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Study on selective reflection properties of chiral nematic liquid crystalline composites with a non-uniform pitch distribution

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The preparation is reported of particles of photopolymerisable monomer/chiral dopant composites with a crystalline (Cr)-chiral nematic (N*) phase transition. By mixing particles with different pitches of the N* phase in the Cr phase and crosslinking the liquid crystal (LC) monomer molecules by photopolymerisation in the planarly oriented N* phase, an N*-LC composite film with a non-uniform pitch distribution was obtained. Experimental results show that the bandwidth of the reflection spectrum and the location of reflection band of the composite films can be controlled accurately by controlling the pitch lengths of the N* phase of the particles. Effects of polymerisation temperature and UV intensity on the non-uniform pitch distribution of N*-LC composite films were investigated.

Keywords: non-uniform pitch distribution; chiral nematic composite; photopolymerisation; selective reflection

1. Introduction

A chiral nematic liquid crystal (N*-LC) is formed when a nematic LC (N-LC) is doped with a chiral dopant. In the N* phase, the long axis of the LC molecules rotates about a helix. The pitch length, P, of the helix corresponding to a 2π molecular rotation is determined by the concentration of the chiral dopant, decreasing with increasing fraction of the chiral dopant. One of the important features of a N*-LC is its unusual optical property of selective reflection of circularly polarised incident light; i.e. light with the same handedness as the N*-LC helix can be reflected within a bandwidth (*1, 2*). The bandwidth of the selective reflection spectrum, $\Delta\lambda$, is given by $\Delta\lambda=\Delta nP$, where Δn is the birefringence. The location of the reflection band, λ, is related to the pitch length, P, and the mean refraction index, n, by $\lambda=nP$. Since the Δn value for colourless organic materials is typically below 0.3, the bandwidth of a single-pitch N*-LC in visible regions is <150 nm. N*-LC composite films with a pitch gradient or non-uniform pitch distribution can reflect light with much wider bandwidths than a single-pitch N*-LC (*3–11*). These types of composite films are very attractive as reflective LC displays (*12, 13*), brightness-enhancement films for LC displays when the bandwidth covers the visible spectrum (*3*), glass films for buildings to block infrared radiation, thus reducing unwanted rays from the sun when the reflection range is located in near-infrared region (*14*), or other optical elements (*4, 15–17*).

N*-LC composite films with a pitch gradient were obtained by Broer *et al.* (*3*) from the photopolymerisation of a composite comprising N*-LC diacrylate monomer/N-LC monoacrylate monomer/dye/photoinitiator. A UV intensity gradient was formed over the film thickness owing to the presence of a UV-absorbing dye. Thus, a pitch gradient was achieved by photo-induced diffusion during the crosslinking reaction occurring in N*-LC and N-LC monomers with different UV reactivities. The N*-LC composite films prepared with a pitch gradient were able to reflect circularly polarised incident light over the wavelength range 400–750 nm (*3*). A systematic study of N*-LC composite films with a non-uniform pitch gradient has also been carried out by Yang and co-workers (*8–11*).

In this paper, a simple method is reported for preparation of N*-LC composite films with a non-uniform pitch distribution. In contrast to the films mentioned above, this novel method does not require complicated synthesis of the N*-LC diacrylate monomer and precise control of UV intensity gradient, whereas $\Delta\lambda$ and λ can be controlled accurately according to experimental design. Effects of polymerisation temperature and UV intensity on the non-uniform pitch distribution of N*-LC composite films were investigated. The mechanisms of formation of the non-uniform pitch distribution were studied in detail and the experiments clarifying the controllable reflection are described.

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2. Experiments

Materials

The photopolymerisable monomer (PPM) 1,4-bis{4-[(6-acryloyloxy)hexyloxy]- benzoyloxy}-2-methylbenzene and chiral dopant ZLI-4572 were used as components of the PPM/chiral dopant composites. PPM was synthesised according to the method suggested by Broer *et al.* (*18*). ZLI-4572 was purchased from Merck Co, Ltd. and used without further purification. 2,2-Dimethoxy-2-phenylacetophenone, a photoinitiator (PI), and the inhibitor *p*-methoxyphenol were purchased from TCI, Ltd. and also used without further purification. Figure 1 shows the chemical structures and phase transition temperatures of PPM and ZLI-4572.

Preparation of PPM/ZLI-4572 composite particles

Different weight ratios of PPM/ZLI-4572 were dissolved in acetone with 50 ppm of inhibitor added to prevent thermal polymerisation. After the acetone was evaporated completely, PPM/ZLI-4572 composites for samples S1–S8 were prepared. Then, samples S1–S8 were crushed using an agate mortar and pestle at room temperature and filtered in a fine mesh filter with a mesh size of 3.0 µm. The particle sizes were measured using a calibrated optical microscope after a monolayer coating of sample particles was deposited on a microscope slide. The compositions of samples S1–S8 are listed in Table 1.

Preparation of mixtures with different pitch of N phase*

Mixtures M1, M2, M3 and M4 were prepared by thoroughly mixing the appropriate weight proportions of particles of samples S1, S2 and S4, samples S2 and S4, samples S2, S3 and S5 and samples S6, S7 and S8, respectively, doping each mixture with 0.5 wt % PI and totalling each final mixture to 100 wt % at room temperature. Then, each mixture was milled and ground again using an agate mortar and pestle for at least 30 min to ensure that an even mixture was obtained. The compositions of mixtures M1–M4 are listed in Table 2.

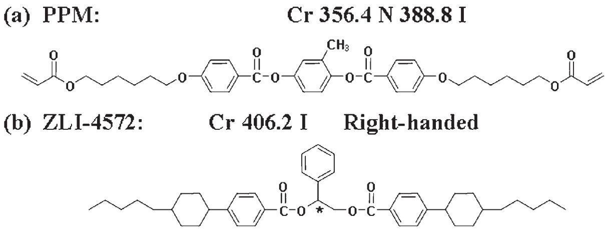

Figure 1. The chemical structures and phase transition temperatures of (a) PPM and (b) ZLI-4572.

Table 1. The compositions of samples S1–S8.

Sample	C6M/ZLI-4572/wt %
S1	98.1/1.9
S2	97.4/2.6
S3	96.6/3.4
S4	95.8/4.2
S5	95.0/5.0
S6	93.7/6.3
S7	91.0/9.0
S8	87.8/12.2

Table 2. The compositions of mixtures M1–M4.

Mixture	Composition/wt %
M1	S1/S2/S4=33.4/33.3/33.3
M2	S2/S4=50.0/50.0
M3	S2/S3/S5=33.4/33.3/33.3
M4	S6/S7/S8=33.4/33.3/33.3

Preparation of N-LC composites films with non-uniform pitch distribution*

Each mixture was heated to the N* phase temperature and kept for 5 min at that temperature without any stirring under vacuum to ensure that no air was left in the mixture. Subsequently, after a 50 µm thick glass cell, the inner surfaces of which had been treated for homogeneous orientation of LC molecules, had been preheated at the same temperature for 10 min, each mixture was filled into the cell by capillary action. The N* phase of the mixture in the cell adopted a planar texture. Finally, the cell was irradiated with UV light (365.0 nm) for about 10 min. Thus, a N*-LC composite film with a permanent helical solid structure was prepared from the photopolymerisation (*19–21*) of the molecules of PPM in the mixture.

Measurements of phase transition temperatures of samples S1–S8

The phase transition temperatures of samples S1–S8 were investigated by differential scanning calorimetry (DSC, Perkin Elmer Pyris 6) at a heating rate of 10.0 K min^{-1} under a dry nitrogen purge.

Measurements of pitch lengths of samples S1–S8

The pitch lengths of the N* phase of samples S1–S8 were measured by the Cano wedge technique (*22*). In this measurement, a wedge-shaped cell with a wedge angle, α, was used and the inner surfaces of its two

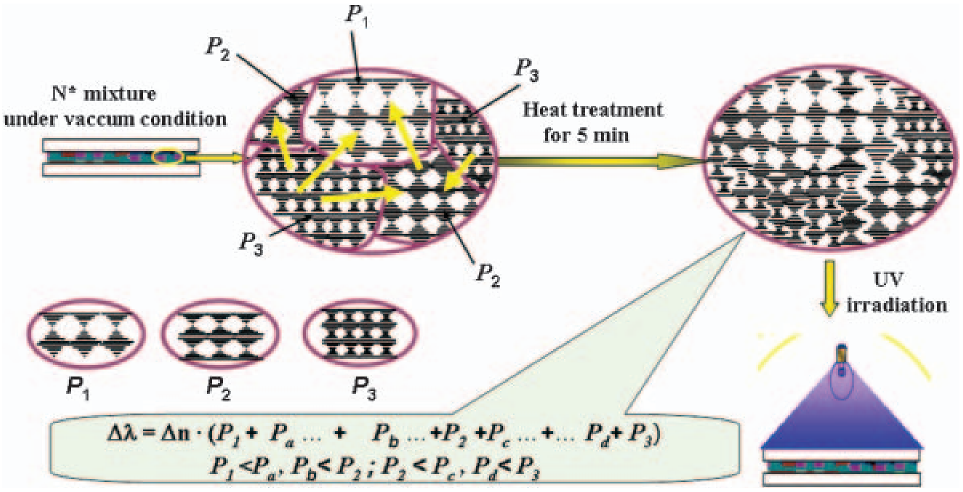

Figure 2. Schematic representation of the preparation of an N*-LC composite film with non-uniform pitch distribution.

glass substrates were treated to provide a homogeneous orientation of LC molecules. After the sample was filled into the cell in the isotropic (I) phase and then cooled to the N* phase, at some temperature a Grandjean–Cano texture formed with disclination lines separated by a distance *l*. The pitch length *P* is determined from $P=2\alpha l$ at that temperature.

Treatment for homogeneous orientation

To obtain homogeneous alignment, a 3.0 wt % polyvinyl alcohol (PVA) aqueous solution was coated onto the inner surfaces of the substrates by spinning casting. The deposited film was dried at 353.2 K for about 30 min, and subsequently rubbed with a textile cloth under a pressure of 2.0 g cm^{-2} along one direction.

Other measurements

The optical textures were observed using a polarising optical microscope (POM, Olympus BX51) equipped with a hot stage calibrated to an accuracy of ±0.1 K (Linkam LK-600PM). The transmission spectra were obtained using a UV/VIS/NIR spectrophotometer (JASCO V570) with the transmittance of an empty cell normalised to 100%. The microstructure of the N*-LC composites film was observed by scanning electron microscopy (SEM, Cambridge S250) with the freeze-fractured surface of the film coated with a thin layer of carbon to eliminate any electric charge problems.

3. Results and discussion

Design of microstructure with non-uniform pitch distribution

Various regions exhibiting different λ and non-uniform pitch gradients in the N*-LC composite films have been proved to be an effective route in broadening $\Delta\lambda$ (*8–11*). Here, the particles of samples S1–S8 with a crystalline (Cr)-N* phase transition are designed to be prepared. By mixing the particles with different pitches of the N* phase in the Cr phase and making the PPM molecules crosslink by photopolymerisation in the planarly oriented N* phase, an N*-LC composite film with a non-uniform pitch distribution will be obtained. A schematic representation of the preparation of an N*-LC composite film with non-uniform pitch distribution is shown in Figure 2.

N-LC composite films prepared from samples S1–S8*

On the basis of POM observation and DSC measurements, the phase diagram of PPM/ZLI-4572 composites was determined (Figure 3). It can be seen

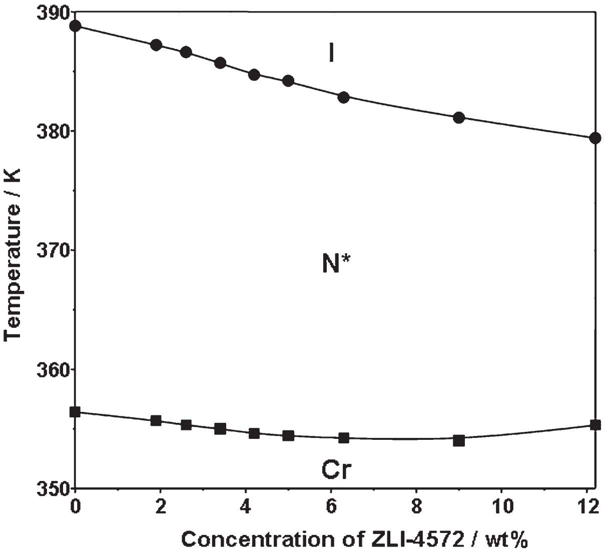

Figure 3. The phase diagram of PPM/ZLI-4572 composites.

from the phase diagram that the temperature range of the N* phase decreases with increasing ZLI-4572 concentration.

Figure 4 shows the dependence on ZLI-4572 concentration of the pitch lengths of the N* phase of samples S1–S8 and the locations of reflection band of the N*-LC composite films prepared from S1–S8. It was found that the pitch lengths of the samples are inversely proportional to the concentration of ZLI-4572. Due to the law of selective reflection, the λ of the N*-LC composite films prepared from S1–S8 shift to shorter wavelength accordingly with increasing concentration of ZLI-4572.

Polymerisation temperature dependence of Δλ in the N-LC composite films prepared from mixtures*

Figure 5 shows the polymerisation temperature dependence of Δλ in the N*-LC composite films prepared from the mixture M1 with UV intensity of 8.4 mW cm^{-2}. It can be seen that the Δλ of curves 3, 1 and 2 increase in that order and that the N*-LC composite film prepared at 368.2 K has a very broad bandwidth covering the wavelength range 1100–2500 nm.

Figure 6 shows optical textures of planar alignment of the N* phase at different temperatures for the mixture M1. It should be mentioned here that the polymerisation temperature of preparation of the N*-LC composite films, the preheating temperature of the glass cell and the filling temperature of the mixture at N* phase are the same (see section on film preparation). As shown in Figure 6, a lower viscosity at higher temperature leads to a better planarly-oriented N* phase. However, it is not difficult to understand that a lower viscosity also induces a faster diffusion of the molecules in different regions. Consequently, the N*-LC composite film prepared at 376.2 K has to have a uniform pitch distribution, which is why the Δλ of curve 3 of Figure 5 is smaller than those of curves 1 and 2. In contrast, a higher viscosity at lower temperature brings a longer diffusion time in filling the N* mixture into the glass cell, which is also inconvenient for preparation of N*-LC composite films with non-uniform pitch distribution.

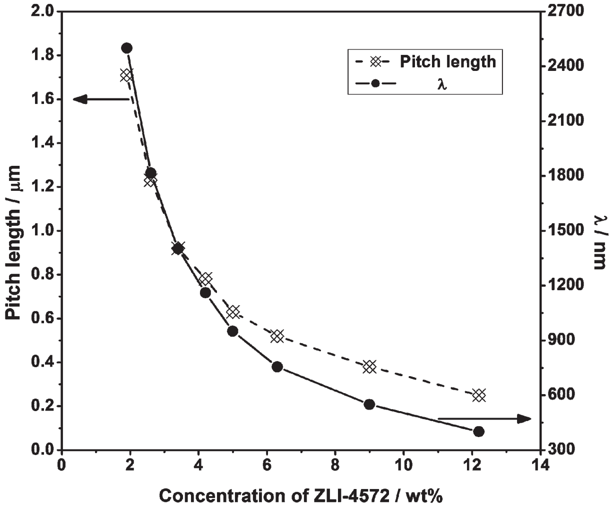

Figure 4. Dependence on ZLI-4572 concentration of the pitch lengths of the N* phase of samples S1–S8 and the locations of reflection band of the N*-LC composite films prepared from S1–S8.

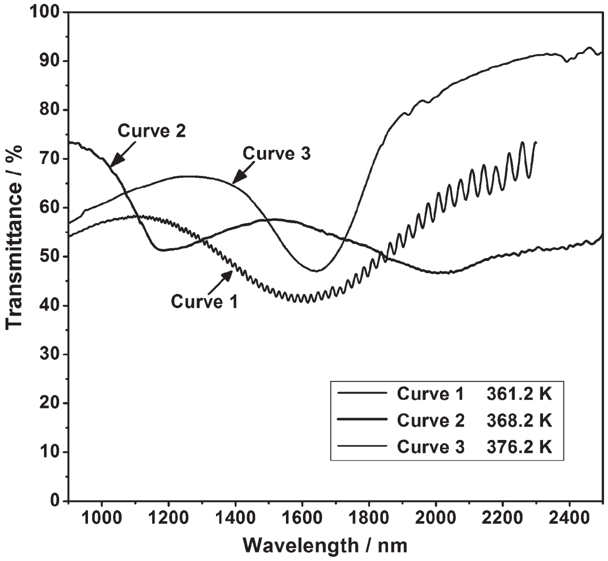

Figure 5. The polymerisation temperature dependence of Δλ in the N*-LC composite film prepared from the mixture M1 with UV intensity of 8.4 mW cm^{-2}.

Figure 7 shows the microstructures of the freeze-fractured surface of the N*-LC composite films prepared at different temperatures. It is clear that there are different pitch lengths in different regions, such as domains I, II, III and IV, as shown in Figure 7(b). Due to the diffusion of the molecules, the pitch length at the interfaces between two domains should be between the values of the two domains. Thus, a non-uniform pitch distribution forms inside of the composite film. In comparison, the N*-LC composite films prepared at 376.2 K or 361.2 K have a uniform pitch distribution or only a little non-uniform pitch distribution, as shown in figures 7(c) and 7(a), respectively. This demonstrates that the above explanation is reasonable.

UV intensity dependence of Δλ in the N-LC composite films prepared from mixtures*

Figure 8 shows the UV intensity dependence of Δλ in the N*-LC composite films prepared from the mixture M1 at 368.2 K. It can be seen that the Δλ

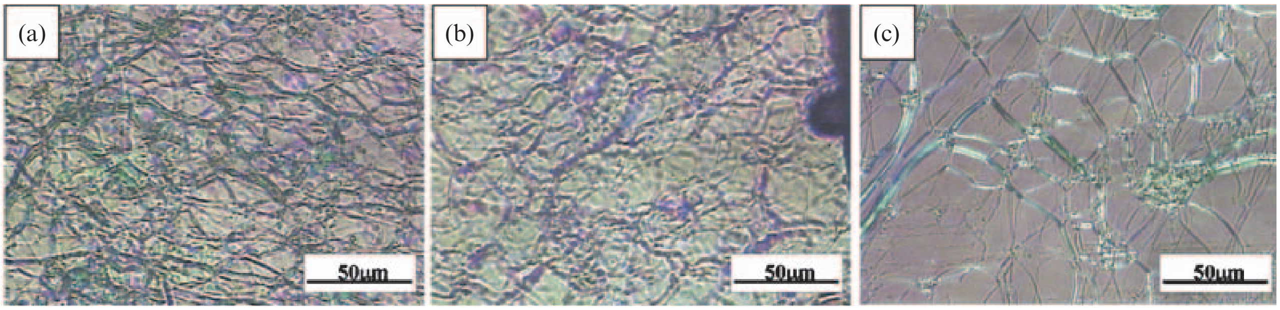

Figure 6. The optical textures of planar alignment of the N* phase at different temperatures for the mixture M1: (a) 361.2 K; (b) 368.2 K; (c) 376.2 K.

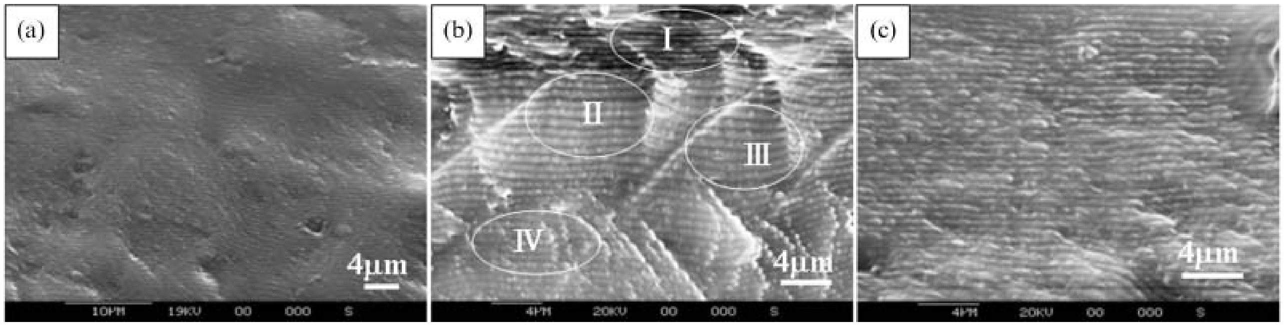

Figure 7. The microstructures of the freeze-fractured surface of the N*-LC composite films prepared at different temperatures: (a) 361.2 K; (b) 368.2 K; (c) 376.2 K.

of curve 1 was much smaller than that of curve 2. The possible reason is that the weak UV intensity is not sufficient for the timely initiation of photopolymerisation and thus induces the formation of a N*-LC composite film with a uniform pitch distribution.

Experiments on controlling reflection in the N-LC composite films prepared from mixtures*

Figures 9(a)–9(c) show the transmission spectra of the N*-LC composite films prepared from samples S1–S8 and mixtures M1–M4 at 368.2 K with UV intensity of 8.4 mW cm^{-2}. It can be seen that the $\Delta\lambda$ of the transmission spectra of the films prepared from mixtures M1–M4 are much broader than those of the films prepared from samples S1–S8 for which the N* phases had a single pitch. The $\Delta\lambda$ of the transmission spectra of the films prepared from mixtures M1–M4 were approximately located in the wavelength ranges 1100–2500 nm, 1100–1900 nm, 900–1900 nm and 400–800 nm, respectively. It can also be seen that the $\Delta\lambda$ of the composite films prepared from the crosslinked mixtures can be controlled accurately by adjusting the distribution of the pitch lengths of the N* phase of the particles before crosslinking, whereas the reflection bands of the composite films can be located in different wavelength ranges by adjusting the average values of the pitch lengths.

Figure 10 shows the microstructures of the freeze-fractured surface of the N*-LC composites films prepared from mixtures M2–M4. As can be seen in Figures 7(b) and 10, the pitch lengths in different regions are different and the maximum and the minimum values are approximately equal to those of

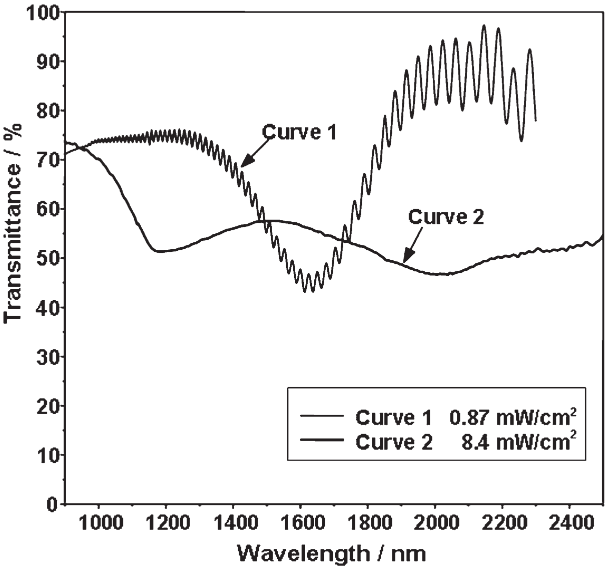

Figure 8. The UV intensity dependence of $\Delta\lambda$ in the N*-LC composite film prepared from the mixture M1 at 368.2 K.

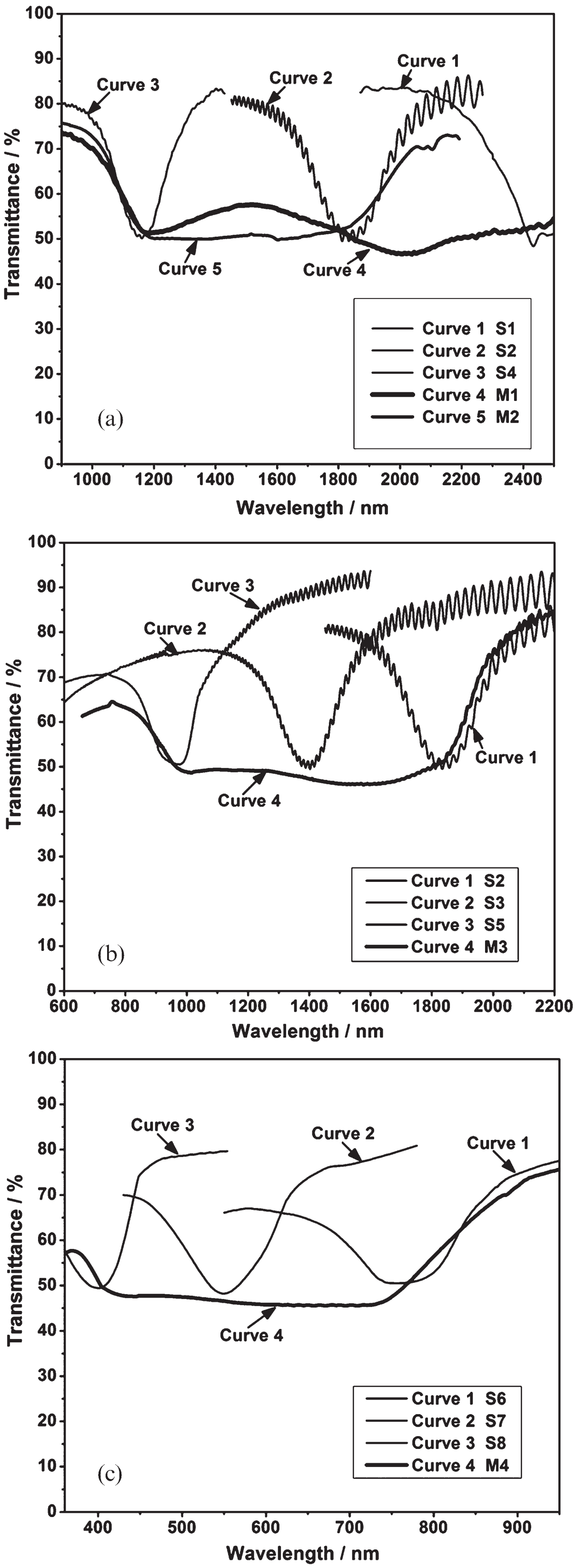

Figure 9. The transmission spectra of the N*-LC composite films prepared from samples S1–S8 and mixtures M1–M4 at 368.2 K with UV intensity of 8.4 mW cm^{-2}.

the N* phases of corresponding samples. These experimental results are in accordance with the microstructure design of the N*-LC composite films with non-uniform pitch distribution mentioned above.

In the experimental method, particles with different pitches of the N* phase were mixed in the Cr phase and polymerised in the planarly oriented N* phase to obtain a non-uniform pitch distribution. Frontiers between local regions with different pitches can be divided into continuous frontiers and discontinuous frontiers. Three possible circumstances of pitch gradient, pitch jump and pitch deformation have been discussed. Due to molecular diffusion, pitch gradient could be obtained between the local regions with the continuous frontiers (*23*), as shown schematically in Figure 11(a). The discontinuous frontiers separate local regions that have different pitches. A coarsened helical texture jumps into a non-helical state at a certain point in the direction parallel to the helix axes (*24, 25*), as shown schematically in Figure 11(b). Correspondingly, deformed helical structures form in the N*-LC composites because of the pitch mismatch between local regions with the discontinuous frontiers in the direction vertical to the helix axes, as shown schematically in Figure 11(c). It has been proved that the pitch inhomogeneity in the deformed helical structures obtained by strain, flow or external fields (*23, 24, 26, 27*) broadens the reflection band and decreases the peak reflectance. This well explains the possible origin of the weak transmitted intensity in Figure 5.

A well-oriented planar texture plays a crucial role in the optical performances of the prepared N*-LC composite films. It is well known that the light scattering phenomenon occurs due to a focal conic texture exhibiting polydomains (*23*). As shown in the POM and SEM photographs mentioned above, the prepared N*-LC composites have a good planar Grandjean texture. The refractive index of the N*-LC composites in the direction vertical to the cell substrate is almost the same. Furthermore, the transmittance spectra are all continuous. Taking the deformed helical structures in local regions with discontinuous frontiers into account, the little light scattering that may arise from the prepared N*-LC composites should be non-apparent and inessential.

4. Conclusions

In this study, particles of PPM/ZLI-4572 composites with a Cr-N* phase transition were prepared. By mixing particles with different pitches of the N* phase in the Cr phase and making PPM molecules

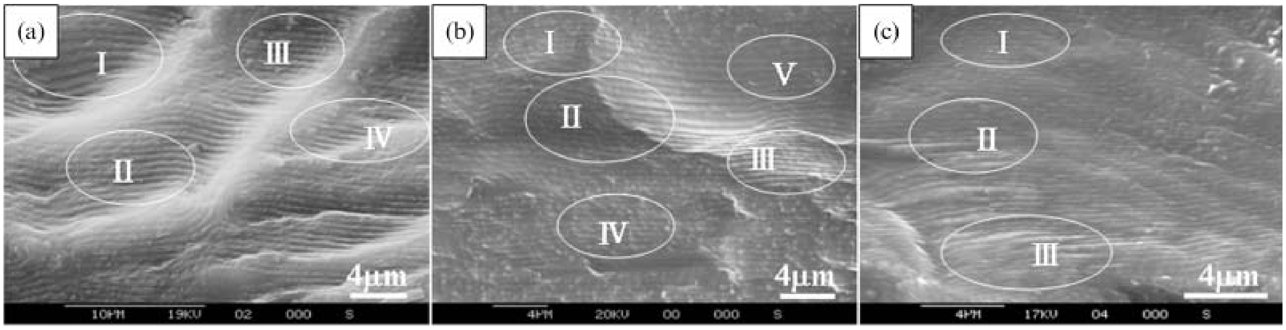

Figure 10. The microstructures of the freeze-fractured surface of the N*-LC composite films prepared from mixtures M2–M4: (a) M2; (b) M3; (c) M4.

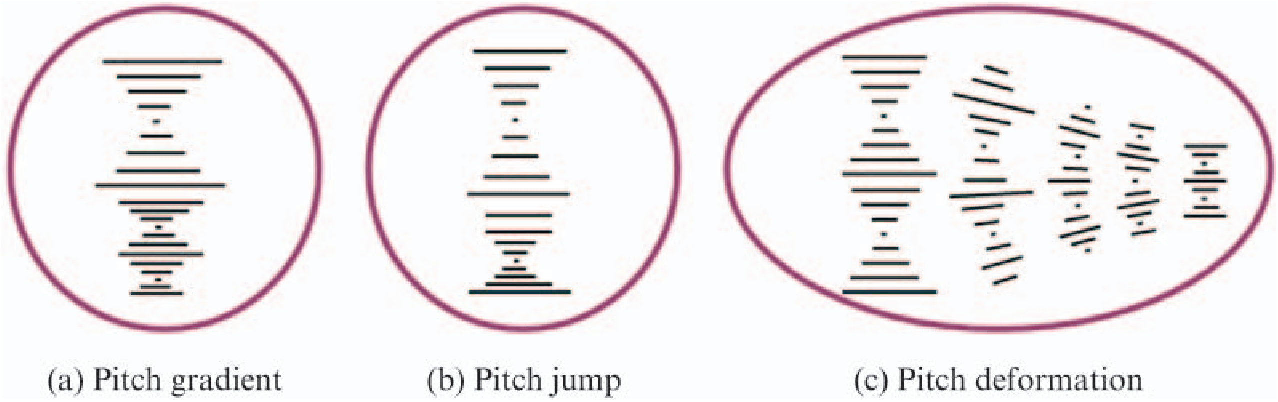
(a) Pitch gradient (b) Pitch jump (c) Pitch deformation

Figure 11. The schematic representation of three possible circumstances in the frontiers between local regions with different pitches: (a) pitch gradient; (b) pitch jump; (c) pitch deformation.

crosslink by photopolymerisation in the planarly oriented N* phase, an N*-LC composite film with a non-uniform pitch distribution was obtained. By adjusting the pitch lengths of the N* phases of the crystalline PPM/ZLI-4572 particles in the mixture before crosslinking, both the λ located in the range of visible or near-infrared region and the $\Delta\lambda$ of the composite films can be controlled accurately. Appropriate polymerisation temperature and UV intensity play important roles in formation of a non-uniform pitch distribution. Higher and lower temperatures lead to form a uniform pitch distribution because of faster molecular diffusion and longer diffusion time, respectively. Weak UV intensity, which is not sufficient to initiate timely photopolymerisation, also induces formation of a uniform pitch distribution.

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