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Orientation and anchoring effects in stretched polymer dispersed nematic liquid crystals

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The induction of liquid crystal orientation through mechanical stretching was investigated for polymer dispersed liquid crystals (PDLCs) by means of infrared dichroism. Using a nematic liquid crystal BL006 and polyacrylic acid as the polymer matrix, it was possible to stretch the PDLC films with BL006 in either the isotropic or the nematic phase. After cooling the films under strain to room temperature, the molecular orientation of BL006 was found to be much higher for films that contained isotropic liquid droplets of BL006 at the time of stretching than for films that had nematic droplets. Stretching PDLC films with isotropic droplets results in no molecular orientation, but the orientation is induced during the subsequent cooling when BL006 goes through the isotropic-to-nematic phase transition. Interestingly for PAA/BL006, the nematic director orients along the long axes of the elongated droplets despite liquid crystal anchoring perpendicular to the polymer interface.

1. Introduction

Polymer-dispersed liquid crystals (PDLCs) are interesting electro-optical materials that are composed of droplets of a low mass liquid crystal dispersed in a polymer matrix [1–5]. Their applications are based mainly on electrically controllable light scattering. Generally, a PDLC cell is prepared by sandwiching a PDLC film between two glass plates coated with a transparent electrode such as indium tin oxide. In the absence of an electric field (the field-off state), the cell appears opaque because of strong light scattering due to the mismatch between the refractive index of the polymer, n_p, and that of the LC droplets. On applying a voltage (the field-on state), the LC molecules can be aligned along the electric field direction so that light sees the ordinary refractive index of the LC, n_o. If n_p is chosen to match n_o, there is little light scattering and the cell becomes transparent. At the field-off state, the effective refractive index of the LC droplets depends on the configuration of the director field and their orientation. For instance, in the case of the bipolar configuration, which is the most common configuration known for PDLC, the symmetrical axes of the droplets are randomly oriented at the field-off state, and, in terms of the LC molecular orientation, there is no orientation at a macroscopic scale. At the field-on state, a macroscopic orientation is achieved by the effect of the electric field.

If a macroscopic and uniform LC orientation is obtained at the field-off state, properties useful for applications may be generated; an example is the scattering polarizer [6, 7]. Orientation can also lead to helical unwinding for ferroelectric liquid crystals dispersed in polymers, giving rise to novel electro-optical effects [8]. We have recently investigated the preparation of oriented PDLC films based on 4-octyl-4′-cyanobiphenyl (8CB) with amorphous polyacrylic acid (PAA) and semicrystalline poly(ε-caprolactone) (PCL) [9, 10]. 8CB was found to have a very low solubility limit in both polymer matrices (< 5 wt %). The films of PAA/8CB can only be stretched at $T > T_g$ of PAA, where 8CB is in the isotropic liquid phase and phase-separated from PAA. It was found [10] that a uniform orientation of 8CB can be achieved under film extensions as small as 20% when the stretched films are cooled to room temperature. The order parameter, determined from infrared dichroism, was close to 0.5. This result is in sharp contrast with PCL/8CB [9] whose films can be stretched at room temperature where 8CB is liquid crystalline. For this PDLC, the stretching-induced orientation is much smaller and increases linearly with film extension, with the order parameter reaching only about 0.3 at 300% extension.

Those results imply the importance of anchoring effects on the induction of the LC orientation in PDLCs. They suggest that in order to obtain a uniform LC orientation in PDLC films, it can be more effective to stretch phase-separated PDLCs with the LC compound in the isotropic phase than in the liquid crystalline phases.

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However, the comparison made between PAA/8CB and PCL/8CB was not straightforward. As two different polymers matrices were utilized, any differences in the parameters such as miscibility and droplet size could also lead to different orientation behaviours. In this paper, we report a study on the PDLC made from PAA and the nematic liquid crystal BL006 that has a high nematic-to-isotropic transition temperature T_{NI} (the clearing temperature) of about 117°C. Using this system, it is possible to stretch the films with BL006 in both the isotropic and nematic phase, and to compare the induced LC orientation. This made it straightforward to confirm the mechanism of, and to reveal further the anchoring effects, on the orientation induction in stretched PDLC films.

2. Experimental

BL006 was purchased from EM Industries, USA. Similar to BL001, which is often named E7, BL006 is a eutectic liquid crystal mixture composed mainly of cyanobiphenyl compounds. PAA was obtained from Aldrich; the sample has an average molecular weight of 450 000 g mol^{-1} and a glass transition temperature $T_g \sim 90$°C. The PDLC films were prepared by dissolving BL006 and PAA in a mixture of THF/ethanol (50/50 v/v) and casting the solution onto the surface of a glass plate. Unless otherwise stated, PDLC films containing 30 wt% of BL006 were used. The cast films, having a thickness of about 30 µm, were dried under vacuum at 80°C for two days in order to remove the solvent and, before the stretching, further heated to 150°C for 10 min for equilibrium. The uniaxial stretching of the films was carried out on a laboratory-made apparatus that was placed inside a thermostat oven; the stretching rate was about 20 mm min^{-1}. Most orientation measurements were performed at room temperature on films that were cooled under strain immediately after the stretching. The orientation measurements at higher temperatures were made using a temperature-controlled stretching device that was directly mounted into the sample compartment of the infrared spectrometer.

The molecular orientation of BL006 was characterized through the determination of the order parameter that is defined as $S = (3 < \cos^2 \theta > - 1)/2$, where θ is the angle between the long axes of BL006 molecules and the stretching direction. The infrared dichroism technique was used to measure S through the relationship $S = (A_{\parallel}/A_{\perp} - 1)/(A_{\parallel}/A_{\perp} + 2)$, where $A_{\parallel}$ and $A_{\perp}$ are the absorbances of the cyano band of BL006 at 2230 cm^{-1} with the infrared beam polarized parallel and perpendicular to the film stretching direction, respectively. An example of the polarized infrared spectra is shown in figure 1. The spectra were recorded on a PAA/BL006-70/30 film stretched at 140°C to a draw ratio $\lambda = 2$, λ being defined as the ratio of film length after stretching to that before stretching. Few bands of BL006 are useful for its orientation measurement because of overlapping with the strong absorption of PAA. The exception is the 2230 cm^{-1} C≡N band; the parallel dichroism in figure 1 is indicative of a macroscopic orientation of BL006 molecules along the stretching direction. Details on the use of infrared dichroism to determine the orientation in stretched PDLC films were reported elsewhere [9, 10]. The polarized infrared spectra were obtained on a Bomem MB-102 FTIR spectrometer having a wire-grid polarizer placed between the sample and the DTGS detector. Other instruments used for the characterization of the samples include a Perkin-Elmer DSC-7 for differential scanning calorimetry (heating rate: 10°C min^{-1}) and a Leitz DMR-P polarizing microscope equipped with an Instec hot stage.

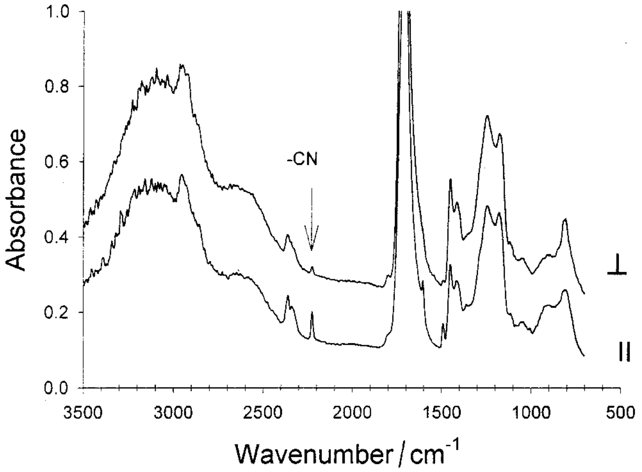

Figure 1. Polarized infrared spectra at room temperature for a PAA/BL006-70/30 film stretched to $\lambda = 2$ at 140°C. The two spectra were recorded with the electric vector of the infrared beam parallel (‖) and perpendicular (⊥) to the stretching direction.

3. Results and discussion

After casting an initially homogeneous solution of PAA with BL006 onto the surface of a glass plate, the liquid crystal phase-separated from the polymer as their common solvent evaporated. The phase separation in the film could easily be observed from the DSC and microscopic measurements. Figure 2 shows the DSC heating curves of PAA/BL006-70/30 and pure BL006. The nematic-to-isotropic transition endotherm in the PDLC film is broadened and apparently shifts to higher temperatures as compared with pure BL006. This is because BL006 is a nematic mixture whose components may have different solubilities in PAA. A quite significant amount of BL006 molecules is indeed dissolved in the polymer matrix as can be seen from the decreased T_g

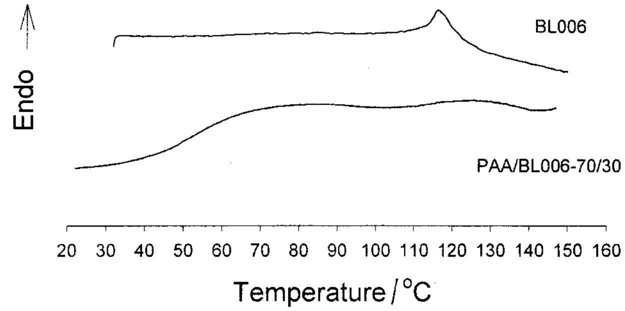

Figure 2. DSC heating curves for PAA/BL006-70/30 and pure BL006.

of PAA to about 55°C. An interesting feature for PAA/BL006 is that once the phase separation occurred in the films, it remained even at high temperatures above T_{NI}. This can be seen from the optical photomicrographs shown in figure 3. Spherical droplets of BL006 are visible at 140°C where BL006 is in the isotropic liquid phase. After the film was stretched at this temperature to $\lambda = 1.5$, the droplets changed their forms from spherical to elliptical with the long axes along the stretching direction. The elongation of the droplets increases as the draw ratio increases.

Using infrared dichroism, the orientation of BL006 was monitored for PDLC films stretched at temperatures below and above T_{NI} and cooled under strain. Figure 4 shows the order parameter measured at room temperature versus draw ratio λ for films stretched at 110 and 140°C. When stretched at 140°C, where BL006 is isotropic, the orientation of BL006 in the films at room temperature develops rapidly as the film extension increases, with $S \sim 0.4$ at $\lambda = 2$. The orientation increase is then slowed down at higher draw ratios. However, when stretched at 110°C, where BL006 is nematic, the stretching-induced orientation increases slowly and, within experimental error, linearly with film extension. As compared with the isotropic phase stretching at 140°C, the nematic phase stretching at 110°C was difficult to perform; the films broke easily. This difficulty was probably caused by the higher viscosity of BL006 in the nematic phase.

At a fixed $\lambda = 2.5$, figure 5 compares the order parameters obtained at different stretching temperatures for films of PAA/BL006-70/30 and also for PAA/BL006-85/15, the latter showing a similar T_{NI} to the former (figure 2). The clearing temperature, taken as the maximum of the melting peak, is indicated. It is clear that the orientation induced by stretching BL006 in the isotropic phase is much higher than that obtained by stretching BL006 in its nematic phase. The absence of a sharp change of the order parameter around T_{NI} reflects the broadness of the liquid crystal melting endotherm in the PDLC film (figure 2). For instance, at 120°C a number of the

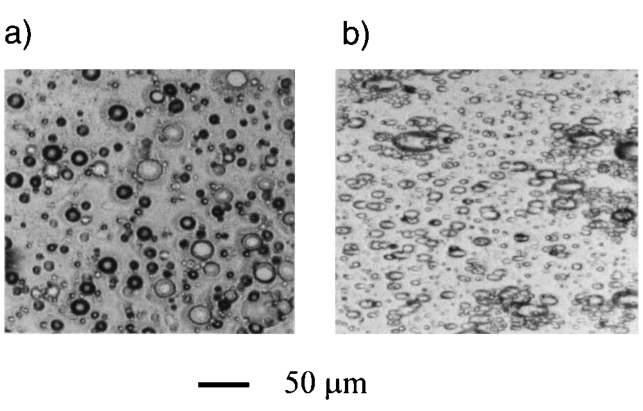

Figure 3. Optical photomicrographs for a PAA/BL006-70/30 film at 140°C before (*a*) and after (*b*) stretching to $\lambda = 1.5$.

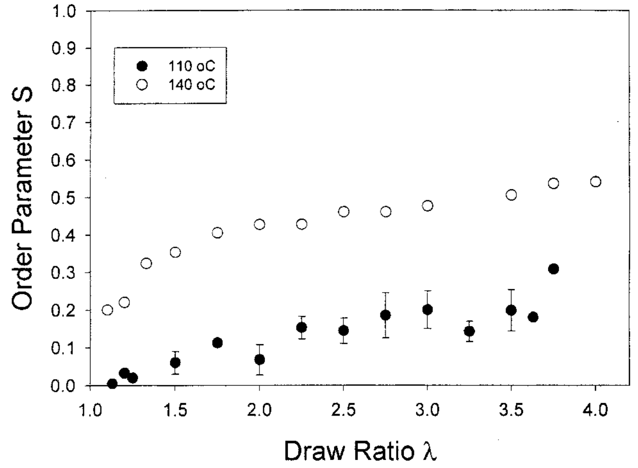

Figure 4. Order parameter measured at room temperature vs. draw ratio for PAA/BL006-70/30 films stretched at 110°C (BL006 in the nematic phase) and 140°C (BL006 in the isotropic phase).

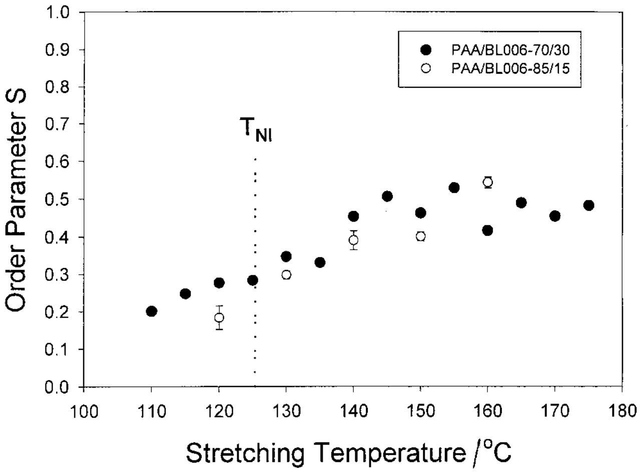

Figure 5. Order parameter measured at room temperature vs. stretching temperature for films of PAA/BL006-70/30 and PAA/BL006-85/15 stretched to $\lambda = 2.5$.

molecules of BL006 are already in the isotropic phase, which may contribute to a higher molecular orientation after the stretching and cooling. Meanwhile, the rest of the BL006 is still nematic and the stretching results in a lower orientation. Because the order parameter that is measured from infrared dichroism is the average orientation over all the BL006 molecules, an intermediate value between those obtained by stretching the films at 110 and 140°C should be observed.

The isotropic phase stretching at 140°C should not give rise to molecular orientation because of the liquid nature of BL006. Therefore the high LC orientation observed at room temperature should be achieved during the cooling of the stretched films. The experiment depicted in figure 6 confirms this. A film of PAA/BL006-70/30 was stretched at 140°C, and the order parameter of BL006 was measured immediately after the stretching. The film was then allowed to cool under strain, and orientation measurements were made at various temperatures during the cooling. It can be seen that the stretching of the liquid droplets of BL006 results in no macroscopic orientation, with the order parameter immediately after stretching having a value close to zero. Orientation appears during the cooling at $T < T_{NI}$ after BL006 undergoes the isotropic liquid-to-nematic phase transition inside the elongated droplets. In contrast, for films stretched at 110°C the small LC orientation measured at room temperature is induced by the action of the stretching.

The above results confirm unambiguously that the stretching of isotropic liquid droplets is much more effective in inducing a uniform LC orientation in PDLC films than the stretching of nematic droplets. This is opposite to what is known for side chain liquid crystalline polymers (SCLCPs) [11], in which the mesogenic groups are linked to the chain backbone through a flexible spacer. In the case of SCLCPs, stretching in liquid crystalline phases is required to achieve a uniform orientation of the mesogenic groups, while stretching in the isotropic phase usually results in no orientation at all. For PDLCs, the LC anchoring at the polymer interface exerts an important effect on the orientation induction. Indeed, when liquid crystalline droplets are stretched, changes in the configuration of the director field inside the droplets and displacement of the defects should be involved. These deformations result in an increase in the elastic free energy and hinder the development of a uniform LC orientation along the stretching direction. When PDLC films are stretched at $T > T_{NI}$, all anchoring effects are erased. During the isotropic-to-nematic phase transition, the elongated geometry is required for making the LC molecules align along the long axes of the droplets.

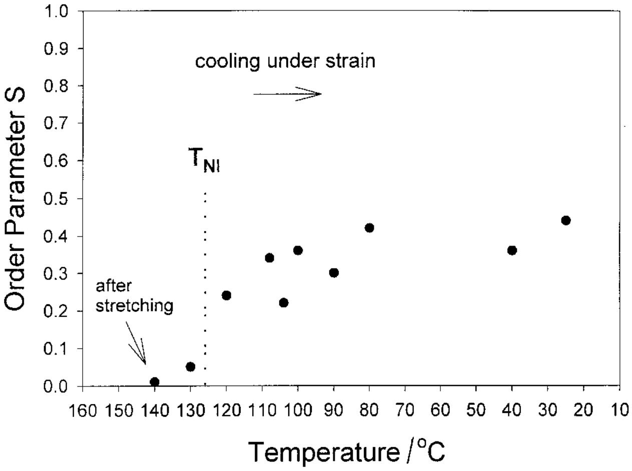

Figure 6. Order parameter vs. temperature for a PAA/BL006-70/30 film cooled under strain after being stretched to $\lambda = 2.5$ at 140°C.

The mechanism for the induction of a uniform LC orientation through the isotropic phase stretching and cooling under strain can be recapitulated by the sketch in figure 7. We consider the bipolar and radial LC droplets, which are the two most representative configurations, resulting respectively from parallel and perpendicular LC anchoring at the polymer interface. When the film is heated to $T > T_{NI}$ before stretching, whatever the configuration, the nematic droplet becomes a liquid droplet without LC anchoring. The subsequent stretching leads to an elongated liquid droplet having no molecular orientation. During the cooling of the stretched film, at the isotropic-to-nematic phase transition, nematic order is spontaneously formed between the molecules inside the droplet. As the droplet is elongated along the stretching direction, qualitatively the interface parallel to the long axis of the droplet is larger than that perpendicular to it. At the moment of the formation of the nematic phase, if the LC anchoring is parallel to the interface, the anchoring effect should favour the LC orientation in the direction of the long axis. This is the case for the

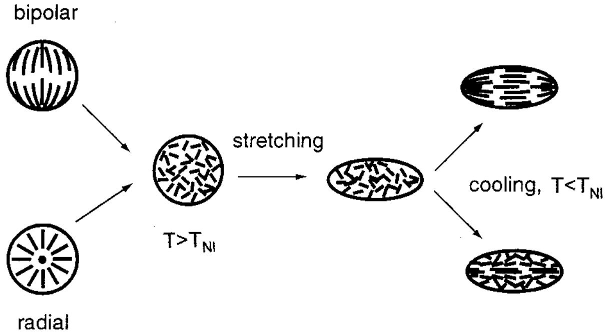

Figure 7. Schematic illustration for the mechanism of orientation induction through the isotropic phase stretching and cooling under strain.

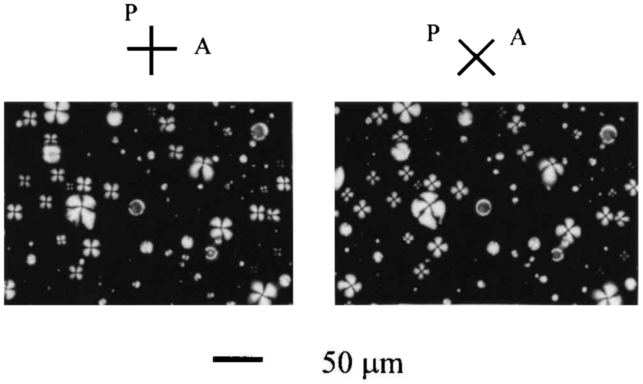

Figure 8. Optical photomicrographs for a PAA/BL006-70/30 film taken at room temperature under crossed polarizers. The positions of the polarizer (P) and analyser (A) are indicated.

system PAA/8CB [10], which easily achieved a uniform LC orientation ($S \sim 0.5$ for $\lambda = 1.2$). For the same reason, if the anchoring at the interface is perpendicular, the anchoring effect may hinder the formation of a uniform orientation along the long axis. Interestingly for the system PAA/BL006, the LC droplets were found to display a radial configuration, suggesting a perpendicular LC anchoring at the interface with PAA.

The radial configuration in the PAA/BL006 system was revealed by observations on a polarizing microscope. Figure 8 shows two optical photomicrographs of a PAA/BL006-70/30 film taken under crossed polarizers. It can be seen that when the crossed polarizers are rotated by 45° without changing the position of the film, the relative orientation of the black cross of the droplets follows the position of the crossed polarizers. Nevertheless, although less effective than the parallel-anchoring PDLC of PAA/8CB, the results of this study still show the induction of LC orientation for PAA/BL006. This suggests that the perpendicular anchoring in PAA/BL006 may be weak, and cannot prevent the molecular orientation in the stretching direction. But if the strength of the perpendicular anchoring is dominant, the situation may be different; a uniform LC orientation in the stretching direction can be difficult to achieve as sketched in figure 7.

4. Conclusions

The nematic liquid crystal BL006 is phase-separated from PAA even in the isotropic liquid phase, forming spherical liquid droplets. Stretching the PDLC films containing liquid droplets results in no molecular orientation of BL006 but transforms the droplets geometry from spherical to elliptical. When the stretched films are cooled under strain, a uniform molecular orientation of BL006 is spontaneously formed upon the transition from the isotropic to the nematic phase. Despite a perpendicular liquid crystal anchoring at the polymer interface for this system, the achieved molecular orientation is parallel to the long axes of the droplets, i.e. in the film stretching direction. The LC orientation induced by stretching isotropic liquid droplets followed by cooling is much greater than the orientation obtained by stretching the PDLC films with nematic droplets. When nematic droplets are stretched, regardless of the nature of the liquid crystal anchoring that can be parallel or perpendicular to the polymer interface, the elongation of the droplets leads to deformation of the director field and displacement of the defects, which raises the elastic free energy. The consequence is a slow and difficult development of a uniform molecular orientation along the stretching direction. The studies show that the key to obtaining a uniform LC orientation in stretched PDLC films at the field-off state is the phase separation for the liquid crystal compound in the isotropic phase.

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