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Control of liquid crystal droplet configuration in polymer dispersed liquid crystal with macro-iniferter polystyrene

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A polystyrene macro-iniferter was applied to control the alignment of liquid crystal molecules at the droplet wall of polymer dispersed liquid crystal (PDLC) films. The aspects of the alignment were monitored by observing the droplet in the PDLC film. With increasing the macro-iniferter polystyrene in the composition, the configuration of LC droplets changes from bipolar to radial. This is because the high concentration of the macro-iniferter polystyrene results in a small surface interaction between the LC and the polymer matrix, which favours the formation of radial configuration. The radial configuration was stable under our conditions. However, increasing the LC and the initiator concentrations resulted in the change from radial to bipolar.

Keywords: polymer dispersed liquid crystal; macroinitiator; iniferter polymerisation; polymerisation induced phase separation; radial configuration

Polymer dispersed liquid crystals (PDLCs) are promising candidate materials for application in the field of electro-optical devices, such as optic shutters, smart windows, optical sensors, memories and flexible display devices (*1–3*). Usually, PDLCs have a bipolar director configuration, which is characterised by a director field parallel to the interfaces with two point defects at opposite ends of the droplets and a cylindrical symmetry. Under application of an electrical field, it can be switched from a cloudy, light-scattering state to a transparent state. However, if PDLCs possess perpendicular alignment of the LC at the cavity wall, the radial director configuration is formed (*4*). These films tend to be relatively transparent because the refractive index difference between neighbouring droplets is not as large as in films of bipolar droplets. The relative transparency of films of radial droplets has been exploited to construct a 'reverse-mode' PDLC film (transparent unpowered state, scattering powered state) (*5*). But such a configuration is not easily achieved in nature in agreement with the Friedel–Creagh–Kmetz (FCK) rule, which predicts the incompatibility between long-term stability and radial configuration (*3, 4*). Some researchers have reported that the addition of small amounts of surfactants (*3–6*), and adopting a polymer matrix with the special structure (*6–9*) can result in the radial configuration. In this paper, we describe a simple method that was adopted to achieve the radial configuration in PDLC films. A polystyrene (PS) macro-iniferter (MI) was synthesised and used to copolymerise with butyl acrylate (BA) for preparation of PDLCs by the process of polymerisation induced phase separation (PIPS). The configuration of LC in the droplet can be easily adjusted by the concentration of MI in PDLC films. Moreover, the effect of the LC concentration on the configuration was also investigated.

The nematic liquid crystal employed was a common eutectic mixture of cyanobiphenyls (E7) ($n_o = 1.521$, $\Delta n = 0.22$, $T_{N\text{-}I} = 60°\text{C}$) obtained from Shi Jia Zhuang Crown Display Material Co., Ltd (Shijiazhung, Henan, China). Styrene (St) and butyl acrylate (BA) (98%, analytical grade, from Tianjing Chemical Reagent Co., China) were passed through a column of silica to remove inhibitors. N,N,N′,N′,N″-pentamethyldiethylenetriamine (PMD ETA) (98%, Jiangsu Liyang Jiangdian Chemical Factory, China), 2,2′-azobis(isobutyronitrile) (AIBN) and other reagents were used as received. The MI shown in Figure 1 was synthesised according to the literature (*10*): a thoroughly dried glass tube containing St (0.1 mol), $Cu(S_2CNEt_2)Cl$ (0.2 mmol), AIBN (0.1 mmol) and PMDETA (0.6 mmol) was sealed under high vacuum. Then, the tube was placed into an oil bath held by a thermostat at 115°C. After 12 h, it was cooled to quench polymerisation. The reaction mixture was diluted in tetrahydrofuran and precipitated into a large amount of methanol, and then dried under vacuum to constant weight at 40°C. $M_n = 20200$, PDI = 1.14, yield: *c.* 80%. The prepolymer was obtained by dissolving different concentrations of MI in BA with a constant weight ratio of the photo-initiator (1104, Changzhou LanDing Sci-Tech. Co., Ltd, Changzhou Jianasu, China)

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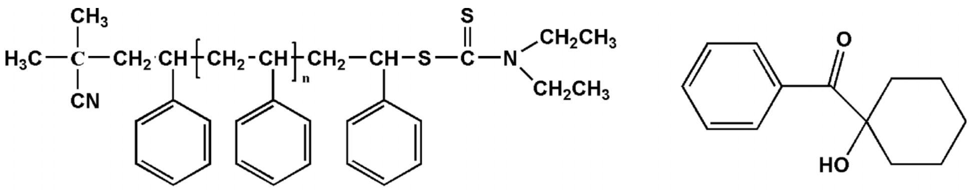


Figure 1. Chemical structures of the compounds used in this study.

Table 1. The composition and polymerization result of samples.

Sample[a]	Compositions (wt%) BA:MI	LC:prepolymer (wt%)
1	100:0	50:50
2	97.5:2.5	50:50
3	92.5:7.5	50:50
4	85:15	50:50
5	85:15	40:60
6	85:15	60:40
7	85:15	80:20

Note: [a]All the samples were prepared by exposing to a 100 W UV light from a distance of 20 cm for 40 min.

(details shown in Table 1). PDLC films were prepared by the method of PIPS from homogeneous solutions of liquid crystal and the prepolymer mixture in glass cells. The cell gap was set to be 19 μm by glass spheres. The cells were exposed to a 100 W UV light from a distance of 20 cm at ambient temperature for 40 min. Molecular weight of the MI was measured with gel permeation chromatography (GPC) on an Agilent 1100 column using PS standards as the calibration. The influence of MI and LC concentration on the polymer matrix morphology was characterised on an Olympus Model BH-2 polarised optical microscope at 25°C.

When a droplet is larger than 5 μm in diameter, it is possible to identify the droplet configuration using an optical microscope. Figure 2 shows photomicrographs of PDLC films of varying concentrations of MI taken between crossed polarisers. When the concentration of MI was lowered or absent, the bipolar configuration is obtained, where the molecules are anchored parallel to the polymer matrix. Its textures appear very complicated with the orientation of the droplet directors connecting the two poles. The various textures of the bipolar droplet are shown in Figure 2; they are consistent with the simulated patterns of other researchers (*4, 7*). When the concentration of MI increases above 7.5 wt%, the radial configuration can be attained as expected, in which the microscopic cross-shaped texture does not change with rotating polarisers (shown in Figure 2(d)).

The bipolar configuration in PDLC with PBA can be simply explained by the FCK rule, where the PBA has a higher surface tension than E7 (*3, 4*). On the other hand, the macro-iniferter used in this study is a kind of PS which bears the ability to initiate the copolymerisation with BA. Early work has demonstrated that the contact angle of the polymer matrix increased with an increase of St content in the copolymer (*11*). A small surface interaction was obtained with high St content in the copolymer (*12, 13*). Usually, low-surface energy favours LC perpendicular alignment in the wall of droplets and a radial structure (*4*). With increasing the MI concentration, the surface tension gradually deceased and at some point it was smaller than the intermolecular forces among the LC molecules and thus formed the radial configuration. In our systems, there was a threshold MI concentration for the onset of the radial configuration (15 wt% in the prepolymer). When MI concentration is below 15 wt%, the bipolar configuration is favoured. If the MI concentration is above 15 wt%, the radial configuration is formed.

Figure 3 shows the morphologies of PDLC films with the same composition under different curing times. It was found that with increasing the curing time, PDLC films always displayed radial configuration under our conditions. However, changing the concentration of the initiator greatly influenced the liquid crystal configurations in PDLC films (Figure 4). When the concentration is 0.05%, no phase separation is induced with 45 min curing. As the concentration of the initiator increases, the configuration changes from radial to bipolar. Our preview work has demonstrated that addition of the initiator in the iniferter system will induce the phase separation of the polymer matrix, which had a great effect on the morphologies of PDLC (*14*). Therefore, the composition of the resultant polymer matrices was changed with increasing the concentration of the initiator. It greatly changed the surface tension of the polymer matrices and thus influenced the liquid crystal configuration. Moreover, increasing the concentration of the initiator will

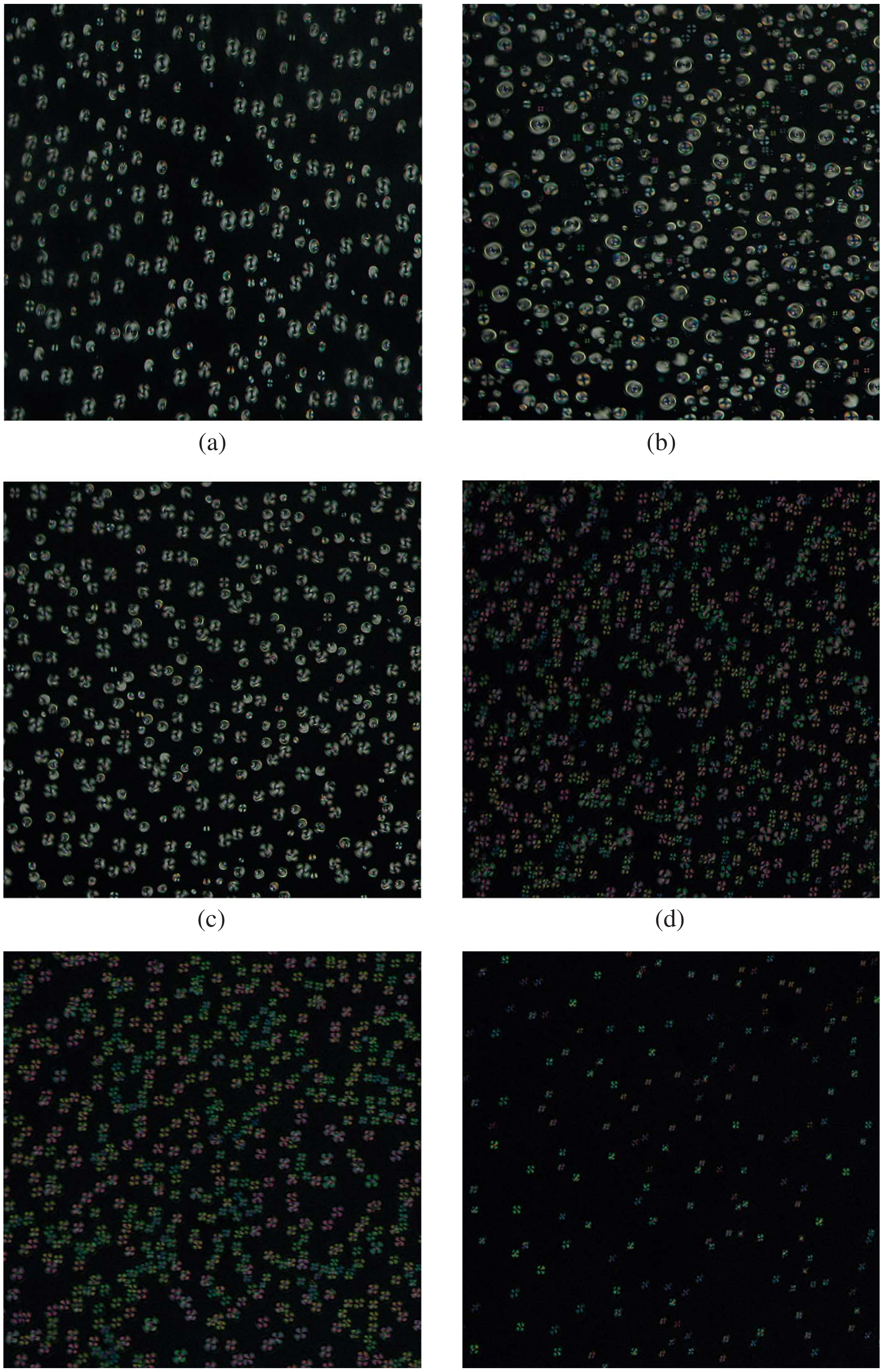
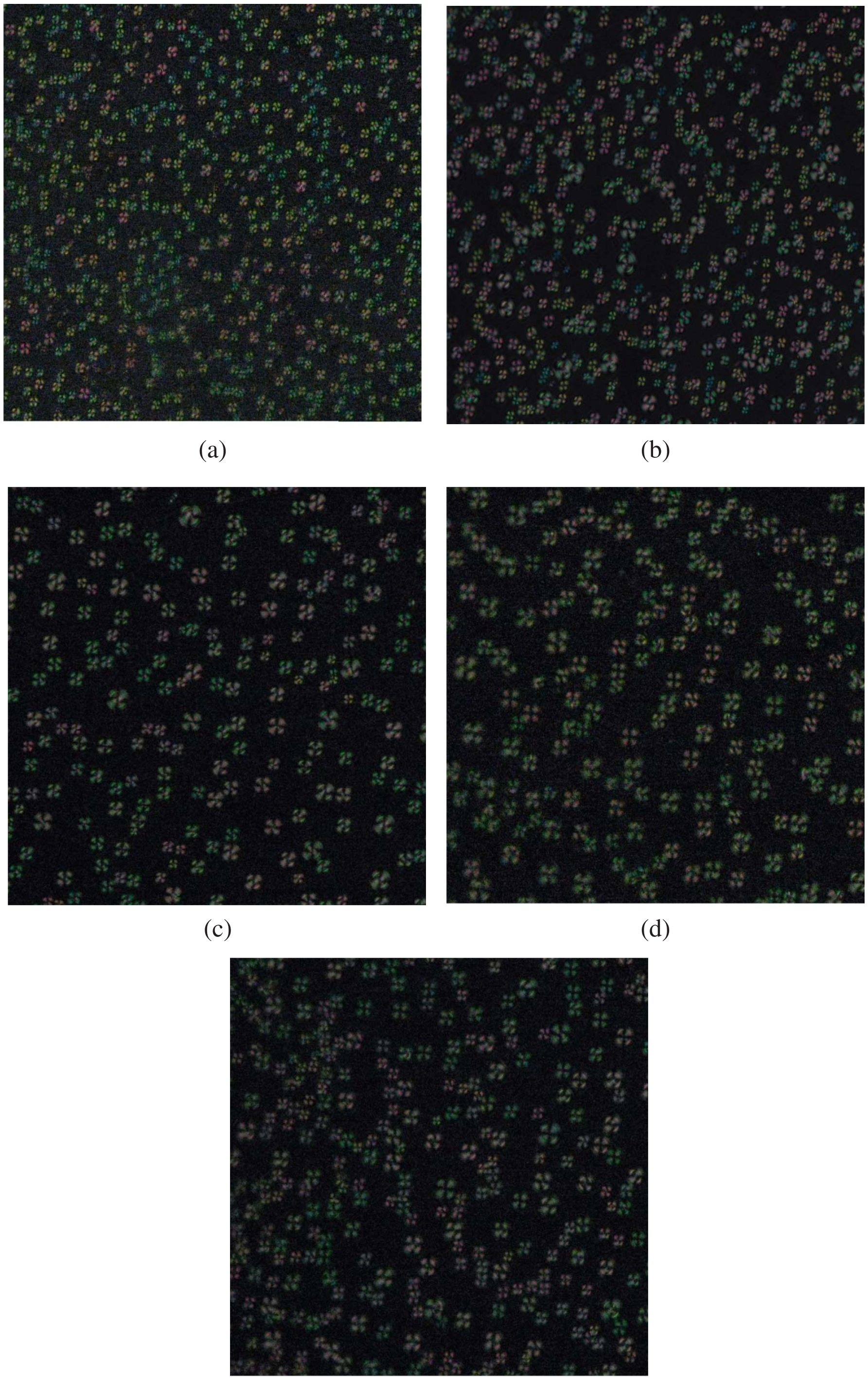


Figure 2. Polarised optical micrographs of polymer/liquid crystal (50/50 by weight) film of different MI concentrations: (a) 0%; (b) 2.5%; (c) 7.5%; (d) 15%; (e) 20%; (f) 30%. Picture area: 320 μm × 320 μm.

decrease the purity of liquid crystals and thus decrease the intermolecular interaction of liquid crystals (*15*). Consequently, increasing the concentration of the initiator favoured the formation of bipolar configurations in PDLC films.

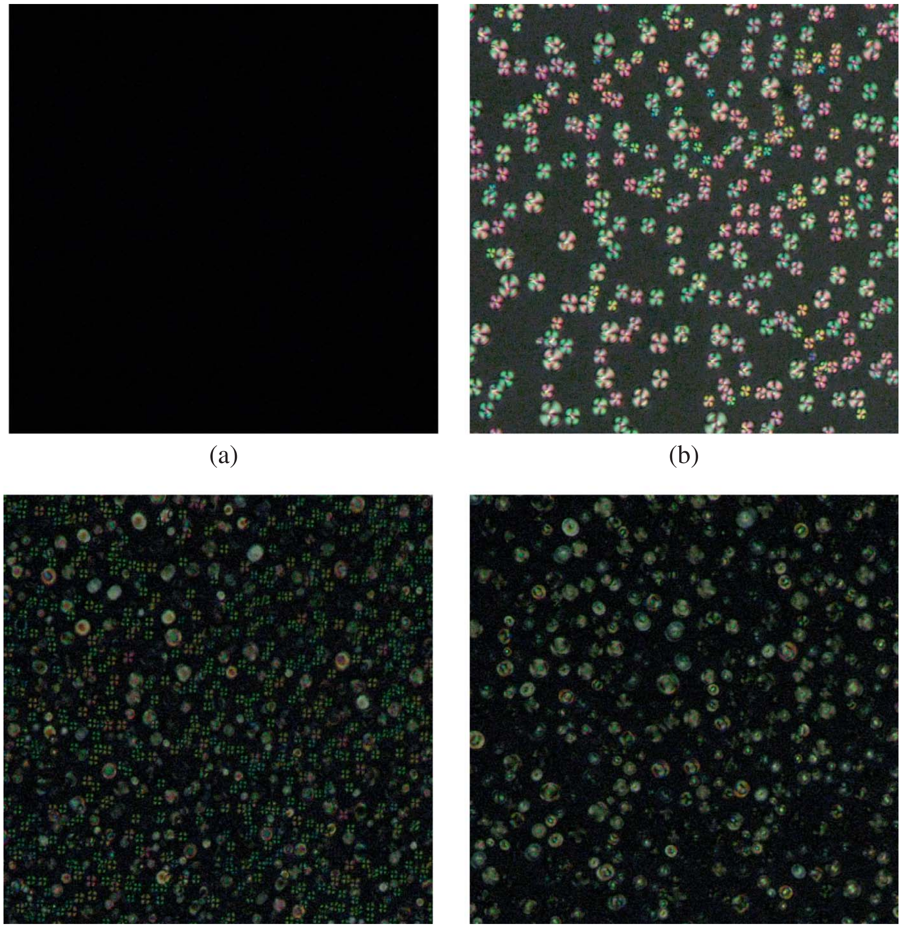
The effect of LC concentration on the configuration of LC droplets was also investigated (shown in Figure 5). It was found that increasing the LC concentration induces formation of the large LC droplet, and changes the LC configuration from radial to bipolar.



(a) (b) (c) (d) (e)

Figure 3. Polarised optical micrographs of PDLC films (MI:BA: E7 = 15:35:50 by weight) under different curing times: (a) 15 min; (b) 30 min; (c) 45 min; (d) 1 h; (e) 2 h. Picture area: 320 μm × 320 μm.

Some work has demonstrated that the large droplet usually favours the radial configuration (*4, 9*), but this is different from our case. In their case, the size of droplets was adjusted by the composition of the polymer with the constant LC concentration, so the influence of LC was negligible. In our case, composition and LC concentration are both changed, and the large droplet was mainly caused by the high LC concentration. This change from radial to bipolar configuration can be explained by the FCK rule. According to this simple semi-empirical rule, when the surface energy of the substrate is relatively low, and the intermolecular


(a) (b)

(c) (d)

Figure 4. Polarised optical micrographs of PDLC films (MI:BA: E7 = 15:35:50 by weight) using different concentrations of initiator 1104: (a) 0.05%; (b) 0.1%; (c) 0.5%; (d) 1%. Picture area: 320 μm × 320 μm.

forces among the LC molecules are stronger than the forces across the interface, the longer axis of the liquid crystal molecules is aligned perpendicular to the surface so as to maximise their intermolecular interactions. In the case that the surface tension of the substrate is greater than that of the liquid crystal molecules, the forces across the interface dominate. Therefore, the surface free energy is minimised if the LC molecules are packed flat, that is, aligned parallel to the substrate. In our case, the macro-iniferter used in this study is a kind of PS which bears the ability to initiate the copolymerisation. Some works have shown that a small surface interaction was obtained with high St content in the polymer matrices (*12, 13*). Consequently, when the liquid crystal content was low, the concentration of PS in the system increased and thus dramatically decreased the surface tension of the substrate. In this situation, the intermolecular forces among the LC molecules dominated and thus formed the radial configuration. With increasing the liquid crystal concentration, the surface tension gradually increased and at some point exceeded the intermolecular forces among the LC molecules and thus formed the bipolar configuration. Therefore, the change from the radial to the bipolar configuration is induced because of the increasing surface tensions of polymer matrices.

In conclusion, we have shown that the addition of the macro-iniferter PS in PDLC films is an effective method to induce the radial configuration. It was found that the radial configuration is very stable even after 2 h of UV curing. However, increasing the LC and the initiator concentration resulted in the transformation of droplet configuration from radial to bipolar. Because the OFF-state transmittance of the radial configuration is all above 70%, it will be a good candidate for the construction of ‘reverse-mode’ PDLC films with LC of a negative dielectric anisotropy. The correlating work is underway in our laboratory and the results will be reported later.

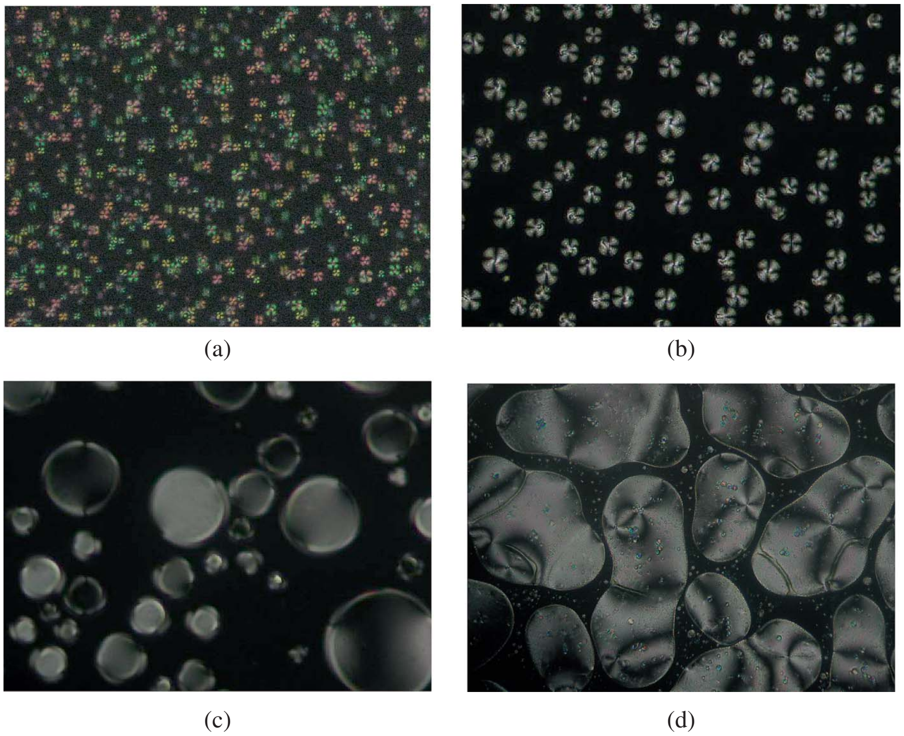

(a) (b) (c) (d)

Figure 5. Polarised optical micrographs of polymer/liquid crystal film of different LC concentrations: (a) 40%; (b) 50%; (c) 60%; (d) 80%. Picture area: 370 μm × 320 μm.

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