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Striped pattern formation in polymer dispersed liquid crystal films

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Composite films of polymer and liquid crystal (LC) have been prepared by a simple solution casting technique. The films obtained exhibit a polymer dispersed liquid crystal structure where LC droplets are dispersed in the polymer matrix. Casting the mixture of polymer solution and LC on a tilted substrate results in a specific texture in which arrays of LC droplets align parallel to each other, i.e. a striped pattern can be formed. The size of the droplets and the spacing between the lines are dependent on the substrate tilt angle and the preparation temperature. By using a dip-coating technique, a similar striped texture appears at a fast dipping velocity. From *in situ* observation of the stripe development, it is seen that the translation of the phase-separating region, accompanying the flow, plays a more important role in the formation of the striped patterns than the flow of the solution itself.

1. Introduction

Composite films of polymer and liquid crystalline (LC) material have attracted much attention from both engineers and scientists, since these films can be used in optical switching devices; a variety of aggregation structures, depending on the preparation conditions, is ascribed to the specific phase separation behaviour. Such composite films are frequently termed 'polymer dispersed liquid crystal' (PDLC) since the film consists of droplets of low molecular mass LC dispersed throughout a polymer matrix [1–3]. PDLCs are particularly promising materials for flexible displays. Monolithically integrated flexible PDLC display devices have recently been reported [4]; the devices exhibit both flexibility and robustness and can be driven by organic transistors.

Other types of LC/polymer composite film have been reported. A polymer ball-type film consists of polymer balls dispersed in a LC matrix [5]. As an intermediate structure between these two types, bicontinuous-type films have been demonstrated, in which both polymer and LC phases are continuous [6].

Simple techniques have been utilized for the preparation of polymer/LC composite films, e.g. solution casting, dip-coating and spin-coating, since quick and easy manufacture is required to reduce production costs [2, 6]. In addition, thin flexible composite films can be

easily fabricated from the mixture of a UV curable resin and a nematic LC [1, 5].

Here it should be noted that conventional PDLC films show specific textures with LC droplets aligned randomly. For a simple scattering device such as an optical switch, it is practically unnecessary to control the alignment order of the droplets precisely. On the other hand, the position and alignment of LC droplets must be controlled in order to alter the scattering or diffracting direction, when PDLC films are applied to a tunable grating for optical computing devices such as spatial optical modulators and optical bidirectional switches. Recent interest in PDLCs therefore stems from their use in stratified layers, namely holographic PDLCs (HPDLCs), for photonics and telecommunication applications [7–10]. By increasing the efficiency of the phase separation process, i.e. by controlling the component concentration and UV curing conditions, submicron (nano-sized) droplets can be formed [7, 9]. For an in-plane alignment of droplets in PDLCs, however, it has only been reported that the application of shear force to a PDLC film before UV exposure results in LC droplets elongated and oriented in the direction of shear [11].

The purpose of this study is to fabricate PDLC films with an in-plane alignment of droplets by modifying two simple methods, solution casting and dip-coating. In order to regulate the alignment, we arrange a flow of the solution in one direction on the substrate. The

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effects of the preparation conditions on the structure are discussed, as observed by microscopy.

2. Experimental

2.1. Preparation of PDLC films

Polystyrene (PS) ($M_w = 10\,000$) was used as the polymer matrix of composite films. As the other component, a low molecular mass LC substance, 4-heptyl-4'-*n*-cyanobiphenyl (7CB) (Merck Co., Ltd.), was used without further purification. The polymer component was dissolved in carbon tetrachloride to form a 2.0 wt% solution. The LC component, 7CB, was added to the solution so that the mass would be the same as that of PS; i.e. the ratio PS:7CB is 1:1 by weight, unless otherwise stated. The glass substrates were washed with acetone and then with pure water to remove contaminants adsorbed on the surface.

A modification of a simple solution casting method was made to give an order to the alignment of the droplets. Firstly, the solution was dropped onto the glass substrate, as shown in figure 1. A flow of the solution was induced by tilting the substrate at various angles. The resulting solution cast films were then dried in air at atmospheric pressure; the solution lost fluidity as the solvent evaporated. Finally, the samples were replaced horizontally on the sample stage of the microscope (see below) after losing fluidity and forming solid films, which were somewhat swollen with the solvent.

As another method to induce flow on the substrate, a dip-coating method was used. The glass substrates were dipped in the solution and then lifted vertically at a constant velocity.

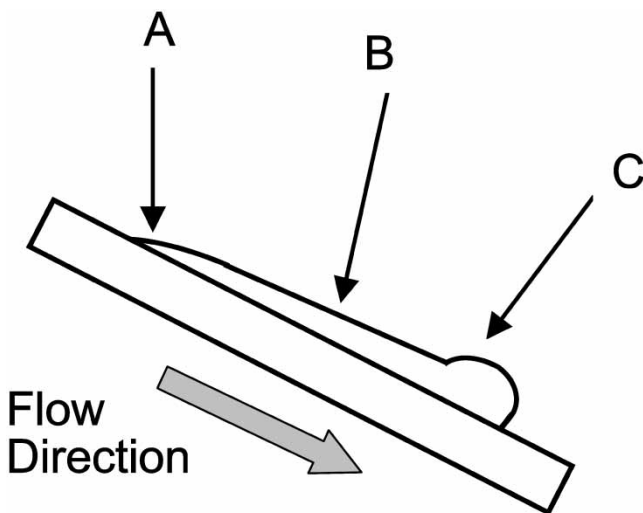


Figure 1. Schematic illustration of the side view of the film on the substrate. The solution is dropped onto point A, and flows spontaneously from A to C.

2.2. Observation of PDLC films

Textures of the PDLC films formed were observed with a polarizing optical microscope (Nikon Optiphot) at a temperature at which 7CB exhibited the nematic phase. The sample temperature was regulated with a hot stage (Mettler FP82HT/FP80). The transition temperature was determined as the temperature at which a nematic droplet first appeared on cooling from the isotropic phase.

3. Results and discussion

3.1. Solution cast films

Figure 2 shows polarizing optical micrographs of the PDLC films cast on tilted glass substrates. The films show a specific striped pattern; each stripe contains ellipsoidal LC droplets aligned linearly. Smaller droplets are formed in the vicinity of the point onto which the solution was dropped (region A), whereas larger droplets and wider spacing between adjacent stripes are observed at the middle of the film (region B). At the end of the film (region C), the solution forms a pool and the resultant film includes larger droplets having irregular shapes with random alignment. Such striped patterns can be observed at PS:7CB ratios ranging from 4:6 to 7:3 by weight. The diameter of the droplet increases with an increase in the 7CB content, whereas the spacing between adjacent stripes is almost independent of the content.

In order to clarify the effect of flow on the texture, the solution was cast onto substrates set at different tilt angles. Figure 3 shows polarizing optical micrographs of the films prepared at different tilting angles. The microscope field of view will hereafter be restricted to region B unless otherwise noted. If the substrate was set horizontally during the film formation, large droplets are dispersed randomly in the matrix. For the samples cast on tilted substrates, a larger tilting angle results in larger line spacing.

The textures are also dependent on the fabrication temperature T_{cast} as shown in figure 4; the diameter of the droplets decreases with an increase in the fabrication temperature. This indicates that the size of the droplets is associated with the rate of phase separation. Figure 5 shows the diameter of the droplets and the depression of nematic–isotropic transition temperature, $T - T_{\text{NI}}$, as a function of the fabrication temperature T_{cast} . The depression $T - T_{\text{NI}}$ may be caused by the existence of PS dissolved as a contaminant in 7CB. The dependence of the depression $T - T_{\text{NI}}$ on the fabrication temperature T_{cast} can be associated with variation of droplet size because the equilibrium between the LC droplets and the PS matrix should be held through the interface, and the relative interfacial area (defined as the ratio of the interfacial

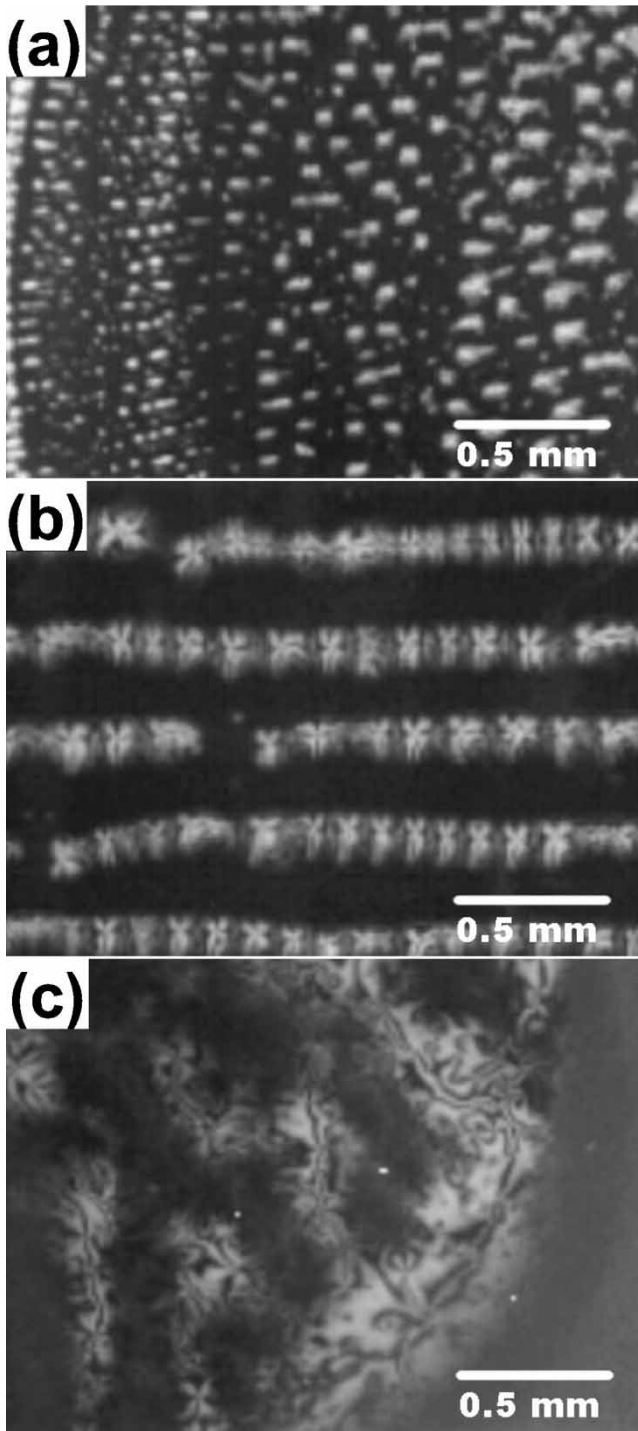


Figure 2. Polarizing optical micrographs of PDLC films (PS/7CB) prepared at 22°C and tilting angle 30°: (a) region A, (b) region B, (c) region C, as represented in Fig. 1. The flow direction corresponds to the horizontal direction of the photographs (from the left to the right).

area to the volume of the droplet) should decrease as the droplet size increases. It was confirmed by microscopy that the transition temperature was dependent on

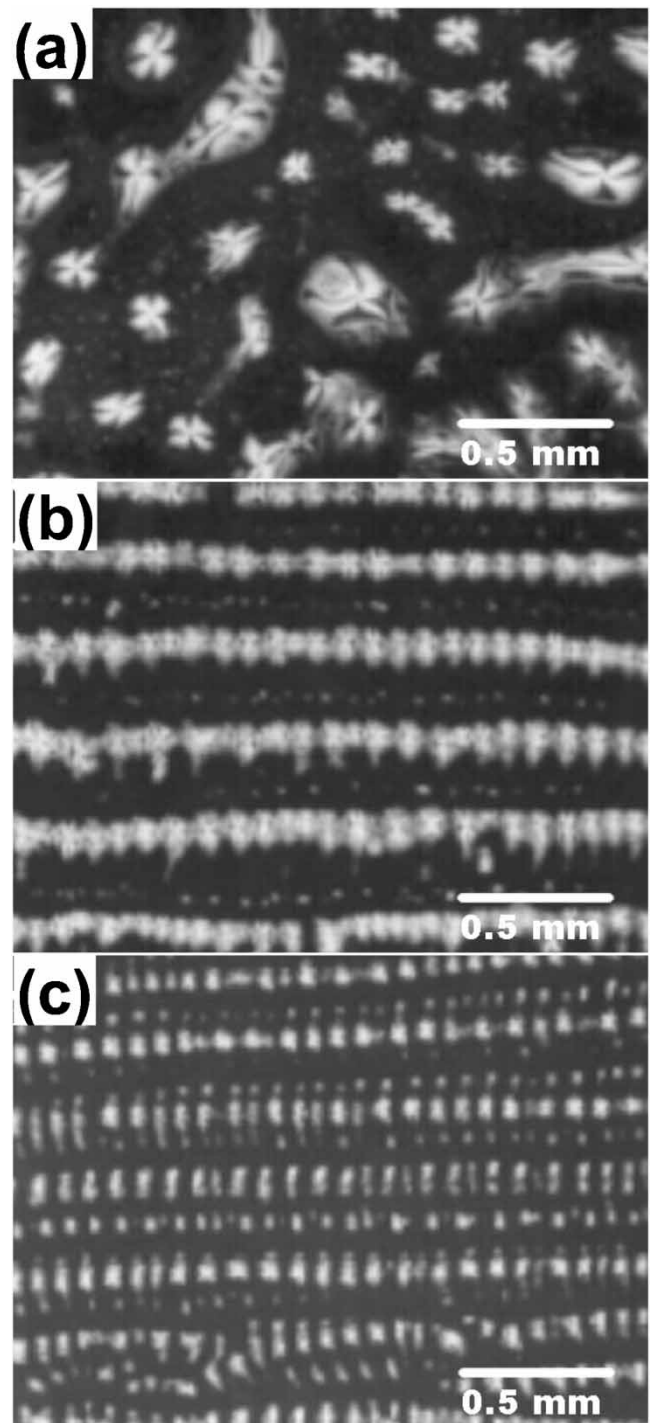


Figure 3. Polarizing optical micrographs of PDLC films (PS/7CB) prepared at 22°C: tilting angle (a) 0°, (b) 30°, (c) 70°. The flow direction corresponds to the horizontal direction of the photographs (from the left to the right).

the droplet diameter, as shown in figure 5. These results indicate that the formation of these textures can be related to the temperature-dependent phase separation

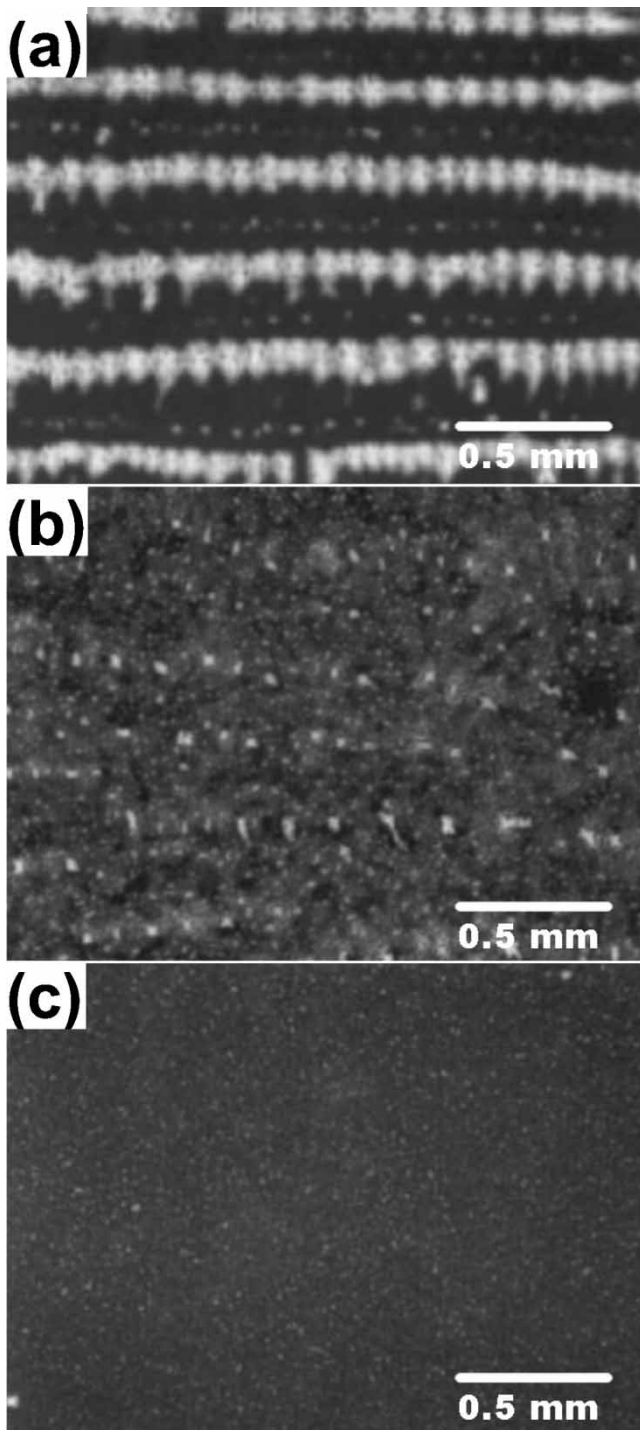


Figure 4. Polarizing optical micrographs of PDLC films (PS/7CB) prepared at a tilting angle of 30° and at a temperature of (a) 22°C , (b) 60°C , (c) 80°C . The flow direction corresponds to the horizontal direction of the photographs (from the left to the right).

behaviour. For varying lengths of alkyl chain in the liquid crystal ($n=5-8$), the longer length gave rise to larger droplets and higher transition temperature. This

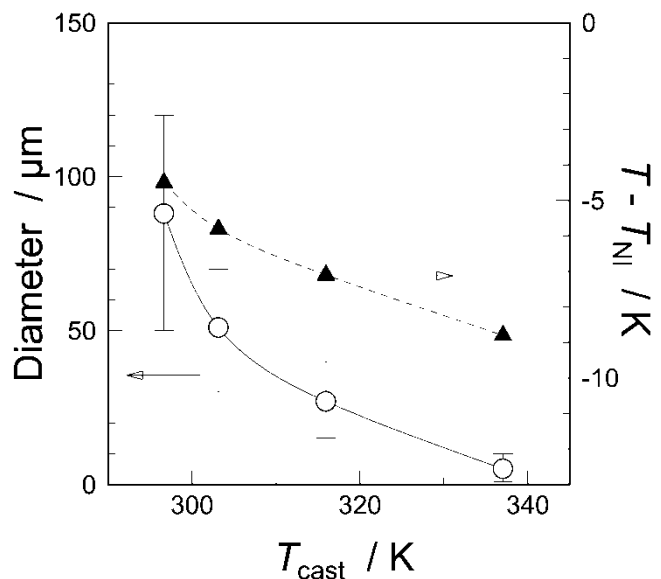


Figure 5. Diameter of the droplets and depression of the nematic–isotropic transition temperature, $T - T_{\text{NI}}$, as a function of the fabrication temperature, T_{cast} .

chain length dependence is related to the decreasing miscibility of PS with $n\text{CB}$ with increase in n .

In order to understand the formation mechanism of these striped patterns, we observed the samples as the solvent was evaporating soon after the solution was cast onto the tilted substrate. Firstly a striped pattern appears within 2 min after casting, as shown in figure 6(a); in this pattern, a brighter band contains the liquid crystal while a darker one consists of the polymer matrix. It is also found that droplets emerge within the brighter bands from the left-hand side of the picture, i.e. the droplets are formed sequentially along the flow direction of the solution. Next, these droplets can be seen more clearly at 5 min after casting, figure 6(b). Lastly, the droplets then become aggregated and grow larger, figure 6(c).

At the boundary between solution and solid film, a fingering instability can be observed as shown in figure 7. Such fingering patterns are sometimes observed for a water–ethanol mixture, known as the ‘tears of wine’ phenomenon [12]. The mechanism of formation of the fingering patterns is ascribed to a gradient of the surface tension in the vicinity of the boundary line, i.e. the Marangoni effect [13]. In a two-component solution, the Marangoni effect can originate from local differences in concentration. The fingering patterns observed in the present study therefore suggest that phase separation would take place in the vicinity of the boundary line. Here it should be noted that an array of

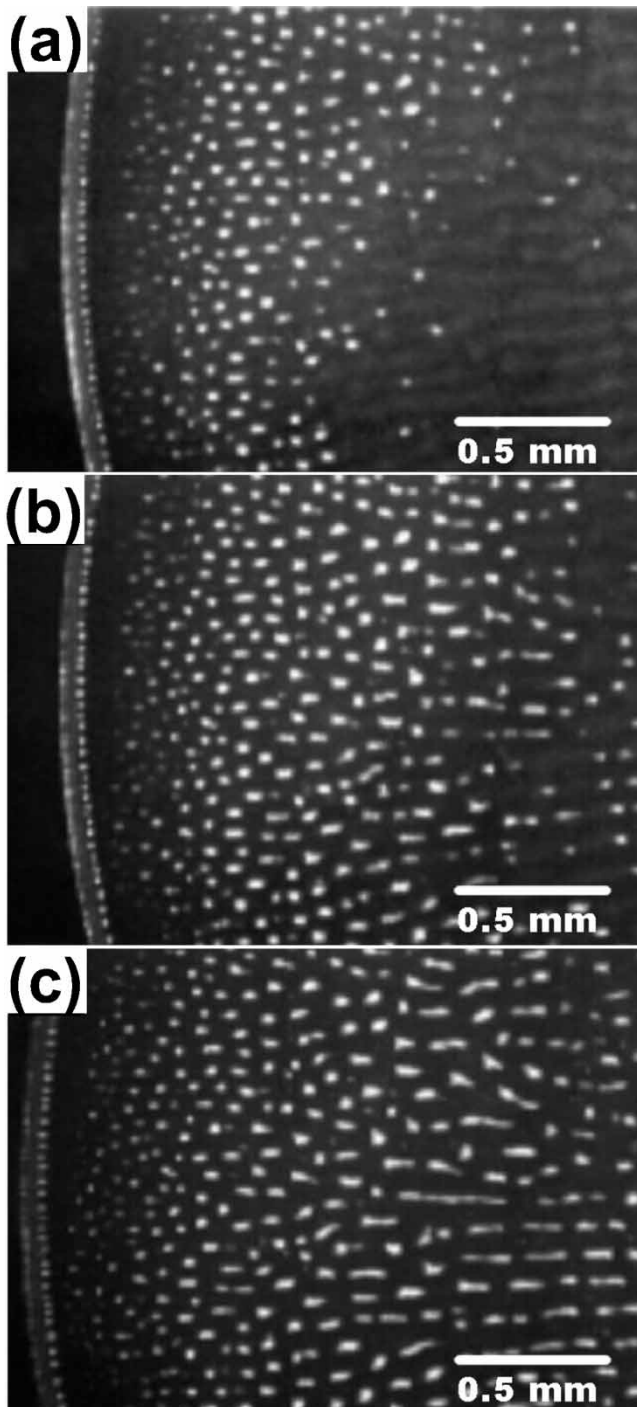


Figure 6. Polarizing optical micrographs of the formation of liquid crystal droplets in region A of PDLC films (PS/7CB) prepared at 22°C and a tilting angle of 30°; obtained at (a) 2 min, (b) 5 min and (c) 20 min after casting the solution onto the substrate. The flow direction corresponds to the horizontal direction of the photographs (from the left to the right).

liquid crystalline droplets is terminated by a dent of the boundary line.

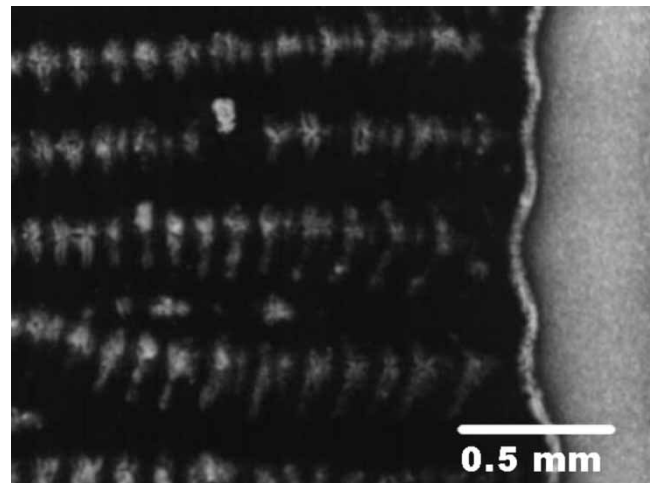


Figure 7. Polarizing optical micrograph of PDLC films (PS/8CB) prepared at 22°C on a tilted substrate. The boundary (frontier line) is located between region B and region C. The flow direction corresponds to the horizontal direction of the photographs (from the left to the right).

3.2. Dip-coated films

Figure 8 shows polarizing optical micrographs of dip-coated PDLC films. At a lift-up velocity of 50 mm min^{-1} , the film contains droplets oriented in lines to form striped patterns, similar to those cast on the tilted substrates. Lower lift-up velocities give rise to droplets without ordered alignment, while no droplets were observed for lowest velocities.

3.3. Formation of striped patterns

It should be noted that, besides these striped PDLCs, similar patterns have been observed in one-component polymer thin films prepared by solution casting [14, 15]. The films exhibit a periodical texture with ordered arrays of submicron polymer aggregates. The formation of arrays in the polymer films is ascribed to the stick and slip motion of the solution and dewetting of the aggregates. A significant difference, however, can be found between the textures of the striped PDLCs and the above one-component polymer films. The direction of the stripes or arrays in the polymer films is perpendicular to the flow direction, whereas that of striped PDLCs is parallel. This indicates that the mechanism for the formation of striped PDLCs is different from that for the ordered polymer films.

In situ observations of the structural development for the striped patterns have prompted the formation model illustrated schematically in figure 9. Firstly, the solvent evaporates from the solution to leave a solid film while the solution is flowing on the substrate. As a consequence of solvent evaporation, a boundary line

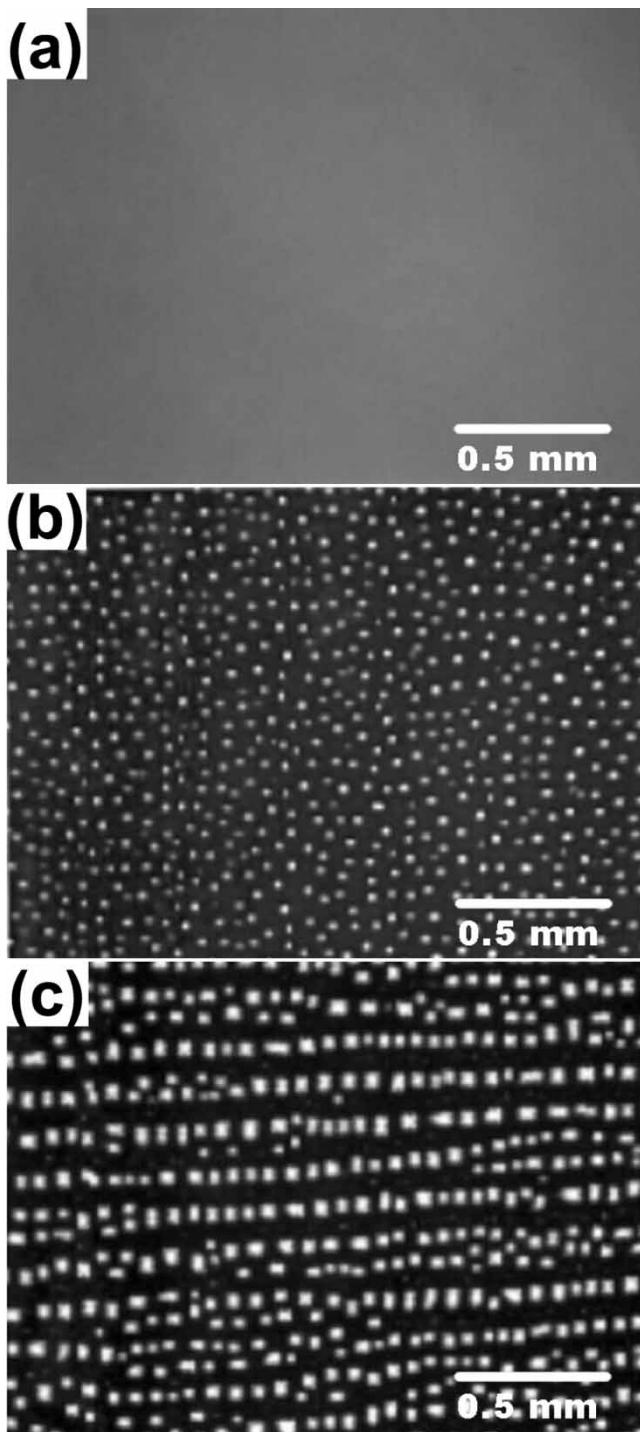


Figure 8. Polarizing optical micrographs of PDLC films (PS/7CB) prepared at 22°C by the dip-coating method. The dipping velocities are (a) 1.0, (b) 10, (c) 50 mm min⁻¹. The flow direction corresponds to the horizontal direction of the photographs (from the left to the right).

separating the solution and the solid film moves downstream, i.e. from left to right in figure 9. Here the solvent, PS and LC are miscible until the

concentration reaches a certain critical value. Next a phase separation takes place in the vicinity of the boundary line, and hence such a boundary line may be termed a frontier line. In the phase separating region, the concentration of the LC component will be spontaneously modified periodically along the frontier line. On the left hand side of the frontier line, the solution loses fluidity and then forms a solid film. Therefore a stable striped structure consisting of LC-rich and PS-rich bands appears, as the frontier line progresses along the flow direction. Lastly, in the LC-rich band, the LC molecules aggregate until droplets emerge to be observed clearly, because the LC molecules exhibit mobility even in the solid film somewhat swollen with solvent. Consequently arrays of droplets are aligned periodically to form a striped pattern in the composite film. Therefore the process that plays an essential role in the formation of striped patterns is the translation of the phase separating region rather than the flow of the solution itself.

3.4. Effect of applied voltage

The droplets in the striped PDLC films exhibited an electro-optical response, similar to conventional PDLCs. Figure 10 shows the effect of applied voltage on the polarizing optical micrograph of a droplet in a striped PDLC film. The LC orientation in the droplets is radial since all the droplets exhibit an internal dark cross in the absence of an electric field [16]. Such radial director configuration is rarely observed in conventional PDLCs; it is actually compatible with the experimental results that *n*CB molecules align perpendicular to the substrate on which PS was dip-coated. As the applied voltage increases, the dark cross becomes thicker. This indicates that the applied voltage causes reorientation of the director to a bipolar configuration. Bright regions remain in the vicinity of the PS/LC interface even at a high field. This suggests that the PS matrix provides a strong perpendicular anchoring at the interface.

With a view to use as a grating device, unfortunately no significant diffraction patterns were observed when a He-Ne laser beam was incident on the film, because the stripe spacing was much larger than the wavelength of the incident light. Precise regulation of the preparation conditions might afford a smaller and uniform spacing of a diffractive nature, which would be essential for high performance optical devices such as photonic crystals and spatial optical modulators.

4. Conclusions

Solvent casting and dip-coating on a tilted substrate afforded PDLC films having a specific texture in which

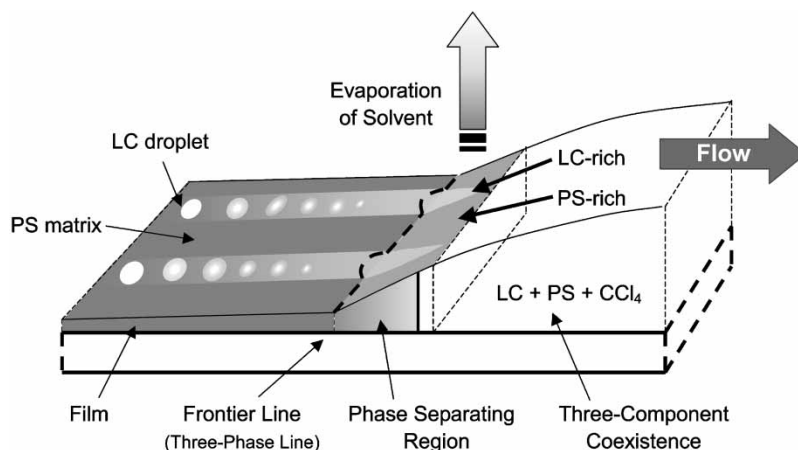


Figure 9. Schematic illustration of the mechanism of the striped pattern formation.

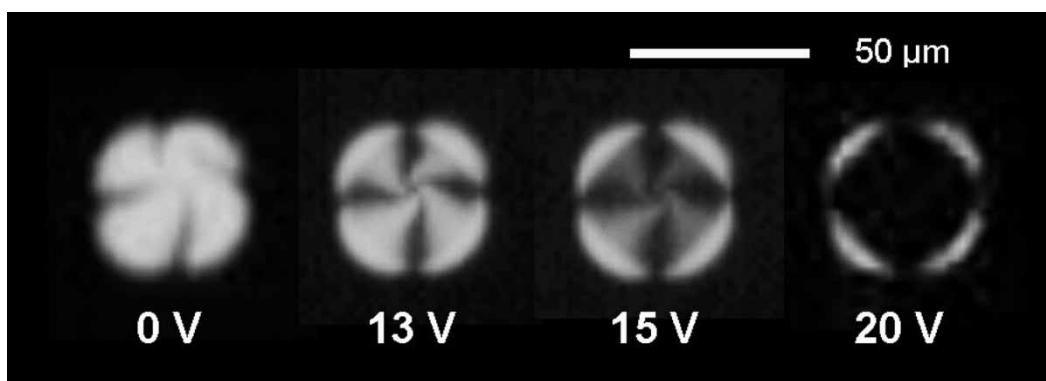


Figure 10. Effect of applied voltage on polarizing microscopic images of a droplet in PDLC films (PS/7CB) prepared at 22°C by the dip-coating method.

arrays of LC droplets align parallel to each other, i.e. a striped pattern can be formed. The size of the droplets and the spacing between the lines are dependent on preparation conditions such as angle of tilt and temperature. Careful *in situ* observations of the development of the patterns indicate that the formation of striped patterns can be ascribed to the downstream translation of the phase-separating region rather than to the flow of the solution itself.

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