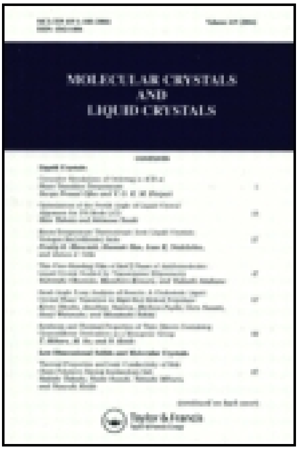

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Orientated Polymer-Dispersed Liquid Crystals

Julien Brazeau [a], Yanick Chenard [a] & Yue Zhao [a]

[a] Departement de chimie, Université de Sherbrooke, Sherbrooke, Quebec, Canada, J1K 2R1

To cite this article: Julien Brazeau, Yanick Chenard & Yue Zhao (1999): Orientated Polymer-Dispersed Liquid Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 329:1, 137-144

To link to this article: http://dx.doi.org/10.1080/10587259908025934

Mol. Cryst. Liq. Cryst., 1999, Vol. 329, pp. 137-144
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Orientated Polymer-Dispersed Liquid Crystals

JULIEN BRAZEAU, YANICK CHENARD and YUE ZHAO*

Departement de chimie, Université de Sherbrooke, Sherbrooke (Quebec), Canada J1K 2R1

Molecular orientation in stretched films of polymer-dispersed liquid crystals (PDLC) was studied by infrared dichroism. The investigated PDLC system is composed of 4'-octyl-4-biphenyl-carbonitrile (8CB) and poly(acrylic acid) (PAA). It was found that a uniform orientation of 8CB can be obtained by stretching PAA/8CB films at T > Tg of PAA, where 8CB is in the liquid state, and then cooling the films to room temperature. The orientation achieved in this way is much higher than that obtained by stretching 8CB in its liquid crystalline phases. The effects of liquid crystal anchoring at the interface on the orientation induction are discussed.

Keywords: polymer-dispersed liquid crystals; molecular orientation; infrared dichroism

INTRODUCTION

Though a large number of works have been dedicated to polymer-dispersed liquid crystals (PDLC)[1,2], apparently, little attention has been paid to PDLC having a macroscopic orientation of LC molecules. The general belief is that elongated LC droplets, usually formed during the fabrication process of PDLC, is undesirable because the driving voltage for LC reorientation at the on-state may be increased. Nevertheless, it is our intention to thoroughly study orientation phenomena in PDLC subjected to a mechanical stretching. The idea is that if a macroscopic and uniform LC orientation can be induced, in purpose, and controlled at the off-state, such oriented PDLC may generate

---

* author for correspondence

some interesting electro-optical effects[3].

The very first PDLC system we studied recently is composed of 4'-octyl-4-biphenyl-carbonitrile (8CB) and poly(ε-caprolactone) (PCL)[4]. 8CB has a low solubility limit in PCL, which is a semi-crystalline polymer and can be cold-drawn at room temperature. It was found that the orientation of 8CB in stretched films increases continuously with film extension, and its orientation parameter reaches about 0.4 at draw ratios of 4-5. An interesting feature revealed in that study is that when PCL/8CB films are stretched at $T > T_{ni}$ of 8CB, some orientation can still be found at room temperature. This behavior is in contrast with what is known for a liquid crystal polymer (LCP) dispersed in a polymer matrix, for which no orientation of mesogens is induced when stretching LCP in its isotropic state[5]. If LC orientation can be obtained by stretching LC in the liquid state, there will be more choices of polymer matrixes suitable for the preparation of oriented PDLC. In this paper, we report investigations on PDLC of 8CB with poly(acrylic acid) (PAA). PAA is amorphous and has a high glass transition temperature T_g. Films of 8CB/PAA can only be stretched at $T > T_g$ of PAA, with 8CB in the liquid state.

EXPERIMENTAL

Both samples of 8CB and PAA were purchased from Aldrich. 8CB has a crystal to smectic-A transition at 24 °C, a smectic-A to nematic transition at 34 °C, and a nematic to isotropic transition (clearing temperature T_{ni}) at 40 °C. PAA has an average molecular weight of 450,000 g/mol, and a measured T_g of 92 °C. Blends of 8CB and PAA were made by dissolving them in ethanol, and the films were prepared by casting the homogeneous solution onto the surface of a glass plate. Phase separation in this PDLC system was induced by solvent evaporation, and the films used for stretching, having a thickness of about 30 μm, were dried under vacuum at 100 °C for two days. Blends containing as much as 50 wt% of 8CB can give rise to films strong enough for mechanical stretching. The uniaxial stretching experiments were carried out on a homemade apparatus, placed inside a thermostat oven, at a rate of about 20 mm/min; the films were cooled under strain at room temperature, immediately after the stretching. Details about the measurements of LC orientation using infrared dichroism were reported elsewhere[4]. Unless otherwise stated, the orientation measurements were performed at room temperature. The instruments used for the characterizations of PDLC include a Perkin-Elmer DSC-7 differential scanning calorimetry, a Leitz DMR-P optical microscope, equipped with an Instec hot stage, and a Bomem MB-102 FTIR spectrometer.

RESULTS AND DISCUSSION

Figure 1 shows the DSC heating curves (second scan) for PAA/8CB of various compositions. Phase separation is clear for all concentrations of 8CB. Even with 5 % of 8CB, a transition peak can be noticed at about 36 °C, indicating that 8CB has a solubility limit below 5 % in PAA. In addition to a slight decrease in T_{ni}, a small smectic-A to nematic transition peak can still be noticed at about 32 °C for all blends. The crystal melting peak is seen only for blends containing 30 % or more 8CB, with a reduced transition enthalpy as compared to pure 8CB. These results can be attributed to interfacial interactions between 8CB and PAA. The T_gs of PAA in those blends appear at around 75-85 °C. This slight decrease of T_g is indication that some 8CB molecules are solubilized in the polymer matrix, acting as a plasticizer. All the films can be stretched at $T > T_g$ of PAA, i.e., above 85 °C.

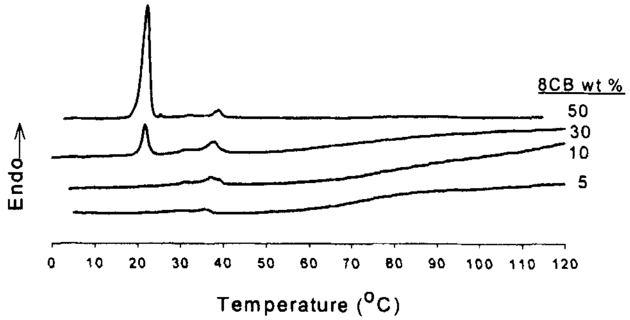

FIGURE 1 DSC curves for PAA/8CB films.

Phase separation in PAA/8CB, over a wide range of temperatures, is also confirmed by optical microscopy. Using PAA/8CB-70/30 as an example, shown in Figure 2 are the photomicrographs for an unstretched film and films stretched to various draw ratios at 130 °C (the draw ratio λ is defined the film length after stretching over that before stretching). All photomicrographs were taken at 130°C, which is some 40 °C above T_g of PAA and 90 °C beyond T_{ni} of 8CB. Spherical droplets of 8CB appear in the unstretched film ($\lambda=1$); their sizes are quit uniform (~ 2 μm in diameter). When the film is stretched to $\lambda=1.5$, an elongation of the droplets along the

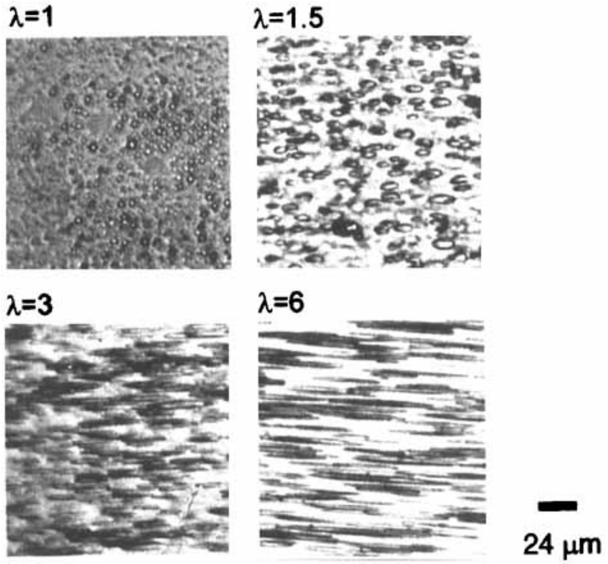

FIGURE 2 Optical photomicrographs for PAA/8CB-70/30 films.

stretching direction is evident. The stretching of the droplets increases with the film extension, as is seen for films stretched to λ=3 and λ=6. At λ=6 (500 % extension), the droplets are transformed to cylinders, which can be as long as 50-60 μm. It is likely that coalescence of the droplets take place at high film extensions. As a matter of fact, for some apparently long cylinders, junctions of different droplets can clearly been observed. Similar results were obtained for all blends, including PAA/8CB-95/5. No solubilization of 8CB in PAA was found when the blends were heated up to 180 °C, which is the temperature limit for the hot stage of the microscope.

Polarized infrared measurements on the stretched films at room temperature indicate orientation of 8CB molecules along the stretching direction. The results obtained for two blends stretched at 130 °C, PAA/8CB-70/30 and PAA/8CB-50/50, are shown in Figure 3, where the orientation parameter F is plotted as a function of draw ratio. The orientation develops rapidly as the film extension increases, reaching a plateau value of about F=0.55 for PAA/8CB-70/30 and F=0.5 for PAA/8CB-50/50. Those values are typical for monodomain formed by nematic liquid crystals ; in other words, a macroscopic and uniform molecular orientation of 8CB is achieved in the stretched films. In the blend containing 30 % of 8CB, the

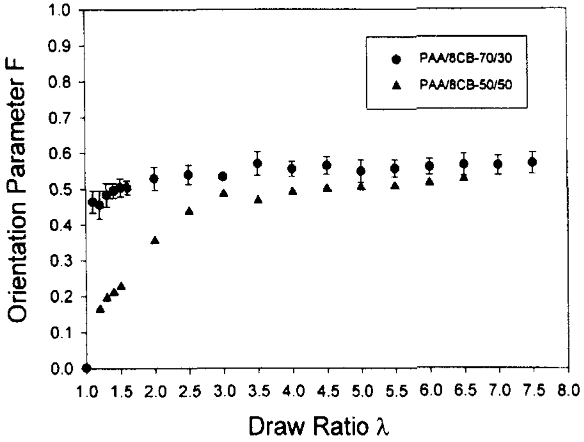

FIGURE 3 Orientation parameter of 8CB vs. draw ratio for PAA/8CB films stretched at 130 °C and cooled to room temperature.

orientation is induced so quickly that at λ≈1.2, F is already close to its plateau value. It is interesting to note that the elliptical droplets at λ=1.5 and the long cylinders at λ=6 (Figure 2) have a similar average molecular orientation of 8CB. For the blend containing 50 % of 8CB, the orientation development is relatively slow: F reaches the plateau value at λ≈3. This behavior may be related to the morphology of the blend. At this high concentration of 8CB, there is coalescence of 8CB droplets before stretching (photomicrographs not shown) and, as compared to PAA/8CB-70/30, the stretching is less effective to elongate all droplets with well-defined long axes. Stretching temperatures ranging from 90 to 130 °C were utilized; no effects on the 8CB orientation were observed.

During the stretching of PAA/8CB at T >T_g of PAA, 8CB is in the liquid state. As a stretching of liquid droplets should not induce a molecular orientation inside them, the uniform orientation, observed at room

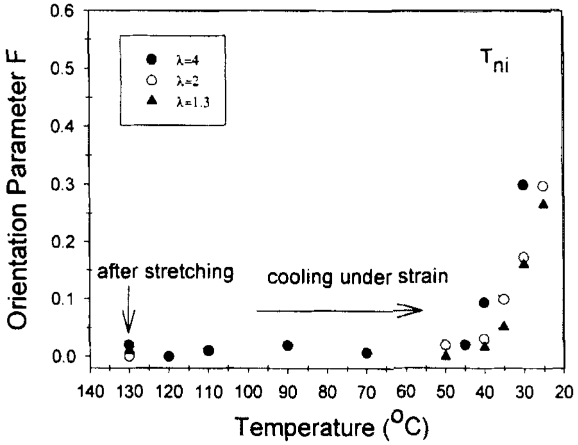

FIGURE 4 Orientation parameter of 8CB vs. temperature for PAA/8CB-70/30 films cooled under strain.

temperature, must be formed during the cooling of the films. This was easily confirmed by the experiments depicted in Figure 4. Using a temperature-controlled stretching device, films of PAA/8CB-70/30 were stretched to three different draw ratios at 130 °C. In each case, the orientation of 8CB was measured immediately after the stretching, at 130 °C, then the film was allowed to cool under strain while the orientation was monitored at several temperatures. It is seen that the stretching induces no orientation of 8CB, and no orientation shows up during the cooling until the liquid-to-nematic phase transition at about 36 °C. For technical reasons, the cooling was made by opening the door of the stretching device, and the actual temperature of the film was estimated to be ~ 2-3 °C higher than the indicated temperature. Therefore, it is during the liquid-to-nematic phase transition that molecules of 8CB inside the elongated droplets are spontaneously aligned along the long axes of the droplets. This orientation remains in the same direction at room temperature where 8CB is in its smectic-A phase. Structure of oriented smectic-A phase in elongated droplets was proposed in the literature [6].

In contrast with 8CB/PAA, for 8CB/PCL [4], no smectic-A to nematic transition peak could be observed from DSC measurements, suggesting that 8CB may be nematic at room temperature in this blend. As mentioned in the Introduction, when films of 8CB/PCL are stretched at room temperature, the resulting orientation increases almost linearly with draw ratio, and F reaches only about 0.4 at λ=4-5 [4]. Therefore, the results suggest that stretching liquid droplets of 8CB, followed by cooling to $T < T_{ni}$, results in higher orientation than stretching directly liquid crystal droplets of 8CB. This observation can be interpreted in terms of the anchoring effects of LC molecules at the polymer interface. Polarizing microscope observations indicate that the nematic droplets of 8CB adopt the bipolar configuration in PAA. This is expected to be also the case for 8CB in PCL, though it is difficult to confirm because of the semi-crystalline polymer matrix. The possible effects of LC anchoring on the stretching-induced orientation is schematically illustrated in Figure 5, using, as an example, a spherical droplet whose axis of symmetry is initially perpendicular to the stretching direction. When the liquid crystal droplet is stretched at $T < T_{ni}$, its long axis should coincide with the axis of symmetry, mainly as a result of the mechanical effect that tends to align the molecules along the stretching direction. But, this transformation process will induce deformation of the director field with respect to the parallel anchoring at the interface, which results in an increase in the elastic free energy and hinders the development of a uniform orientation of LC molecules. Understandably, continuously increasing the droplet elongation will overcome more and more memory effects of anchoring, leading to a continuous increase in the molecular orientation. In the case where the

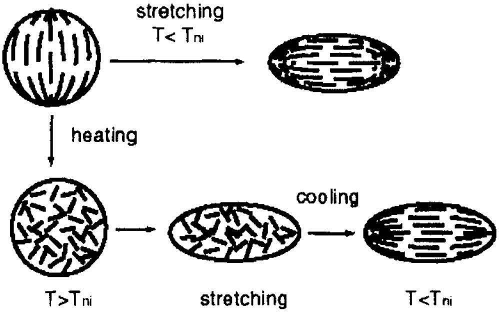

FIGURE 5 Schematic illustration for stretching of a bipolar droplet.

bipolar droplet is heated to $T > T_{ni}$ before stretching, it becomes a liquid droplet, and any memory effects of anchoring are erased. The stretching elongates the liquid droplet, which has no molecular orientation as long as $T > T_{ni}$. While cooling the elongated droplet to $T < T_{ni}$, the phase transition takes place at $T = T_{ni}$; as the area of interface parallel to the long axis of the elongated droplet is larger than that perpendicular to it, the parallel anchoring of LC molecules at the interface should result in a dominant effect that imposes the director field along the long axis of the droplet. This explains the great ease with which a uniform orientation is induced. For 8CB/PAA, the smectic-A phase is formed at lower temperatures while the molecular orientation remains in the same direction. As a final remark, mechanical deformation of liquid droplets can be easier than liquid crystal droplets because of lower viscosity or higher fluidity for a liquid.

CONCLUSION

A uniform molecular orientation of 8CB can be obtained by stretching films of PAA/8CB at $T > T_g$ of PAA, where 8CB is in the liquid state, followed by cooling the stretched films to room temperature. The orientation is easier to be induced in this way than stretching films with 8CB in its liquid crystalline phases. Effects of liquid crystal anchoring at the polymer interface can explain this observation. The finding means more choices of polymer matrices that can be used to prepare oriented PDLC through mechanical effects.

Acknowledgments

We thank 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 for their continuing financial support for our studies.

References

[1] P.S. Drzaic, *Liquid Crystal Dispersions* (World Scientific, New Jersey, 1995).
[2] G.P. Crawford and S. Zumer, eds. *Liquid Crystals in Complex Geometries* (Taylor & Francis, London, 1996).
[3] O.A. Aphonin, Y.V. Panina, A.B. Pravdin and D.A. Yakovlev, *Lig. Cryst.* **15,** 395 (1993).
[4] J. Brazeau, Y. Chenard and Y. Zhao, *Can. J. Chem.* in press.
[5] H. Lei and Y. Zhao, *Polymer,* **35,** 104 (1994).
[6] H. Molsen and H.-S. Kitzerow, *J. Appl. Phys.* **75,** 710 (1994).