



Effect of electric field on phase separation of polymer dispersed liquid crystal

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Abstract

The kinetics of the polymerization induced phase separation of liquid crystal (LC)/monomer mixture has been investigated by means of depolarized light intensity technique and polarized light microscope (PLM). To examine the effect of the electric field, a DC electric field was applied across the mixtures during the phase separation process. The kinetic study indicates that the phase separation process is accelerated when the electric field is applied. The morphologies of the formed polymer dispersed liquid crystal (PDLC) films were observed by PLM. The electric field applied during the phase separation process yields the PDLC with small LC domains and fine morphologies. The clearing temperature (T_{NI}) of the formed PDLC films was measured by the PLM and it is found that the T_{NI} increases with the applied electric field intensity.

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1. Introduction

Liquid crystal (LC) has been used as electro-optical materials in a variety of applications, such as twisted-nematic LC (TN-LC) and super-twisted nematic LC (STN-LC) flat-panel displays. Over the past decade, a new way to disperse the LC and polymer: polymer dispersed liquid crystal (PDLC) has been developed, where the low molecular weight LC is trapped as domains embedded within a polymer matrix [1]. For PDLC, its optical response is based on the electrically controlled light scattering properties of the LC domains. In its normal off-state, a PDLC film can strongly scatter light and appears cloudy. A sufficient strong electric field can reorient the LC molecules and make the film transparent (on-state). As opposed to the traditional TN-LC and

STN-LC devices, PDLC based devices do not require alignment layers, stringent thickness control or polarizers. Therefore, the PDLC is of potential use in electro-optical devices, such as flexible displays, switchable privacy windows and other light control devices.

PDLC can be made in a variety of ways, such as polymerization induced phase separation (PIPS), thermally induced phase separation (TIPS), solvent induced phase separation (SIPS) and microencapsulation process (MP) [2,3]. PIPS has been considered to be the most popular one, since the fabrication process is relatively simple, clean and solvent-free. The matrix materials used in the PIPS include photo-curable and thermal-curable monomers.

PDLC has been the focus of immense theoretical and experimental investigations for fundamental scientific reasons and potential applications. These studies [1,4–9] include synthesis of new material, phase behavior, morphological characterization, phase separation kinetics, theoretical simulation and electro-optical properties. Many investigations show that the phase behavior

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and phase separation process are the important factors for controlling the fabrication and the final electro-optical behavior of the films [4–6].

Some reports [7,8] have involved the reversed-mode PDLC materials prepared by the application of the electric field during the fabrication process. However, to author's knowledge, the effect of the electric field on the phase separation process of the LC/monomer mixtures and the T_{NI} of the formed PDLC films have not been reported so far. It is the aim of this work to show the effect of the DC electric field on the phase separation process and the T_{NI} .

In the present work, methylmethacrylate (MMA) and epoxy resin were used as matrix material and polymerized respectively by UV power and thermally. A DC electric field was applied during the phase separation process and the effect of the electric field on the phase separation process, morphologies and the clearing temperature (T_{NI}) of the formed PDLC films have been studied. The phase separation kinetics was investigated by means of the depolarized light intensity (DLI) technique. The polarized light microscope (PLM) was utilized to observe the morphologies and measure the T_{NI} of the formed PDLC films. The obtained results show that the phase separation process, morphologies and T_{NI} were strongly influenced by the electric field.

2. Experimental

Matrix material: MMA with the dielectric constant $\epsilon = 6.23$ was purchased from Shanghai Feida Co. Ltd., epoxy resin (E51) with the dielectric constant $\epsilon = 4.0$ was purchased from Shanghai Resin Plant (the chemical formula of E51 is shown in Fig. 1). A eutectic nematic LC (TEB) with $T_{KN} = -20$ and 62 °C, and a single component nematic LC (7CB) with $T_{KN} = 30$ and 59 °C were purchased from Tsinghua Yawang LC Materials Co. Ltd. and Yantai Viliant LC Materials Co. Ltd. The dielectric constant ϵ of TEB and 7CB is 14.9 and 12.9, respectively.

The kinetics of the phase separation process was measured by the DLI apparatus designed by the Institute of Chemistry, Academic Sinica, which has been approved to be a useful technique in following the phase transition process in the LC system [10,11]. The detailed description of DLI apparatus could be found elsewhere

[12]. In the present work, the DLI apparatus measures the intensity change of the depolarized light of the samples during the phase separation process of the LC/monomer mixture.

The PDLC was prepared by standard method, PIPS. The matrix material, low molecular weight LC and cure agent (or photo-initiator) were weighted, hand mixed for several minutes, heated well above the clearing point of the LC. The mixture was then sandwiched between two ITO films, subjected to a constant pressure to drive off the air bubbles. The thickness of all the samples was fixed at $30 \mu\text{m}$. For the epoxy system, the prepared samples were immediately put into the cell of the DLI apparatus to follow the phase separation process by detecting the DLI changes at a constant temperature of 50 °C. And for the MMA system, the samples were intermittently taken out of the UV cure box and quickly put into the cell of the DLI apparatus to detect the intensity of the depolarized light, then quickly returned to the UV cure box again. Such intermittent taking of samples has neglectable effect on the PIPS process [13]. The instrument output was 400 mw/cm^2 in the 365 nm wavelength. The distance between the UV lamp and sample was 60 cm and the illuminated area was 1 cm^2 . All the photo-polymerizations were carried out isothermally at 50 °C.

To investigate the effect of the electric field on the phase separation process and T_{NI} , a DC electric field was applied across the samples during the phase separation process. The intensity of the electric field was from 1.50 to $2.17 \text{ V}/\mu\text{m}$.

For the optical microscopy experiment, a Leitz-Ortholux II polarized light microscope was used. The T_{NI} of the formed PDLC films were observed under cross-polarizer during heating the samples on the hot stage with a programmable temperature controller. All T_{NI} measurements were performed with the same heating rate of 1 °C/min.

3. Results and discussion

3.1. Effect of the electric field on the phase separation

In our previous work, the DLI technique has been proved to be a valuable method in following the phase transition in LC polymers [10,12,14,15]. The intensity of

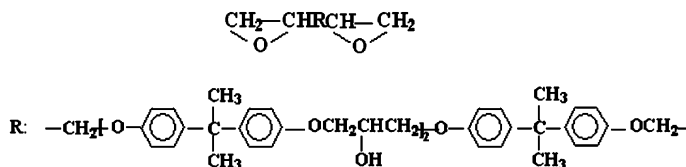


Fig. 1. Chemical formulation of the epoxy resin of E51.

the transmitted depolarized light is quite sensitive to the appearance of the ordered texture during the phase separation of the LC/monomer systems. The intensity of the depolarized light (I) is recorded as a function of time (t) in the phase separation process. Assuming that I is proportional to the fraction of the LCs formed at time t , at any stage of the phase separation, the fraction of the LC component can be expressed as

$$X_t = (I_t - I_0)/(I_\infty - I_0) \quad (1)$$

where I_t is the intensity of the depolarized light at time t , I_0 and I_∞ are the intensity values before and after phase separation [7]. Since the phase separation process and the LC formation process take place almost simultaneously especially for the samples with high LC content [16], the X_t could be served as a measure of the kinetics of the PIPS process of the LC/monomer mixture. In the present work, we also define that the phase separation rate equals the half phase separation time $t_{1/2}$ when $I_t = (I_0 + I_\infty)/2$.

Fig. 2 shows typical DLI curves for the PIPS process of the 7CB/MMA mixtures under electric field with various intensities. During the phase separation, at the initial stage, since the LC dissolves in the monomers and forms a homogeneous solution, the $I_0 = 0$. As the onset of the polymerization, the monomers react, which leads to a poor compatibility between the LC and matrix material. Owing to the LC being incompatible with the polymer matrix, phase separation occurs. The separated LC nuclears and domains are formed. Because the intensity of transmitted depolarized light is quite sensitive to the appearance of the ordered texture (LC domains), the I_t increases from 0 with the phase separation. As the polymerization continues, the viscosity of the system rapidly increases. Due to the high viscosity,

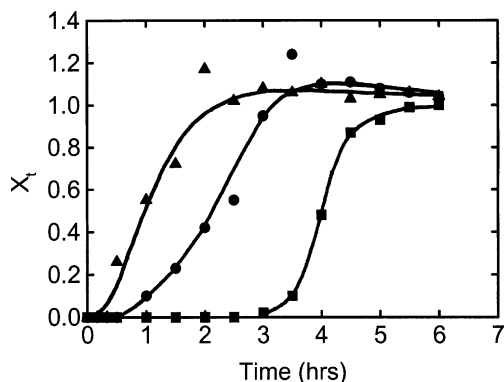


Fig. 2. DLI curves for the phase separation of 7CB/MMA (75/25, wt/wt) under electrical field with intensity of (■) 0 V/μm, (●) 1.50 V/μm, (▲) 2.00 V/μm, where the fraction of the LC component (X_t) formed during the phase separation process is plotted versus time (t).

the diffusion of the LC molecules become more difficult and the phase separation decelerates. As some unreacted monomers still polymerize, the phase separation continues, which causes adjustment of the formed morphology [17].

When the electric field is applied, the phase separation is sharply accelerated as it can be seen from Fig. 2. The phase separation can be detected in 60 min and the half time of the phase separation the $t_{1/2}$ equals 135 min under 1.50 V/μm. But without electric field the phase separation was not observed until 180 min and the $t_{1/2}$ equals 230 min. When the intensity of the electric field increased to 2.00 V/μm, the $t_{1/2}$ becomes only 60 min. Similar results were also obtained for other three systems: (1) TEB/MMA; (2) TEB/E51; (3) 7CB/E51.

More detailed $t_{1/2}$ values of all the four systems are summarized in Fig. 3, where the $t_{1/2}$ is plotted versus electric field intensity. The $t_{1/2}$ values decrease with electric field intensity for all the systems examined. This phenomenon may be explained on the basis of the difference between the dielectric constant of the LC and the matrix material (monomer). For the homogeneous mixture before phase separation, the dielectric constant of the LC is much higher than that of the matrix material (monomer) (see the experimental part), therefore the electro-polarized intensity of the LC is larger than that of the matrix material (monomer) under the same electric field [18]. The LC is more likely to be orderly aligned and aggregate than the system without applying the electric field, so the driving force of the phase separation becomes strong. The higher the electric field intensity, the stronger the driving force. This could lead to the earlier phase separation and shorter phase separation time.

Fig. 4 shows the $t_{1/2}$ value versus LC content for all the four systems at a constant electrical intensity. It is observed that the $t_{1/2}$ value decreases as the LC content

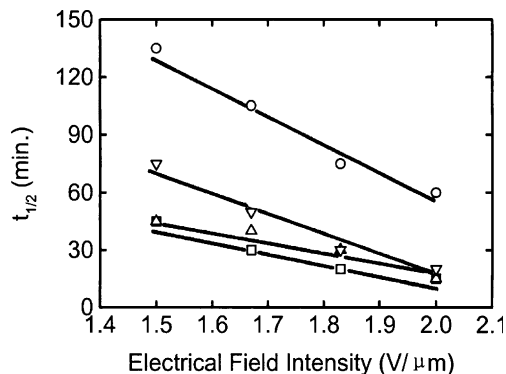


Fig. 3. Dependence of the phase separation rate $t_{1/2}$ on the intensity of the applied electrical field for various systems (□) TEB/MMA, (○) 7CB/MMA, (Δ) TEB/E51, (▽) 7CB/E51. The LC content is 75 wt%.

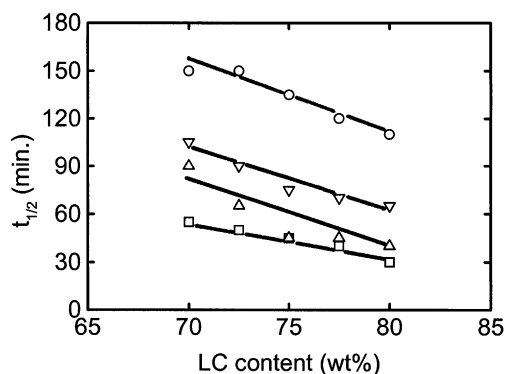


Fig. 4. Dependence of the phase separation rate $t_{1/2}$ on the LC content for various systems (\square) TEB/MMA, (\circ) 7CB/MMA, (\triangle) TEB/E51, (∇) 7CB/E51. The intensity of the applied electrical field is $1.50 \text{ V}/\mu\text{m}$.

increases. This reveals that the LC content also affects the phase separation rate. In the absence of the electric field, this kind of phenomenon can also be found.

From the $t_{1/2}$ values in Figs. 3 and 4, it can be noted that the phase separation rate of the 7CB systems is slower than that of the TEB systems. It is also found that the induction time of the 7CB systems is longer than that of the TEB systems and this long induction time cannot be shortened much in the presence of the electric

field. According to Kyu et al. [19], such difference may be attributed to the difference between these two kinds of LC. For TEB, it is a multi-component LC and contain many different kinds of LC. These components have different affinities to the matrix material. The components with poorer affinities to the matrix material may separate from the matrix earlier, which gives rise to higher phase separation rate and shorter induction time for the TEB systems. On the other hand, 7CB is a pure LC. So the phase separation of this system cannot be detected until the polymer chain becomes long enough and the component is incompatible with the matrix material.

3.2. Effect of the electric field on the clearing temperature (T_{NI}) of the formed PDLC films

The external electric field not only has remarkable influence on the kinetics of the phase separation but also the formed morphologies and subsequent clearing temperatures (T_{NI}) of the PDLC films.

Fig. 5 shows the morphologies of the 7CB/PMMA films that were polymerized under electric field with various intensities. Prepared without electric field, the LC domains are rather large and coarse. But in the presence of the electric field, due to the effect of the electric field, the phase separation becomes faster,

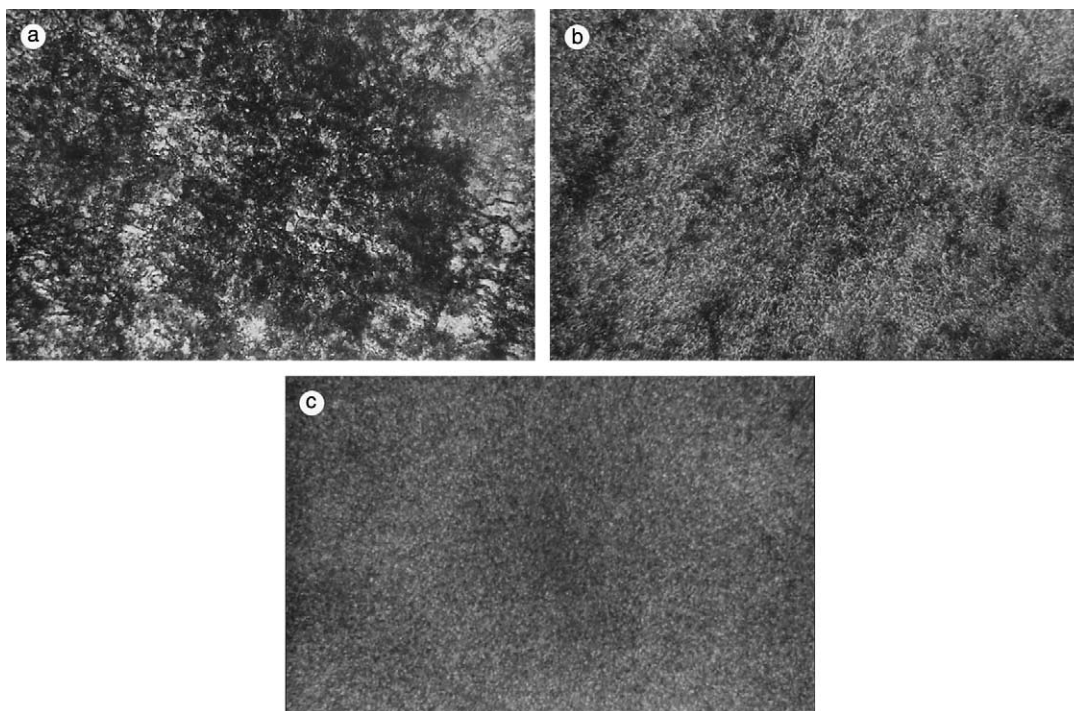


Fig. 5. Morphologies of 7CB/MMA (75/25, wt/wt) films prepared under electrical field with intensity of (a) $0 \text{ V}/\mu\text{m}$, (b) $1.50 \text{ V}/\mu\text{m}$, (c) $2.00 \text{ V}/\mu\text{m}$ (crossed polars $\times 320$).

which has been discussed in the former section. For this effect, the domains have less chance to move and collide with each other, and the growing LC domains is arrested by the polymer chains or networks early. So small domains and fine morphologies forms, as it can be seen from Fig. 5. As for other three systems, the effect of the electric field on the morphologies shows strong resemblance to that of the 7CB/PMMA films.

Fig. 6 shows the clearing temperature (T_{NI}) of the 7CB/PMMA films, for which the electric field with various intensities was applied during the phase separation process. It can be seen that the T_{NI} of the 7CB/PMMA films increases with the intensity of the applied electric field. For example, as for the mixture containing 70 wt% 7CB, the T_{NI} equals 35 °C when the electric field is absent. But under 1.67 V/ μm , the T_{NI} can be increased to 37 °C. And the T_{NI} can be even increased to 40 °C when the electric field intensity equals 2.00 V/ μm . In the present work, such experiments have also been performed on other three systems. The same result that the T_{NI} increases with the electric field intensity was obtained.

Fig. 7 shows the T_{NI} values as a function of electric field intensity for all the four systems. The effect of the electric field on the T_{NI} is more explicitly exhibited. It can be seen that the T_{NI} increases with the electric field intensity for all the four systems examined.

It is well known that, during the phase separation process, the dissolved LC separates from the increasing polymer chains with the progression of the polymerization and is segregated by the polymer chains or polymer network [2,20]. Subsequently, the LC domains come into existence. For ideal condition, the LC and monomers are completely separated after polymerization and the T_{NI} just equals that of the pure LC. But in fact, some monomers and LC are mutually dissolved and some monomers leave in the LC domains after polymerization. For this reason, the purity of the LC domain decreases, which leads to the lower T_{NI} of the PDLC films [20].

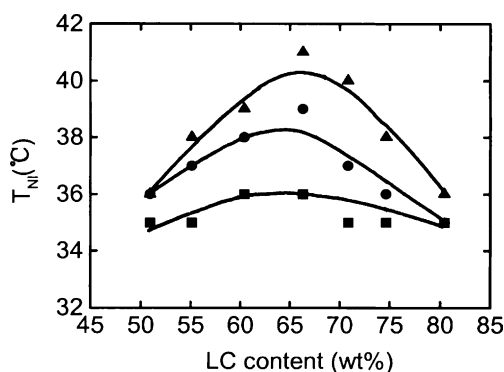


Fig. 6. Plots of clearing temperature T_{NI} versus LC content for 7CB/PMMA films prepared under electrical field with intensity of (■) 0 V/ μm , (●) 1.67 V/ μm , (▲) 2.00 V/ μm .

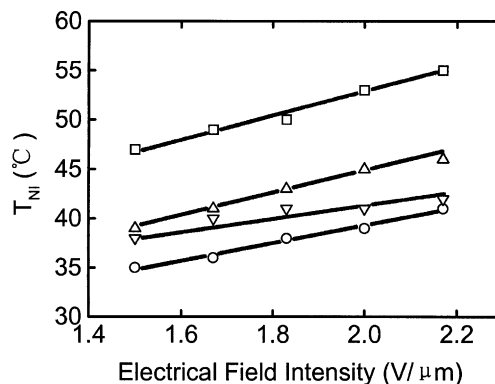


Fig. 7. Dependence of the clearing temperature T_{NI} of PDLC films on the electrical field intensity for various systems (□) TEB/MMA, (○) 7CB/MMA, (Δ) TEB/E51, (▽) 7CB/E51. The LC content is 60 wt%.

In the present work, it is noted that the T_{NI} for 7CB/PMMA are well below the values of the pure LC. The lower T_{NI} could be attributed to the well mutual solubility between the LC and matrix material, even the LC content is high or low. This explanation can get support from the evidence that the broadness of the T_{NI} is relative wider than that of the pure one. In a separate experiment (7CB/MMA system), it was shown that the T_{NI} exhibits a tendency of increase when the LC content increases from 80 to 95 wt%. However, when the LC content is too high, the sample becomes difficult to be cured and forms a film. For the system, where the LC content is lower than 50 wt%, no phase separation occurs. Therefore, the change of the T_{NI} cannot be observed.

When an electric field is applied during the phase separation process, as mentioned above, due to the higher dielectric constant, the electro-polarized intensity of the LC is larger than that of the matrix material under the same electric field, which then results in the increasing driving force of the phase separation process. Due to this increasing driving force, less monomer may leave in the LC after phase separation, thereafter the purity of the LC domains and the T_{NI} increases. The higher the intensity of the electric fields, the higher the purity, which then raises the T_{NI} .

It has been demonstrated that, for nematic LC, only they in the nematic phase contribute positively to electro-optical performance in PDLC [13]. So the operational temperature range of this kind of material is the nematic range of the LC. In this work, the PDLC films with higher T_{NI} (or wide operational temperature range) were obtained when the electric field was applied during the phase separation process. Such results obtained through the investigation may find important applications in the fabrication of the PDLC films.

4. Conclusion

In this work, the external DC electric field with different intensities was applied during the phase separation process for various LC/monomer systems. The effect of the electric field on the phase separation rate, morphologies and the clearing temperature (T_{NI}) of the formed PDLC films were studied. The obtained results are summarized as follows:

- (1) The phase separation process can be accelerated by the electric field applied during the phase separation process.
- (2) The electric field applied during the phase separation process yields the PDLC films with small LC domains and fine morphologies.
- (3) The clearing temperature (T_{NI}) of the formed PDLC films are raised by the electric field applied during the phase separation process. And the higher T_{NI} can widen the operational temperature range of the PDLC films.

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