similar to the preparation using surface orientation layers, this optical alignment and fixation technique needs polymerization to be carried out in the LC phases, with azobenzene monomer surrounded by oriented LC molecules. This statement was made on the basis of the fact that attempts of conducting polymerization in the isotropic phase failed to produce samples having retained LC orientation. This is understandable because, on one hand, the long-range LC orientation can be effectively induced by the optical alignment of azobenzene only in the LC phases and, on the other hand, the anisotropy (or orientation) of the network should be enhanced when it is emerged from the oriented environment.

However, it is interesting to have a closer look into the question about polymerization in the LC or isotropic phase by taking into account the particular feature of the optical alignment of azobenzene, which is the basis of the proposed optical approach. When azobenzene molecules are exposed to linearly polarized light, it is well-known that they tend to align their long axes perpendicular to the polarization direction as a result of repeated cycles of trans−cis photoisomerization and thermally induced cis−trans back-isomerization.[12] For mixtures composed of a reactive azobenzene monomer and a LC compound, Figure 1 sketches a new possibility. Under irradiation, the optical alignment of azobenzene monomer should occur regardless of the phase of the LC compound, even in the isotropic phase. The difference as compared with irradiation in the LC phases is

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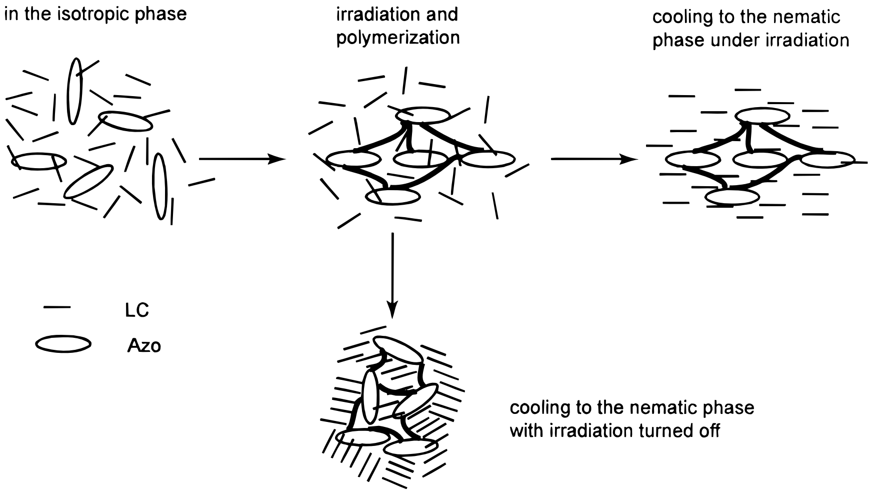


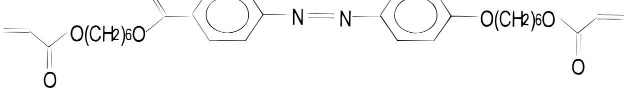
Figure 1. Sketch for the formation of anisotropic azobenzene network in the isotropic phase and its effects on the induction of long-range liquid crystal orientation in the nematic phase.

that in the isotropic phase no orientation of the LC molecules can be induced by the azobenzene orientation. The question that can be raised is whether polymerization of oriented azobenzene monomer in the isotropic phase can still result in an anisotropic network. Should this be the case, two situations are conceivable. If the irradiation is turned off after polymerization and before cooling the sample, the anisotropic network could be relaxed or rearranged in the isotropic medium, and after the sample is cooled into the LC phases (nematic phase in Figure 1), what is obtained is an isotropic network that contains polydomain LC without long-range LC orientation. In the previous studies,[10] the irradiation was indeed turned off right after polymerization. However, if the irradiation remained after polymerization and during cooling of the sample, the anisotropy of the azobenzene network could persist and induce the LC orientation upon the isotropic-to-nematic phase transition. Once in the LC phases, the irradiation can be turned off, and the LC orientation could be preserved by the azobenzene network.

In this paper, we report on a study that supports the mechanism sketched in Figure 1. LC anisotropic gels were obtained by polymerization of optically aligned azobenzene monomer in the isotropic phase of the LC. The results are the first demonstration of anisotropic polymer networks formed in the isotropic phase that, in turn, can induce and stabilize the long-range LC orientation. This development is of interest because, in principle, the approach enables the use of thermal polymerization to produce the stabilizing network in many systems without the need of keeping the LC in its LC phases, thus overcoming the conflict between the polymerization temperature and the LC phases.

Experimental Section

The chemical structure of the used azobenzene diacrylate monomer is shown below. The method for its synthesis was already reported.[8] This monomer is nonmesogenic, showing only a crystal melting endotherm at 51 °C. Its maximum absorption band is centered at $\lambda = 360$ nm.



Two nematic LCs, E7 and BL006, were used in this study. The samples were purchased from EM Industries. Both E7 and BL006 are nematic mixtures mainly composed of cyanobiphenyl compounds. The clearing temperature T_{ni} (nematic-to-isotropic transition) of BL006 is about 115 °C, while that of E7 is much lower, at about 58 °C.

The following conditions were used in the experiments. A calculated amount of the azobenzene monomer was dissolved in either E7 or BL006, containing also 2 wt % of azobis(isobutyronitrile) (AIBN) as the initiator. The mixture was warmed to about 45 °C in order to ensure homogeneous mixing without initiating polymerization. A thin film of about 5 μm thick was then cast from the mixture, between two CaF_2 windows that are transparent to UV and infrared, and then placed inside a thermostat hot stage. Using a 450 W xenon lamp combined with a polarizer and a monochromator, the irradiation was generally applied to the film before the heating started ($\lambda = 358$ nm, irradiation intensity ~ 2 mW/cm^2, and irradiation area ~ 10 mm^2). While always under irradiation, the film was heated to a chosen temperature for thermal polymerization. As it took several minutes before the mixture could reach an elevated temperature for effective polymerization (>70 °C), the azobenzene monomer was aligned prior to polymerization. In some cases, we used a preirradiation in the nematic phase for 20 min, ensuring the alignment of the azobenzene monomer before the rapid heating to the polymerization temperature. But no noticeable differences in the results were observed. Polymerization last from 10 min to 1 h depending on the temperature used, and after polymerization, the film was cooled slowly. During the whole process, the irradiation remained. It was turned off only when the sample reached room temperature. Acronyms for studied samples are used in the text. For instance, E7/network-90/10 indicates the LC used and the weight ratio of LC to the azobenzene monomer (9:1).

The long-range LC orientation in the samples was characterized using infrared dichroism. Details about the measurement of the order parameter have already been reported.[8] Typically, after turning off the irradiation, each obtained sample was heated from room temperature into the isotropic phase and cooled back to room temperature. Then the heating–cooling cycle was repeated. During the whole process, polarized infrared spectra were recorded at different temperatures on a Bomem MB-200 FTIR spectrometer, equipped with a wire-grid polarizer and a DTGS detector. A homemade thermostat sample holder (±2 °C) was used for those measurements. The relative low concentrations of azobenzene moieties in the samples as well as the overlapping of the infrared bands made it difficult to observe the alignment of the azobenzene groups. Instead, polarized UV spectroscopy was used to assess the alignment of azobenzene. An HP-8452A UV–vis spectro-

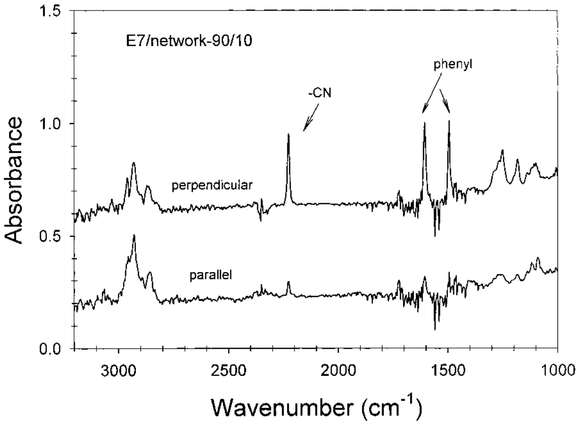


Figure 2. Polarized infrared spectra for a film of E7/network-90/10 polymerized at 120 °C. The two spectra were recorded at room temperature after the film was cooled from the isotropic phase, the infrared beam being polarized parallel and perpendicular to the polarization direction of the UV irradiation.

photometer was used to take the spectra. Observations of scanning electron microscopy (SEM) were conducted on a JEOL JSC-840A system, and an optical Leitz MP-polarizing microscope, equipped with a tilting compensator B, was used for the birefringence measurements.

Results and Discussion

With the azobenzene monomer polymerized in the isotropic phase while under exposure to linearly polarized light, the formed azobenzene network is indeed anisotropic and can induce a long-range LC orientation when the isotropic-to-nematic phase transition occurs during the cooling of the sample. Figure 2 shows an example of the polarized infrared spectra for a film of E7/network-90/10 obtained by polymerization at 120 °C, which is some 70 °C above T_{ni} of E7 in the mixture. The spectra were taken after cooling the sample to room temperature, with infrared beam polarized parallel and perpendicular to the polarization direction of the UV irradiation. The strong perpendicular dichroism appeared for the −CN band at 2227 cm^{-1} (assigned to E7 only) and for the phenyl bands at 1493 and 1605 cm^{1} (from both E7 and azobenzene) is indicative of a uniform LC orientation in the direction of the azobenzene alignment, i.e., perpendicular to the irradiation polarization. The film was then subjected to two heating−cooling cycles in the absence of irradiation. Changes in the order parameter of E7 were measured as a function of temperature, and the results are shown in Figure 3. Similar to samples prepared using optical alignment in the LC phases,[10,11] the LC orientation decreases only slowly upon heating prior to the isotropic transition. The orientation is lost in the isotropic phase but is recovered when the sample is cooled back into the nematic phase. The second heating−cooling cycle shows no difference. The alignment of azobenzene moieties on the anisotropic network for this E7/network-90/10 film is seen from the polarized UV spectra shown in Figure 4, taken at room temperature after the first heating−cooling cycle without irradiation. The absorption band of azobenzene at around 360 nm is much more intense for the spectrum recorded with the UV beam polarized perpendicular to the polarization direction of the alignment irradiation. Furthermore, the morphology of the anisotropic azobenzene network in E7/network-90/10 was investigated by SEM. For this experiment, a film was prepared between two slides under the same conditions as described above. During the preparation procedure, one area of the film was exposed to linearly polarized light, and the rest was prevented from exposure. Afterward, E7 was extracted by immerging the sample in hexane.[1] Figure 5 shows the SEM pictures (top view) for both irradiated and nonirradiated areas. The fiberlike azobenzene network in the irradiated area is indeed aligned perpendicular to the polarization direction, while no alignment can be noticed for the nonirradiated area.

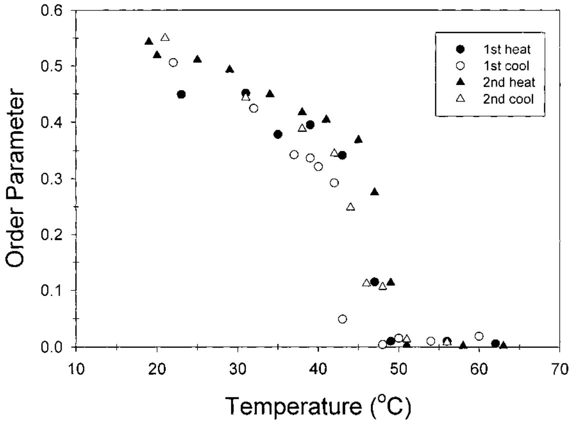


Figure 3. Order parameter of E7 vs temperature for E7/network-90/10 polymerized at 120 °C. The film was subjected to two heating (closed symbols) and cooling (open symbols) cycles in the absence of irradiation.

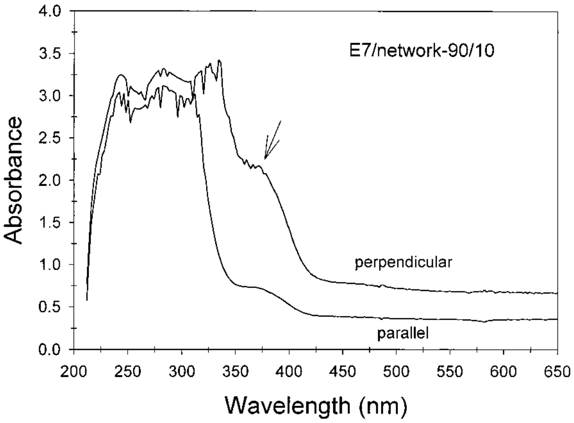


Figure 4. Polarized UV spectra for E7/network-90/10 polymerized at 120 °C. The spectra were recorded at room temperature after the film was subjected to a heating−cooling cycle in the absence of irradiation. The incident beam was polarized parallel and perpendicular to the polarization direction of the irradiation for alignment.

The effect of the concentration of azobenzene monomer was investigated. Similar to samples prepared by polymerization in the nematic phase,[10] lower LC orientation was obtained with 5% of monomer in the mixture. One advantage of forming anisotropic network in the isotropic phase of the LC compound is the possibility of using high monomer concentrations without the concern about the conflict between the polymerization temperature and the LC phases. With the same degree of phase separation, a denser, oriented azobenzene network should lead to a higher LC orientation. The results obtained by polymerizing two mixtures containing 20 and 30% of monomer, at 120 °C, are shown in Figure 6, where the order parameter of E7 is plotted as a function of temperature during the heating−cooling cycle. (Only data for the first cycle are shown for the sake of clarity.) Two observations can be made. First, as compared to

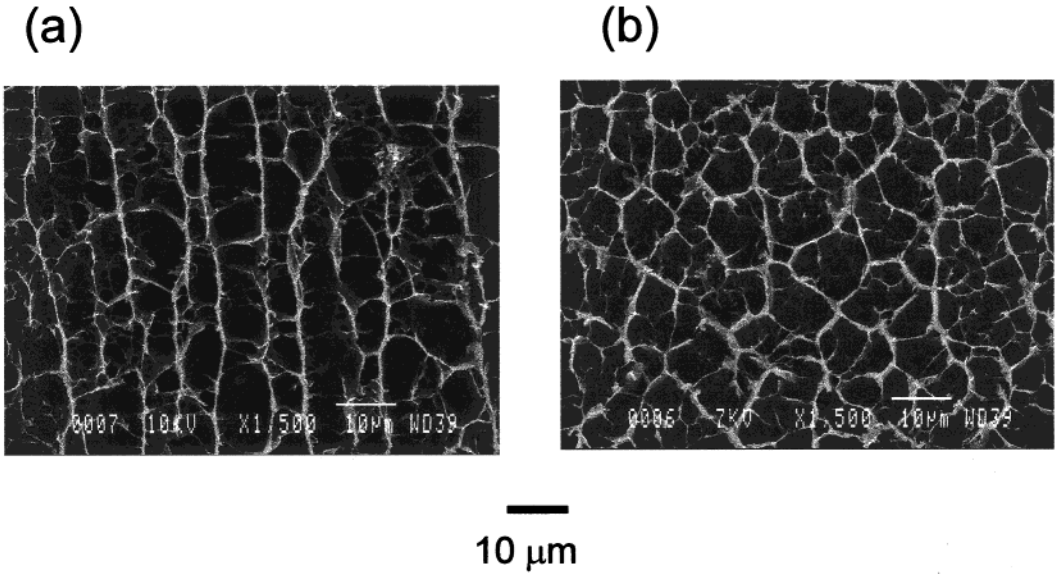


Figure 5. SEM pictures (top view) for a film of E7/network-90/10 polymerized at 120 °C: (a) irradiated area and (b) nonirradiated area.

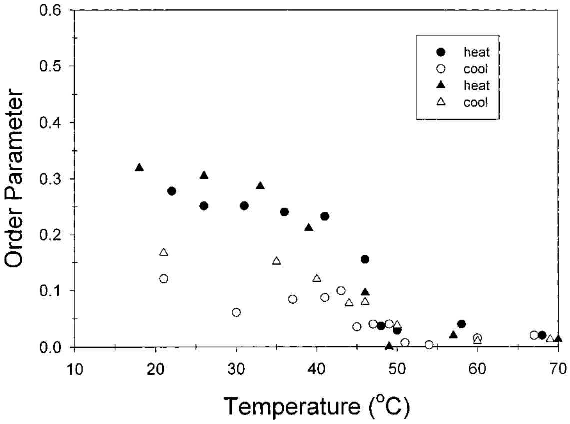


Figure 6. Order parameter of E7 vs temperature for E7/network-80/20 (circles) and E7/network-70/30 (triangles) polymerized at 120 °C. Both films were subjected to heating and cooling in the absence of irradiation.

the sample containing 10% of monomer, these two higher concentrations of azobenzene monomer resulted in lower LC orientation induced by the network. Second, after being heated into the isotropic phase without irradiation, the LC orientation is only partly recovered during the cooling. The results imply that at higher monomer concentrations the miscibility between E7 and the monomer may decrease and the degree of phase separation arising from polymerization may be more important. Another possible explanation is that the low irradiation intensity, generated by the UV lamp used, could only align part of the molecules of monomer so that the network formed upon polymerization would be less anisotropic. This factor, however, seems to be not the cause since a sample of E7/network-80/20 prepared under irradiation of a UV laser (~1 W/cm^2) showed a similar low LC orientation.[13] On the other hand, the partial LC orientation recovery after the sample was heated into the isotropic phase may be related to a loss of the network anisotropy.

To investigate the influence of the polymerization temperature on the LC orientation, the three mixtures of E7/monomer were also polymerized at 90 °C, which is about 40 °C above T_{ni} of E7. Similar to the samples prepared by polymerization at 120 °C, the best result was obtained with 10% of monomer, displaying higher LC orientation. However, with the same monomer concentration, polymerization at 90 °C resulted in lower LC orientation than polymerization at 120 °C. On heating the highest LC orientation has an order parameter of about 0.36, 0.25, and 0.15 for the samples containing respectively 10, 20, and 30% of the azobenzene network, while upon cooling from the isotropic phase the recovered LC orientation exhibits an order parameter of about 0.25, 0.2, and 0.08, respectively. Again, differences in the extent of phase separation between E7 and the azobenzene network may explain the effects of the polymerization temperature. Thermal polymerization, initiated by AIBN, is much faster to proceed at 120 °C than at 90 °C. Faster polymerization means faster gelation that limits more effectively phase separation between the azobenzene network and E7. It is also noted that with polymerization at 90 °C the sample of E7/network-70/30 shows a lower induced LC orientation than E7/network-80/20, while with polymerization at 120 °C, no significant difference appears for both samples (Figure 6).

BL006 has a much higher T_{ni} than E7. In its mixtures with 10 and 20% of azobenzene monomer, T_{ni} is lowered to about 100 and 80 °C, respectively. Those two mixtures were polymerized at two temperatures, 120 and 150 °C, in the isotropic phase. For both mixtures polymerized at both temperatures, the induced orientation of BL006 is lower than that of E7 and is recoverable during the cooling, as can be seen from Figure 7 for the samples polymerized at 120 °C (with only the data obtained for the first heating–cooling cycle). For polymerization at 150 °C, the observed order parameter on both heating and cooling is about 0.17 and 0.05 for the samples containing respectively 10 and 20% of azobenzene network. More heating–cooling cycles resulted in no differences. The different behaviors for E7 and BL006 may be related to their different isotropic transition temperatures; BL006 has a T_{ni} that is almost 60 °C higher than that of E7. For BL006, the polymerization temperatures are relatively closer to the nematic phase, and consequently, the azobenzene monomer and its resulting network are in an isotropic medium that has

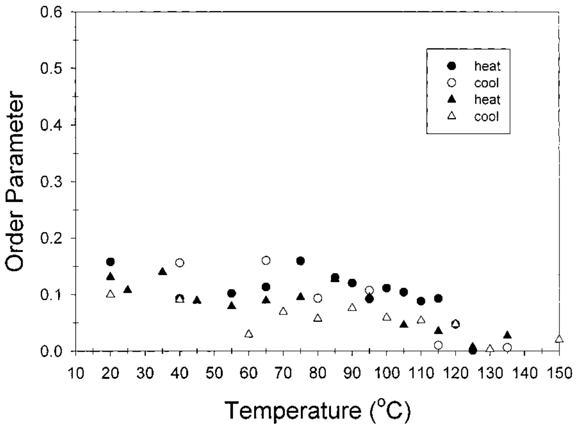


Figure 7. Order parameter of BL006 vs temperature for BL006/network-90/10 (circles) and BL006/network-80/20 (triangles) polymerized at 120 °C. Both films were subjected to heating and cooling in the absence of irradiation.

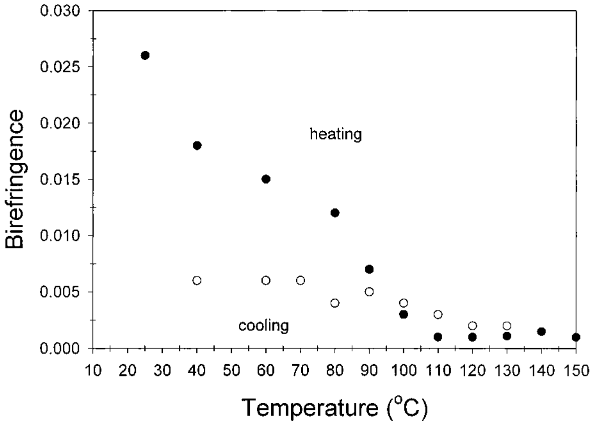


Figure 8. Birefringence vs temperature for a film of BL006/network-80/20 polymerized at 120 °C inside a 4 μm electrooptic cell with rubbed inner surfaces. The film was subjected to heating (closed symbols) and cooling (open symbols).

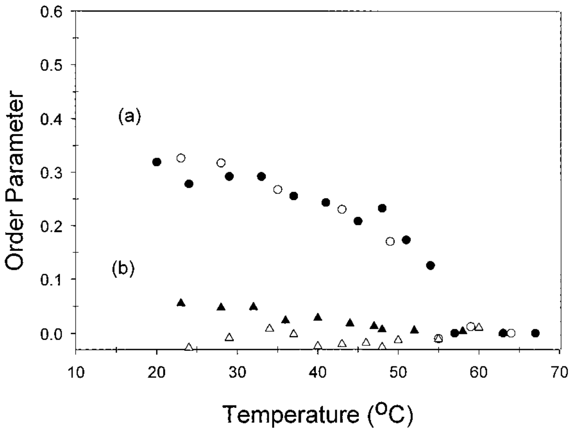


Figure 9. Order parameter of E7 vs temperature for films of E7/network-90/10 prepared (a) with irradiation applied only after polymerization at 120 °C (circles) and (b) with irradiation on during polymerization at 120 °C but turned off afterward, prior to the cooling (triangles). The films were subjected to heating (closed symbols) and cooling (open symbols) in the absence of irradiation.

a higher viscosity. The viscosity factor could lead to lower alignment of the azobenzene network under irradiation, which induces lower LC orientation in the nematic phase. Similar to samples of E7/network, the use of a higher concentration of azobenzene monomer resulted in a lower orientation of BL006, particularly for the sample polymerized at 150 °C.

Unfortunately for all samples prepared between CaF_2 windows, their birefringence could not be reliably determined using a compensator because the films are not homogeneous which causes light scattering. However, for samples irradiated and polymerized inside electrooptic cells, it was possible to do the measurements. Figure 8 shows the birefringence of a BL006/network-80/20 film, measured during the heating–cooling cycle and in the absence of irradiation. In this experiment, the BL006/monomer mixture was inserted into a 4 μm cell with rubbed inner surfaces (purchased from Displaytech). The irradiation was applied with the polarization direction making an angle of 45° with respect to the rubbing direction; after polymerization at 120 °C, the sample was cooled under irradiation to room temperature. First, observation on optical microscope under crossed polarizers indicates that, upon the isotropic-to-nematic phase transition, the LC molecules are indeed oriented under the effect of the anisotropic network rather than being aligned by the surface orientation layers, since the maximum extinction shows up when the rubbing direction is at 45° with respect of the crossed polarizers. Maximum transmission should be observed if the LC molecules were oriented in the rubbing direction. Second, from the data in Figure 8, it is seen that upon heating the birefringence decreases and drops to almost zero in the isotropic phase. But even at temperatures above 120 °C, there is always a small residual birefringence that should arise from the anisotropic azobenzene network. Upon cooling, unlike the samples prepared on CaF_2 windows using the same condition (Figure 7), the birefringence is only partially recovered, with the extinction axis still at 45° to the rubbing direction. This result suggests that, after being heated in the isotropic phase in the absence of irradiation, the anisotropy of the network is lost to some extent. During the subsequent cooling, the effect of the remaining anisotropic network may be weakened by the surface orientation layers that tend to align the LC molecules in the rubbing direction. The consequence is a decreased LC orientation as revealed by the observed marginally recovered birefringence.

From the above results, it seems clear that the presence of an anisotropic azobenzene network during the first isotropic-to-nematic phase transition of the LC, right after polymerization, is crucial for inducing the LC orientation. Once aligned, the LC molecules, in turn, exert a stabilizing effect on the network and, consequently, subsequent heating to the isotropic phase without irradiation can no longer randomize the azobenzene network. It is interesting to know whether polymerization of oriented azobenzene monomer (mixture exposed to irradiation before starting polymerization) is absolutely required. We used the E7/monomer-90/10 mixture and carried out polymerization without irradiation at 120 °C. Only after polymerization, irradiation was applied while the mixture was allowed to cool to room temperature. Under this condition, the formed azobenzene network should be isotropic after polymerization, but the subsequent irradiation could align azobenzene moieties on the network, which leads to aligned network before E7 enters into the nematic phase during the cooling. The obtained results are shown in Figure 9. Similar to samples prepared with irradiation applied before polymerization, a long-range LC orientation is also observed and recoverable after the isotropic transition. However, the induced LC orientation is lower than that obtained by polymerization under irradiation (Figure 3). This result suggests that applying irradiation before polymerization, which aligns the azobenzene monomer, is more effective to form the anisotropic polymer network that induces the long-range LC orientation.

Using the same mixture, we also performed the experiment in which irradiation was applied before polymerization but turned off right after polymerization when the cooling started.[10] The results are also shown in Figure 9. Only a slight orientation of E7 is obtained as can be noticed at the beginning of the heating. The orientation is lost once the sample is heated into the isotropic state, and no orientation is recovered. This observation confirms the results, obtained by using BL006, reported in the previous paper.[10] If irradiation is turned off after polymerization in the isotropic phase, the anisotropic network, which is initially formed under irradiation, can be rearranged into an isotropic network before the liquid-to-nematic phase transition and induces no LC orientation in the LC phases.

Conclusion

Using azobenzene−diacrylate monomer dissolved in a nematic LC, anisotropic polymer network can be obtained in the isotropic phase through optical alignment of azobenzene under linearly polarized light. The irradiation can be applied either before or after polymerization but should be held during the cooling and the liquid-to-nematic phase transition. When the LC enters into the nematic phase, the anisotropic network, formed in the isotropic phase, is able to induce a long-range LC orientation. Then, in the absence of irradiation, when the sample is heated again into the isotropic phase and cooled back to the nematic phase, the LC orientation can be partially or completely recovered. Better LC orientation is achieved with relatively low concentrations of the azobenzene monomer (∼10%) than with high concentrations (20 and 30%) as well as for samples made from the low-T_{ni} nematic E7 than from the high-T_{ni} BL006.

Acknowledgment. We thank Dr. Pierre Magny for assisting the electron microscopy observations. 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 acknowledged.

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