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A study of electro-optical properties of PDLC films prepared by dual UV and heat curing

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Polymer-dispersed liquid crystal (PDLC) films were prepared by dual UV and heat curing from UV- and heat-curable monomers. For PDLC films with a certain amount of the UV- and heat-curable monomers, the mesh size (the size of LC domains) of the polymer network could be adjusted by adjusting the relative content of the two types of monomers, enabling the electro-optical properties of the film to be optimised.

Keywords: polymer-dispersed liquid crystal; UV curing; heat curing; electro-optical properties

1. Introduction

Polymer-dispersed liquid crystal (PDLC) films are composite materials that consist of micron-sized liquid crystal (LC) droplets embedded in a solid polymer matrix (*1*). They have been the subject of intensive studies because of both fundamental interest and potential applications. Their unique optical and electro-optical properties make them suitable for applications in various technological fields, such as flexible large-scale displays, smart windows and other devices (*2–4*).

A PDLC film exhibits transparent and light-scattering states in the electric field-on and field-off states, respectively. In the field-off state, surface anchoring of the LC to the polymer wall causes a non-uniform director field in the LC droplets (*5–11*). Thus the PDLC film scatters light due to the mismatch between the effective refractive index (n_{eff}) of the LC and the refractive index of the polymer (n_{p}). In the field-on state, LCs of positive anisotropy tend to align themselves with the directors parallel to the field direction. In this state, the refractive index for incident light is equal to the ordinary refractive index (n_{o}), and if n_{o} is matched with n_{p}, the films become transparent.

The most common methods for the preparation of PDLC films are the phase separation methods, including polymerization-induced phase separation (PIPS), thermally induced phase separation (TIPS) and solvent evaporation induced phase separation (SIPS) (*5*). Nicoletta *et al.* (*6*) investigated the electro-optical properties of PDLC films obtained by a two-step phase separation process, which was performed by TIPS at the first step and then by PIPS for the second step. In this work, PDLC films were prepared by a two-step UV curing and heat curing process, according to the PIPS method.

In this paper, we report the results of a detailed study of the electro-optical and morphological properties of PDLC films that produced by a dual UV and heat curing procedure. That is, the PDLC films were first cured under UV radiation and then subjected to a heat curing process. The effects of UV and heat curing processes on the electro-optical properties of PDLC films have been studied.

2. Experimental

In this study, the UV curable monomers were a mixture of isobornyl methacrylate, 2-hydroxypropyl acrylate, 3,5,5-trimethylhexyl acrylate, 1,4-butanediol diacrylate and 3-(trimethoxysilyl)propyl acrylate (all provided by Aldrich Co. Ltd.). The heat curable monomers used were a mixture of diglycidyl ether of bisphenol A (DGEBA) resin (DER 332, with an average degree of polymerization $n=0.03$, Dow Chemicals Co. Ltd.), polyoxypropylene diamine (Jeffamine D-400, Huntsman Co. Ltd.) and epoxy acrylate (EA, Tianjin Tianjiao Chem. Co. Ltd.), which were mixed with a stoichiometric ratio: amino hydrogen/epoxide functions=1.0. Figure 1 shows the chemical structures of these materials.

The nematic LC (SLC1717, $T_{\mathrm{NI}}=365.2\,\mathrm{K}$, $n_{\mathrm{o}}=1.519$, $n_{\mathrm{e}}=1.720$, Shijiazhuang Yongsheng Huatsing Liquid Crystal Co. Ltd.) was added at a content of 68.0 wt % to curable monomers with 2.0 wt % Irgacure 651 (Jingjiang Hongtai Chem. Co. Ltd.) as UV initiator.

In this work, PDLC films were prepared by the means of a dual UV and heat curing process and the following method (*10*) was adopted in the UV curing process. The homogeneous solution, as listed in Table 1, was sandwiched between two pieces of

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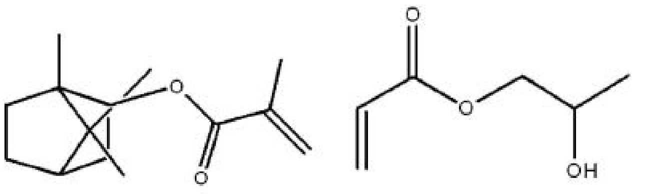
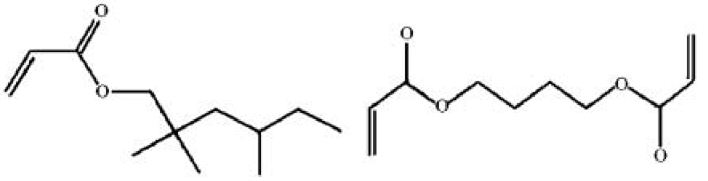
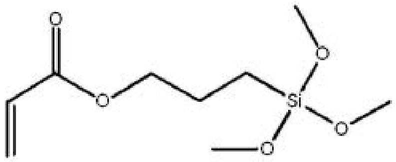


(a) isobornyl methacrylate (b) 2-hydroxypropyl acrylate

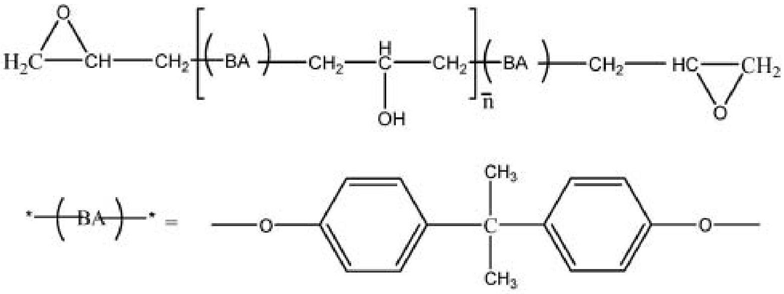


(c) 3,5,5-trimethylhexyl acrylate (d) 1,4-butanediol diacrylate



(e) 3-(trimethoxysilyl)propyl acrylate

DGEBA, *n* = 0.03



Jeffamine D-400

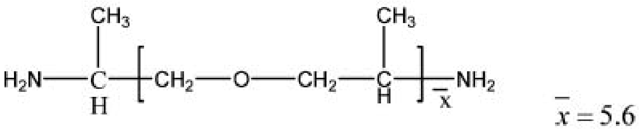


Figure 1. The chemical structures of the UV- and heat-curable monomers.

indium tin oxide (ITO)-coated plastic films and cured by a UV lamp (20.0 mW cm^{-2}, 365 nm) for 10.0 min at 273.2 K before being heated in an oven at 363.2 K for various times, as also shown in Table 1. The thickness of the films was adjusted to 20.0 μm by using glass bead spacers.

The electro-optical properties of the PDLC films were measured using an LCD parameters tester (LCT-5016C, Changchun Liancheng Instrument Co. Ltd.). A halogen laser beam (560 nm) was used as the incident light source. The transmittance of the PDLC films was recoded by a photodiode, and the response of the photodiode was monitored by a digital storage oscilloscope. An electric field square wave (100 Hz) was used and the distance between the PDLC film and photodiode was 300 mm.

Table 1. The compositions and the heat curing conditions of the samples studied.

Sample	UV curable monomers/wt %	Heat curable monomers/wt %	SLC1717/wt %	Photo-initiator/wt %	Heat curing time/h
1	20.0	10.0	68.0	2.0	0
2	20.0	10.0	68.0	2.0	1.0
3	20.0	10.0	68.0	2.0	2.0
4	20.0	10.0	68.0	2.0	3.0
5	20.0	10.0	68.0	2.0	4.0
6	20.0	10.0	68.0	2.0	5.0
7	30.0	0	68.0	2.0	5.0
8	25.0	5.0	68.0	2.0	5.0
9	20.0	10.0	68.0	2.0	5.0
10	15.0	15.0	68.0	2.0	5.0
11	10.0	20.0	68.0	2.0	5.0
12	5.0	25.0	68.0	2.0	5.0
13	0	30.0	68.0	2.0	5.0

UV–visible spectra of off-state PDLC films were measured using a UV/visible/NIR spectrophotometer (Jasco V-570). The wavelengths studied were in the range 300–800 nm and the results were recorded with an incident angle, $\delta=0°$.

The sol/gel fractions were obtained to determine the reaction degree for the various UV and heat curing conditions. First of all, a homogeneous solution of UV-curable monomers/heat-curable monomers/SLC1717/Irgacure 651 (20.0/10.0/68.0/2.0, by weight) was sandwiched between two pieces of ITO plastic films. Then, the UV curing and heat curing processes were applied. The heat curing process was stepped by a sufficient UV curing procedure that lasted for 10.0 min. After the UV and heat curing process, the solid films, which were also adjusted to 20.0 μm by glass bead spacers, were peeled off from the ITO films. The soluble materials in the solid films were extracted in acetone for 72 h and then the extracted films were dried in vacuum at 333.2 K for 10 h. The gel fraction was taken as the ratio of the weight of the extracted film to that of the non-extracted one and five parallel groups of samples were weighed to obtain an average value.

The morphology of the polymer network of the PDLC films was studied by scanning electron microscopy (SEM, Cambridge S360). The film was first separated, and then dipped into *n*-hexane for 24 h at room temperature, and then the polymer network was dried for 12 h under vacuum. The films were sputtered with carbon before the observation of the microstructure of the polymer network under SEM.

3. Results and discussion

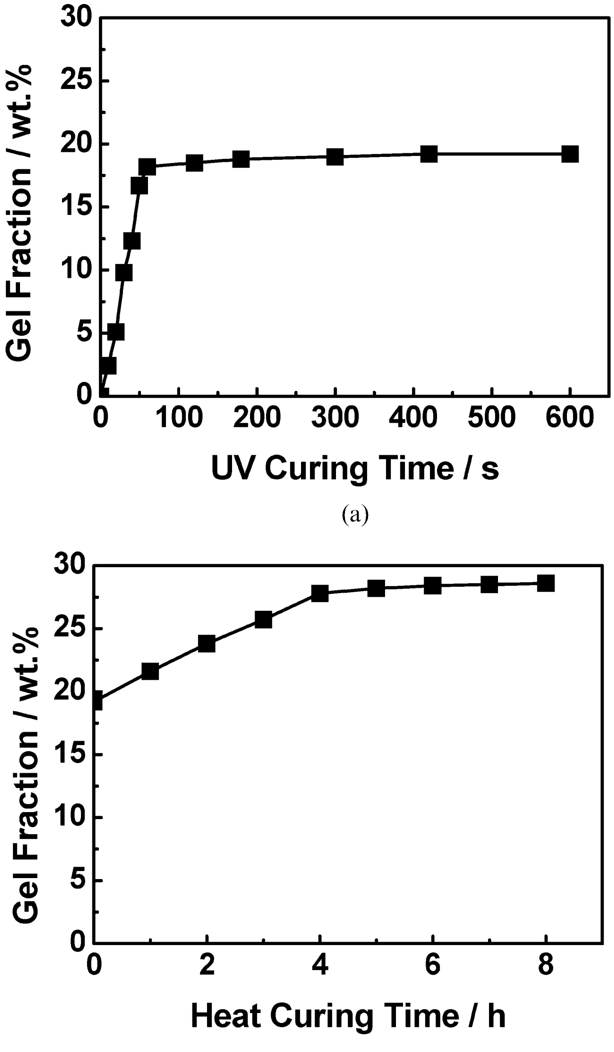
Sol/gel fractions of the dual UV and heat cured films from curable monomers

Figure 2 (a) shows the dependence on UV curing time of the gel fraction of the samples prepared by UV curing and Figure 2(b) shows the dependence on heat curing time of the gel fraction of the samples after they had been UV cured for 10 min. In this experiment, the weight ratio of the UV-curable monomers/heat-curable monomers/SLC1717/Irgacure 651 was 20.0/10.0/68.0/2.0 and the solid films were peeled off from the ITO films after specific curing process. The gel fraction of the samples increased markedly after the first 2 min of UV radiation, and then it remained almost constant at about 19.2 wt %, as shown in Figure 2(a). Figure 2(b) shows that the gel fraction of the samples increased with heat curing time and changed little from a value of about 28.2 wt % after a heat curing time of 5.0 h. The result indicates that the UV monomers had reacted almost completely in the UV curing stage and seldom participated in the following heat curing process. Meanwhile, the result also means that the heat curable monomers did not take part in the UV curing process.

Morphology of polymer matrix in PDLC films

Figure 3 shows the SEM micrographs of samples 1, 4 and 6 obtained with different heat curing times, i.e. 0.0 h, 3.0 h and 5.0 h, respectively. As can be seen in Figure 3, the crosslinking density of the samples monotonically increased with the heat curing time; in other words, the mesh size of the polymer network decreased with the duration of the heat curing process. After the UV curing process, the polymer network that formed from the UV-curable monomers is shown in Figure 3 (a). More heat-curable monomers had taken part in the crosslinking process with increasing duration of the heat curing process. Therefore, the mesh size of the polymer network decreased with increasing heat curing time.

Figure 4 shows the SEM micrographs of the polymer network in samples 7–13, which contained different relative contents of the UV- and heat-curable monomers, as listed in Table 1. The mesh



(a)

(b)

Figure 2. The time dependence of the gel fractions for the samples prepared by (a) UV curing and (b) heat curing after being UV cured for 10.0 min.

sizes of the polymer network in samples 7–9 decreased, whereas those in samples 10–13 increased in the sequence.

Figure 5 shows the SEM micrographs of the polymer network formed from the UV curable monomers in samples 7–12 before application of the heat curing process. No polymer network formed in sample 13 before the heat curing process because it did not contain any UV curable monomers. As shown in Figure 5, the mesh size of the polymer network in samples 7–12 increased in the sequence. This is due to the fact that the content of the UV-curable monomers in samples 7–12 decreased in the sequence. In particular, the polymer network had collapsed somewhat in samples 10–12 after the extraction *n*-hexane because the content of the UV-curable monomers in the samples was so small that the initially formed polymer network was not strong enough to hold itself together. Although the

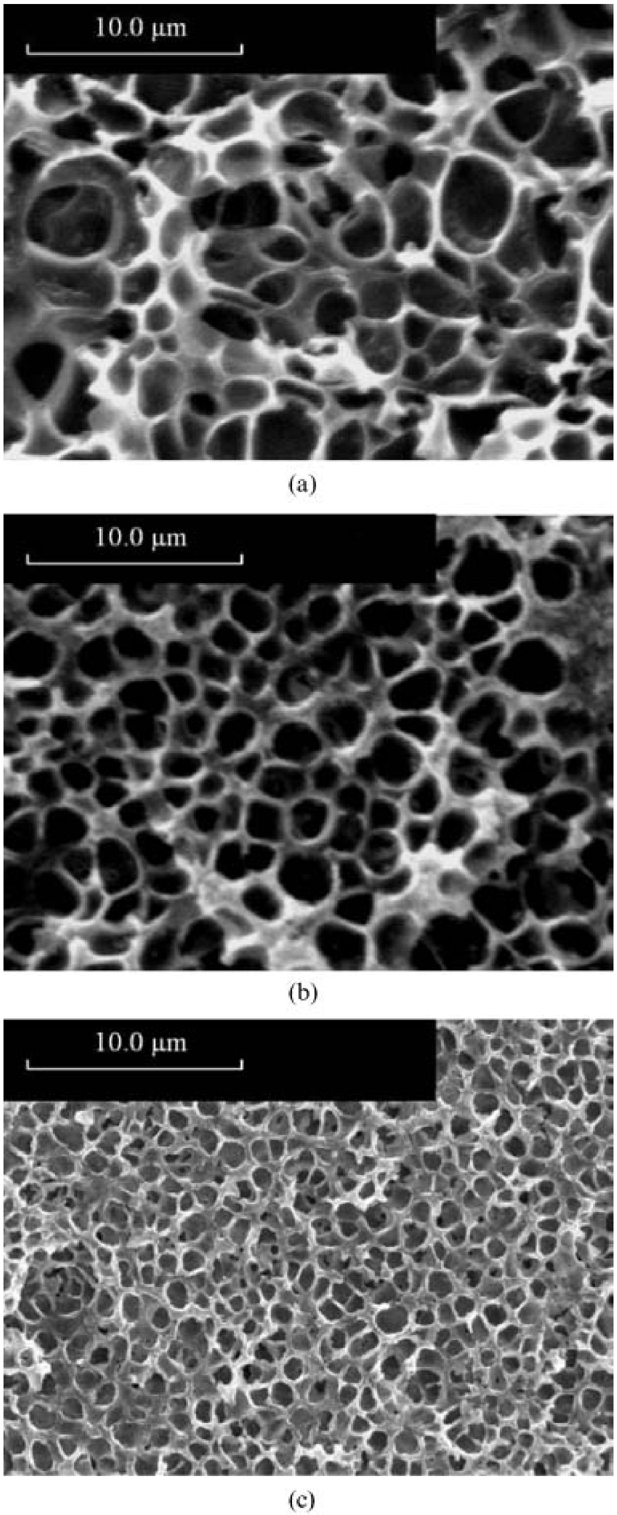
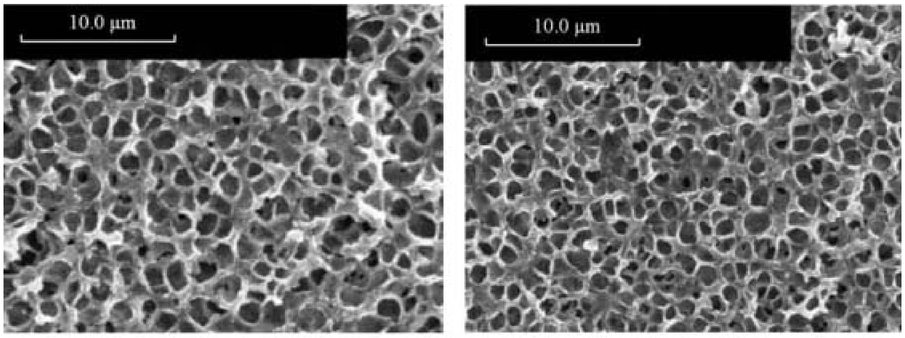
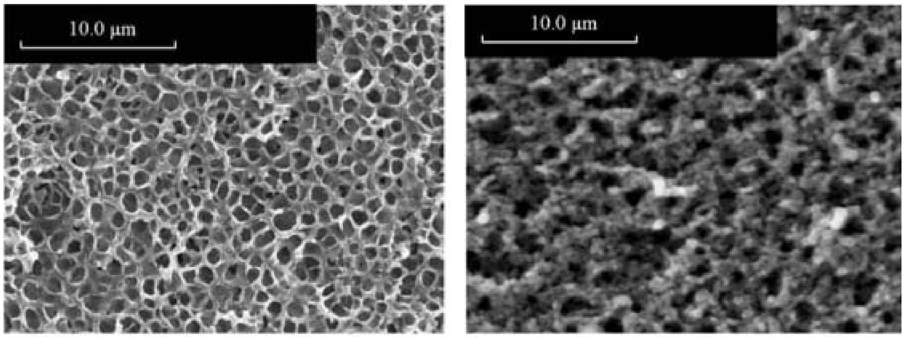


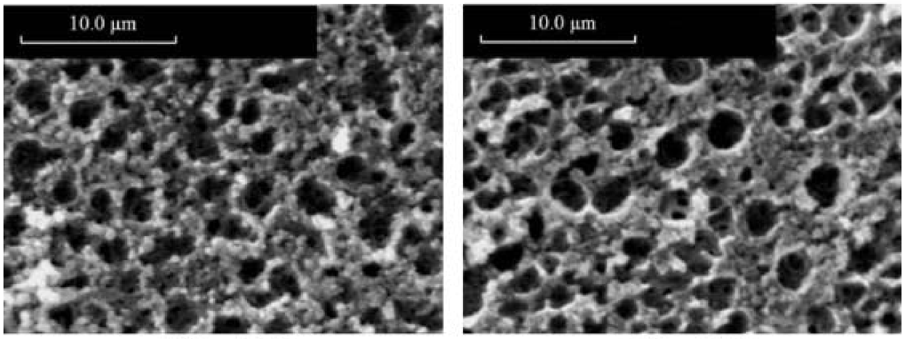
Figure 3. SEM micrographs of the polymer network of the samples (a) 1, (b) 4 and (c) 6 with different heat curing time.



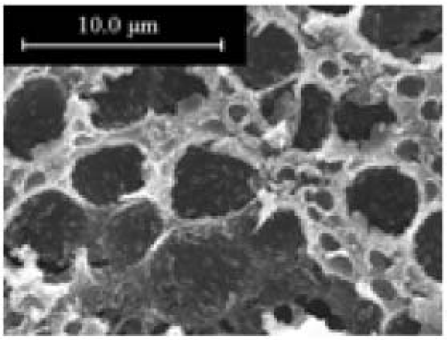
(a) Sample 7 (b) Sample 8



(c) Sample 9 (d) Sample 10



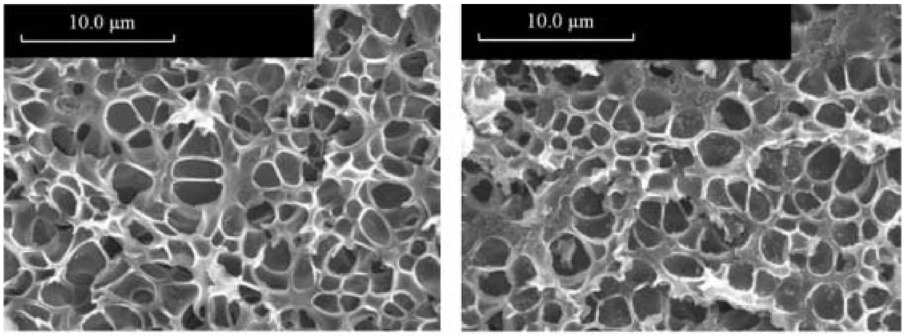
(e) Sample 11 (f) Sample 12



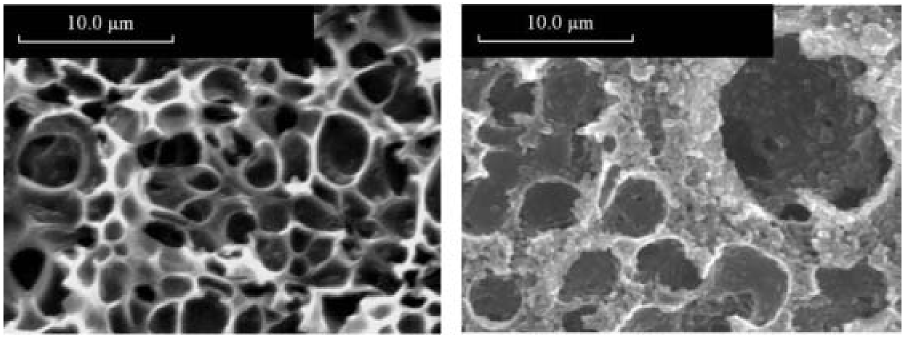
(g) Sample 13

Figure 4. SEM micrographs of the polymer network in samples 7–13 after dual UV and heat curing.

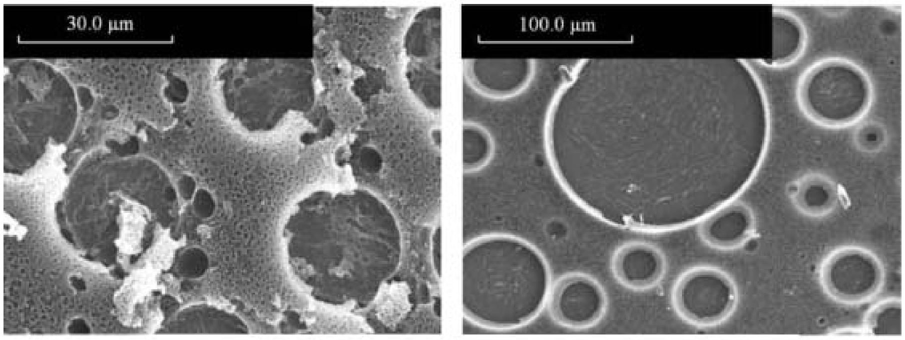
mesh size of the polymer network in samples 7–9, which were formed only by UV curing, increased in the sequence, as shown in Figure 5, the mesh size was still small enough to restrain the diffusion of the molecules of the heat curable monomers during heat curing. Therefore, the eventually formed mesh size of the polymer network in samples 7–9 after heat curing decreased with increasing content of the heat-curable



(a) Sample 7 (b) Sample 8



(c) Sample 9 (d) Sample 10



(e) Sample 11 (f) Sample 12

Figure 5. SEM micrographs of the polymer network in samples 7–12 after UV curing only.

monomers. However, the tendency for the mesh size of the polymer network in samples 9–12, which were also formed only by UV curing, increased so much in the sequence, and that the effect of the polymer network restraining the diffusion of the molecules of the heat-curable monomers during heat curing in samples 9–12 decreased markedly in the sequence. As a result, the eventually formed mesh size of the polymer network in samples 9–12 after heat curing increased, even though the content of the heat-curable monomers increased in the sequence. Actually, the mesh size of sample 13 prepared by dual UV and heat curing followed the same tendency as described above. Therefore, by adjusting the relative content of the UV- and heat-curable monomers, the eventual mesh size of the polymer network could be optimised.

Electro-optical properties of PDLC films

Figure 6 shows the voltage dependences of the transmittance of samples 1–6. As can be seen in Figure 6, the threshold voltage (V_{th}) and the saturation voltage (V_{sat}) of samples 1–6 increased in the sequence. Here, the V_{th} and the V_{sat} are defined as the voltage required for transmittance to reach 10% and 90%, respectively.

Figure 7(a) shows the voltage dependence of the transmittance of samples 7–9 and Figure 7(b) shows the same for samples 9–13. As can be seen in Figures 7, the V_{th} and V_{sat} values of samples 7–9 increased in the sequence, but those of samples 9–13 decreased in the sequence. It is well known that V_{th} is inversely proportional to the domain size of the LC in PDLC films. Larger domains provide the films with

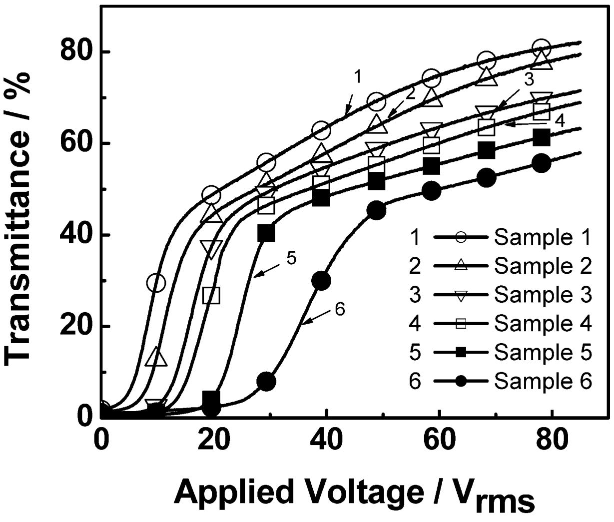


Figure 6. The applied electric field (100 Hz) dependence of the transmittance of samples 1–6.

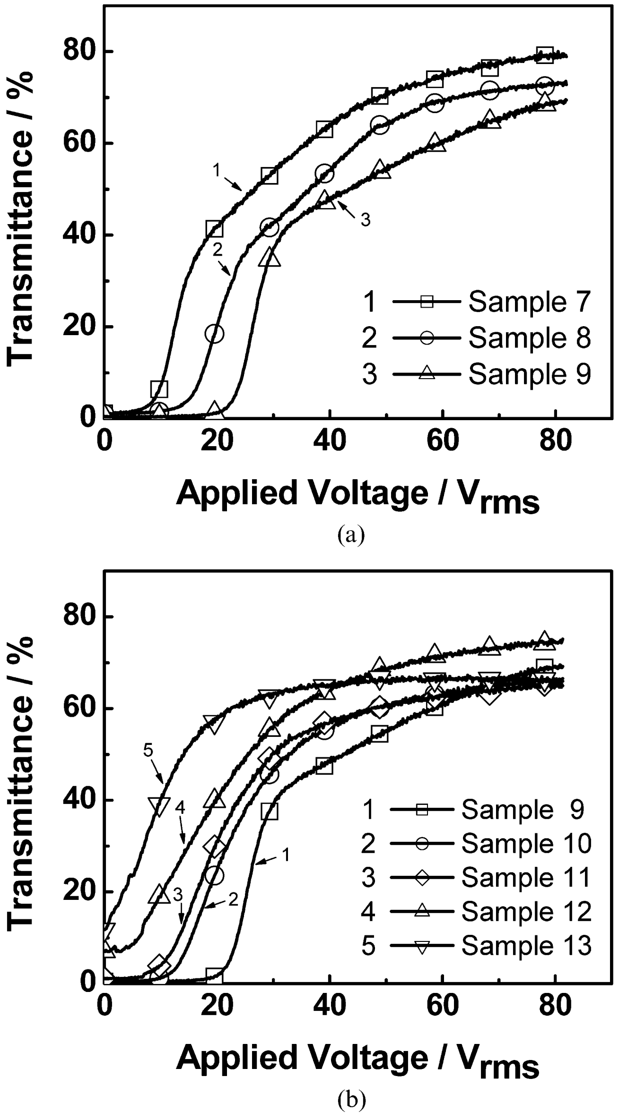
less polymer–LC interfaces and lower overall anchoring energy. V_{th} is a linear function of the reciprocal size of the domain R (the mesh size of the polymer network) according to

$$V_{th} \cong \frac{d}{R}\left[\frac{K\left(\omega^2-1\right)}{\varepsilon_0 \Delta\varepsilon}\right]^{\frac{1}{2}}, \qquad (1)$$

where d is the film thickness, R is the domain radius, K is the effective elastic constant, $\Delta\varepsilon$ is the dielectric anisotropy, ω is the aspect ratio of an elongated droplet and ε_0 is the vacuum dielectric constant. Since the mesh sizes of the polymer network in samples 7–9 decreased and those of samples 9–13 increased in the sequence, the V_{th} of samples 7–9 increased and those of samples 9–13 decreased in the sequence, respectively. Usually, the V_{sat} changes with the V_{th} synchronously.

Figures 8–9 show the UV–visible spectra of the off-state PDLC films of samples 1–6 and 7–13, respectively. As can be seen in these figures, the transmittance of the off-state PDLC films decreased with decreasing mesh size of the polymer network, which can be attributed to the fact that the light-scattering centres in the samples increased with decreasing the mesh size.

Figure 10 shows the applied voltage dependences of the rise time (τ_{R}) and the decay time (τ_{D}) for samples 1 and 6, respectively. τ_{R} and τ_{D} are defined as the time required for transmittance change from 10.0 to 90.0% upon turn on, and from 90.0 to 10.0% upon turn off, respectively. Generally, smaller domains of the LC result in larger τ_{R} since the molecules of the LC have to overcome more surface anchoring energy, and larger applied voltage gives smaller τ_{R} (*12*). Therfore, the τ_{R} of sample 6 was larger than that of sample 1 when the applied voltage was the same.



(a)

(b)

Figure 7. The voltage dependence of the transmittance for (a) samples 7–9 and (b) samples 9–13.

Smaller domains of the LC result in smaller τ_{D} since the surface anchoring energy of the polymer network on the LC is larger (*13*). Hence, the τ_{D} of sample 6 was smaller than that of sample 1. The τ_{D} is a response after switching off and is expected to be independent of the applied voltage. However, our results show a small increase of the τ_{D} with the increase in voltage. In this regard, Jain and Rout (*14*) proposed that the alignment of the LC molecules along the field would complete at high applied voltage, which involves much greater distortion of the director and in turn a greater restoring energy.

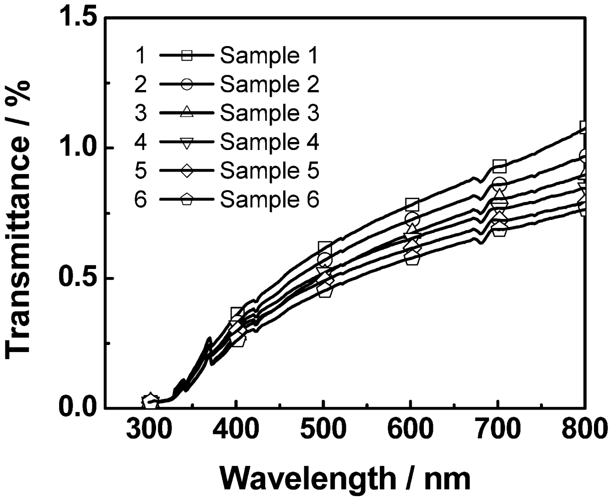
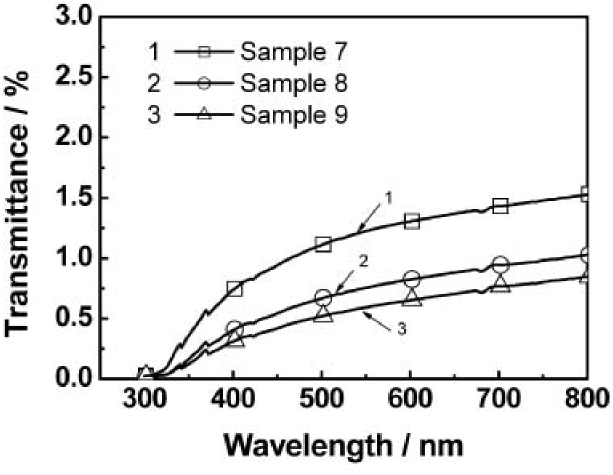
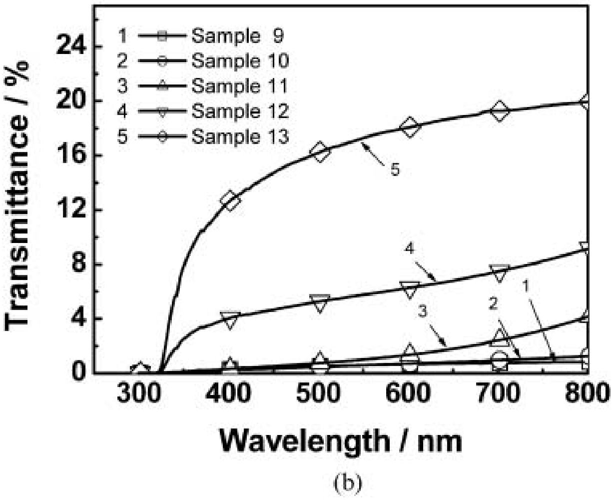


Figure 8. Dependence of UV–visible spectra of off-state PDLC films on heat curing time.

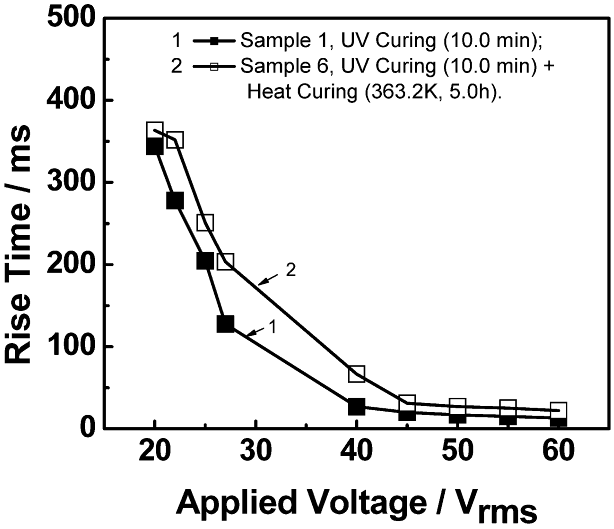


(a)



(b)

Figure 9. Dependence of UV–visible spectra of off-state PDLC films on relative contents of UV curable monomers to heat curable monomers.



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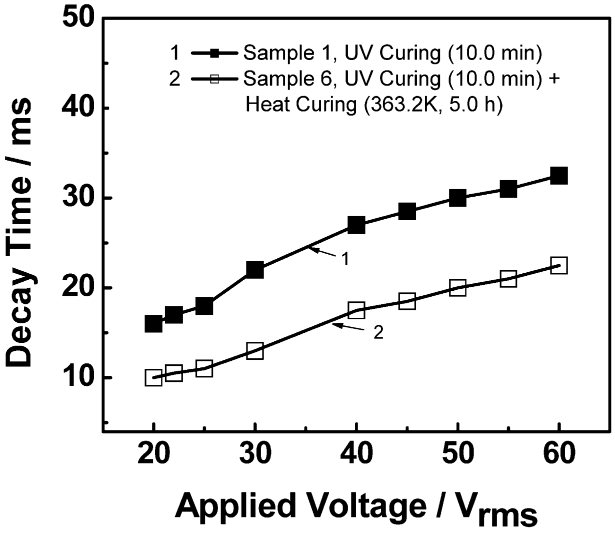

(b)

Figure 10. The applied electric field (128 Hz) dependence of the (a) rise time and (b) decay time as a function of heat curing process.

Therefore, the τ_D increased a little with the increase in voltage.

4. Conclusion

PDLC films prepared by dual UV and heat curing have been investigated. For PDLC films with a certain amount of UV- and heat-curable monomers, the mesh size (the size of LC domains) of the polymer network decreased after crosslinking of the heat-curable monomers. By adjusting the relative content of the UV- and heat-curable monomers, the mesh size of the polymer network could be regulated, and then the electro-optical properties of the film could be optimised.

Acknowledgements

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