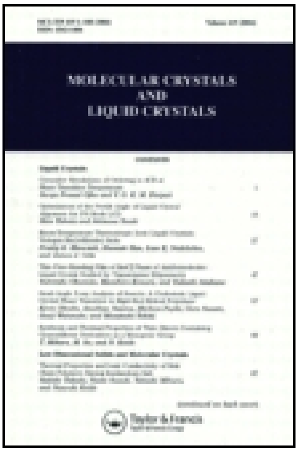

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Effects of 2-Hydroxypropyl Acrylate on Electro-Optical Properties of Polymer-Dispersed Liquid Crystal Films and Elasticity of Polymer Network

Liping Wang [a], Hailian Yang [a], Chengming Zhao [a], Lipei Zhang [a] & Huai Yang [a]

[a] Department of Materials Physics and Chemistry, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing, P.R. China

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LIPING WANG, HAILIAN YANG, CHENGMING ZHAO, LIPEI ZHANG, AND HUAI YANG

Department of Materials Physics and Chemistry, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing, P.R. China

Polymer-dispersed liquid crystal (PDLC) films were fabricated between two indium tin oxide (ITO) film substrates by means of polymerization-induced phase separation, and the electro-optical properties of the PDLC films were investigated. For the preparation of one PDLC film, 1,4-butanediol diacrylate (BDDA), butyl methacrylate (BMA), and 2-hydroxypropyl acrylate (HPA) were used as monomers, whereas for that of the other, no HPA was used. The experimental results are compared for the HPA-containing and HPA-free PDLC film. The HPA-containing one shows a larger elasticity for the polymer matrix and a higher adhesion strength between the two ITO films. Moreover, the electro-optical properties and the thermal stability are significantly improved for the HPA-containing PDLC film. The role of monomer HPA on the morphology, stability, and electro-optical properties of the PDLC film is discussed.

Keywords Elasticity; networks; polymer-dispersed liquid crystal (PDLC); thermal properties; thin films

Introduction

In recent years, polymer-dispersed liquid crystal (PDLC) films have attracted considerable attention due to their application in information display technology [1]. The PDLC is a composite material that consists of micrometer-sized liquid crystal (LC) droplets incorporated into a polymer matrix. For the PDLC-based display devices, an applied electric field to the transparent electrodes sandwiching the PDLC films can control light-scattering properties of the LC droplets. Upon an appropriate electric field, the PDLC films may switch from a light-scattering opaque state (OFF state) to a transparent one (ON state). This provides opportunities to fabricate a new type of LC display panel that does not need back-light, alignment film, polarizer,

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Address correspondence to Huai Yang, Department of Materials Physics and Chemistry, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China. E-mail: yanghuai@mater.ustb.edu.cn

and strict controlling thickness of the LC thin films [2–5]. Therefore, devices based on the PDLC films have many advantages, such as high lightness, wide viewing angles, and the ease of fabricating large area displays [6]. Conventionally, the PDLC films are formed by polymerization-induced phase separation (PIPS), thermally induced phase separation (TIPS), or solvent-induced phase separation (SIPS) of homogeneous LC/monomer mixtures sandwiched between two substrates. As far as large area display is concerned, PIPS is one of the most inexpensive and convenient fabrication methods to prepare the PDLC films [7–11].

In the PIPS process, phase separation is induced by reducing solubility of LC, which is achieved by increasing the length of polymer chains or forming polymer network. The electro-optical properties are determined principally by composition, curing rate and extent, and the immiscibility of LC with the monomers. Furthermore, the size and distribution of the LC droplets affect the electro-optical performance of the PDLC films significantly. In order to improve the electro-optical properties of the PDLC films, the main object is to decrease driving voltage while keeping a high contrast ratio. The lower driving voltage should result in less energy consumption and faster response under the same electric field strength [12]. Generally, the driving voltage can be reduced via enlarging the holes in polymer network, which can be actualized by selecting appropriate monomers with various molecular structure or controlling preparation technics [13,14]. In addition, the mechanical properties of the polymer network are important to the electro-optical properties of PDLC films. Good mechanical properties of polymer matrix are crucial to improve the stability of polymer network and the electro-optical properties of PDLC films [15]. If the mechanical strength is appropriate, the polymer network is then stable under the influence of an applied electric field. Furthermore, it is difficult to distort the network after switching the PDLC films many times, and the electro-optical properties can thus be eligible. On the other hand, the PDLC films with the appropriate mechanical strength and elasticity should exhibit an outstanding durability under some processing treatment, such as bending, heating, or cooling [16].

In this article, two PDLC films were prepared by light-induced polymerization of photopolymerizable monomers in nematic LC/monomers composites where three acrylate monomers with different structures were used. The electro-optical properties and electro-optical and thermal stabilities of the two PDLC films were investigated, and the effect of elasticity on the properties of the PDLC films was discussed.

Experimental

Materials

The low-molecular-weight liquid crystal used is a nematic type liquid crystal mixture SLC7011-100 ($n_0 = 1.673$, $\Delta n = 0.165$), which was supplied by Slichem Liquid Crystal Material Co. Ltd. 1,4-Butanediol diacrylate (BDDA), butyl methacrylate (BMA), 2-hydroxypropyl acrylate (HPA), and Irgacure 651 were purchased from Aldrich Chemical Co. All chemicals were used without further purification.

Preparation of the PDLC Films

Three monomers 1,4-butanediol diacrylate (BDDA), butyl methacrylate (BMA), and 2-hydroxypropyl acrylate (HPA) were used to prepare the PDLC films by using the

Table 1. The constituents and preparation condition

Sample	Components (wt%)				Light intensity (mW/cm^2)	Temperature (°C)
	LC	BDDA	BMA	HPA		
1	80	10	10	0	25	25
2	80	3	3	14	25	25

photo-polymerization induced phase separation. Two samples, one comprising 1,4-butanediol diacrylate (BDDA)/butyl methacrylate (BMA)/liquid crystal (LC), the other comprising BDDA/BMA/2-hydroxypropyl acrylate (HPA)/LC, were prepared. For sample 1 (HPA-free), a typical preparation is as follows. First, the mixture comprising an appropriate amount (as shown in Table 1) of monomers (BDDA, BMA) and LC was mixed using a magnetic stirrer. Then 5 wt% Irgacure 651 and 20 μm polycarbonate or polyimide (Mylar) film spacers were added to the mixture as an initiator and a film thickness controller, respectively. Next, the clearing point was measured to be 6°C and 15°C for samples 1 and 2, respectively. After that, the mixture was cast onto a conductive resinous substrate, which had previously been coated with a transparent thin layer of indium tin oxide (ITO), followed by a rolling press. Finally, the PDLC film was obtained by irradiation with a UV lamp (PS135 UVflood, Labino Ab Co. Ltd., power 100 mW/cm^2, $\lambda = 365$ nm) of the predetermined mixtures at a constant temperature with various curing intensity. The film was cured for sufficient time till the precursors polymerized completely. Sample 2 (HPA-containing) was prepared in the same way except that HPA was added in the mixture at the very beginning.

Measurements

The light transmission properties of the PDLC films were measured using a LCT-5016C LCD parameters tester (Changchun Liancheng Apparatus Co. Ltd.) equipped with a 75 W halogen tungsten lamp and a 632.8 nm wavelength filter. The transmittance of the samples was recorded with an oscilloscope-monitored photodiode. A 100 Hz square-wave electric field was applied to the samples 300 mm apart from the photodiode. Morphologies of polymer were studied with scanning electron microscopy (SEM, Cambridge S160). Samples for the SEM measurement were prepared by the extraction of the LC in the PDLC films with cyclohexane for 1 h.

The adhesion intensity of the PDLC films was measured using a universal testing machine (Shimadzu AG-20kNIC) with a moving speed of 50 mm/min. Film samples were cut into pieces with 100 × 25 mm. The measurements of tensile strength were carried out on a Rheometric Scientific testing machine (Minimat-Firmware Vsn 3.1) with a stretch rate of 5 mm/min for samples of 50 × 20 mm. All measurements were carried out at ambient temperature.

Results and Discussion

Stability Properties of the PDLC Films

The composition and preparation conditions of the samples prepared by PIPS are listed in Table 1. The applied voltage-transmittance curves of the samples are shown

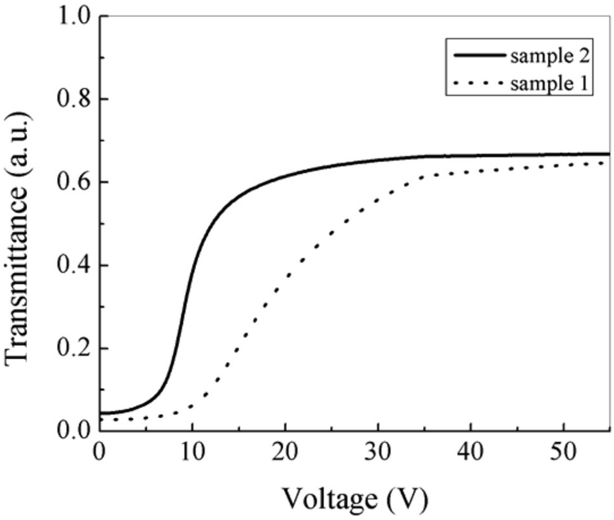


Figure 1. Transmittance vs. applied voltage for samples 1 and 2.

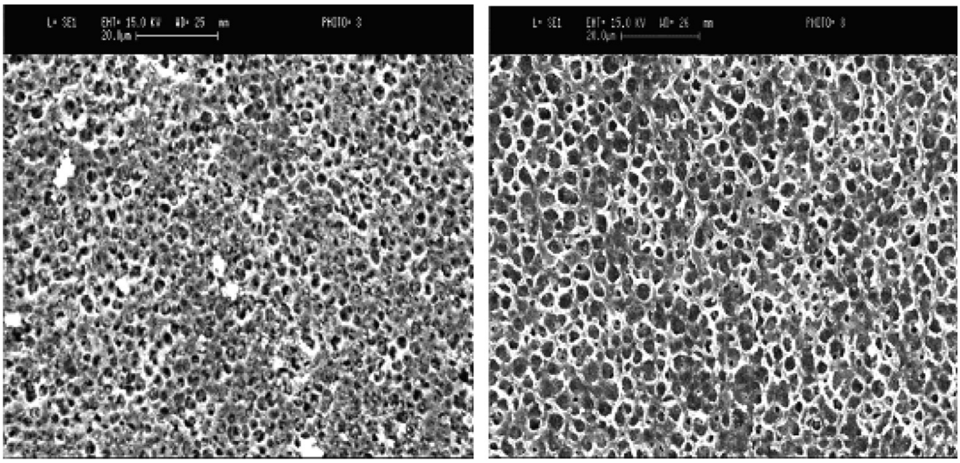
in Fig. 1. The threshold and saturation voltages are listed in Table 2, where threshold voltage (V_{10}) is the one with 10% transmittance, saturation voltage (V_{90}) is the one with 90% transmittance, and contrast is the ratio of maximum and minimum transmittance.

When the applied voltage is lower than the threshold voltage, the symmetry axis of the LC droplets is randomly oriented, and the PDLC film thus remains opaque in appearance. When the applied voltage reaches the specific threshold voltage, the refractive indices of the LC droplets and the polymer matrix are matched, and the film therefore turns into transparent. For the PDLC films prepared at the same condition, sample 2 (with HPA) shows threshold and saturation voltages smaller than those of the sample 1 (free of HPA), whereas the HPA-free sample exhibit an applied voltage-transmittance curve steeper than that of the one containing HPA. Meanwhile, the contrast of sample 2 is about 20% lower than that of sample 1. This suggests that adding HPA results in reducing the threshold and saturation voltages and improving the steepness of the PDLC films.

With respect to the polymerization of the monomer with different components, polymer matrix with variable morphology may be formed. The structure of polymer network in turn affects the electro-optical properties of PDLC films. The film morphology (droplet volume, density, and size) plays a major role on the contrast ratio, which is influenced by the different percentages of photochrome (from opaque to transparent), rather than by the refractive index matching [17]. Figure 2 shows the SEM images of the polymer network of the two samples. From the analysis of the

Table 2. The electro-optical parameters of the samples

Sample	Threshold voltage (V)	Saturation voltage (V)	Contrast
1	10.3	33.6	24
2	5.9	18.5	20



(a) (b)

Figure 2. The SEM images of polymer network of the samples 1 (a) and 2 (b) (×1000).

SEM images for each sample, there is not much difference in the LC droplet size. However, the polymer network holes of sample 2 are larger and more uniform than those of sample 1. The smaller hole should contribute to a higher threshold and saturation voltages and higher steepness. Generally, the contrast decreases when the holes of polymer network become larger. In addition, the contrast of sample 2 is up to 20 with much reduced voltages, as shown in Table 2. The above results indicate that sample 2 has better integrated properties. Because the holes were originally filled by the LC droplets, comparing Figs. 1 and 2, it is shown that a higher switching voltage is required for the film with smaller LC droplets and a lower switching voltage for the one with larger LC droplets. When a PDLC film with small droplets is tested at low frequency, more space-charge occurs at the LC droplet–polymer interface, resulting in an appreciable increase of the dielectric permittivity of the matrix [13]. This should reduce the field across the LC droplets and increase the switching voltage.

The interaction between the polar groups in the LC molecules and the hydroxyl groups (–OH) in HPA molecules could diminish the holes of polymer network. However, the fact is that the holes enlarge for the sample with –OH. This can be attributed to the competition between the diminution and enlargement. On the one hand, the interaction between –OH and polar groups, –CN, causes a decrease of the hole sizes in the polymer network. On the other hand, the significant shrinkage of the HPA-containing polymer increases the hole sizes. The result suggests that the effect of shrinkage-accompanied HPA polymerization is greater than the interaction mentioned above. This is main reason for the hole enlargement.

To investigate this shrinkage, two contrast experiments were carried out, in which two kinds of monomer mixtures of samples 1 and 2 were filled in a $10^4\,mm^3$ mold, and a photo-polymerization was induced with UV light in the same condition. The volume changes of the two polymers are shown in Table 3. It can be seen that the AV/V for sample 2 is much larger than that for sample 1, which indicates that the monomer mixture of the sample 2 shrinks dramatically. This large shrinkage can subsequently surpass the interaction between the polar groups,

Table 3. Volume changes of the two kinds of polymers

Sample	ΔV (mm^3)	$\Delta V/V$ (%)
1	18.94	0.19
2	1020.98	10.20

−OH and −CN, eventually resulting in enlargement of the holes in the polymer network. That is why the threshold and saturation voltages decrease and the contrast reduces for sample 2.

Thermal and Electro-Optical Stability of the PDLC Films

Figure 3 shows the photos of the samples 1 and 2 after heated in an oven at 120°C for 2 h and kept at room temperature for one day. After heating at high temperature, white spots appeared in the film of sample 1, whereas no such change was observed for sample 2. When the film is heated at high temperature, the LC droplets change in the distorted polymer network or the air previously dissolved vanishes. The occurrence and growth of white spots therefore represent the instability of the polymer network at an elevated temperature. The result indicates that sample 2 is much more stable than sample 1 against heating. Hence, the sample with hydroxyl groups has a better thermal stability compared to the one without hydroxyl groups.

Figures 4a and 4b show the electro-optical properties of samples 1 and 2 before and after applying an electric field 500 times. For sample 1, the contrast and the response time on the OFF state (t_{off}) changes significantly on applying electricity. The contrast decreases from 24 to 12 and the t_{off} increases from 3 to 10 ms. For sample 2, little change can be seen in the contrast and the t_{off} as well. Apparently, applying electricity a great number of times affects the transmittance more for sample 1 than for sample 2. This indicates that the electro-optical properties of the sample with hydroxyl groups are more stable.

Adding HPA to the monomers improves both the thermal stability of the thin film and enhances the stability of the electro-optical properties, which are the main characteristic of PDLC films. Two reasons can be involved for this improvement,

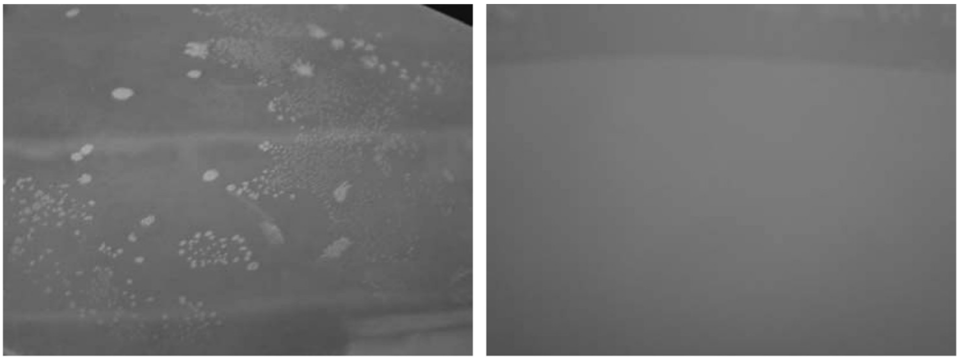

(a) (b)

Figure 3. The film pictures of samples 1 (a) and 2 (b) after heating.

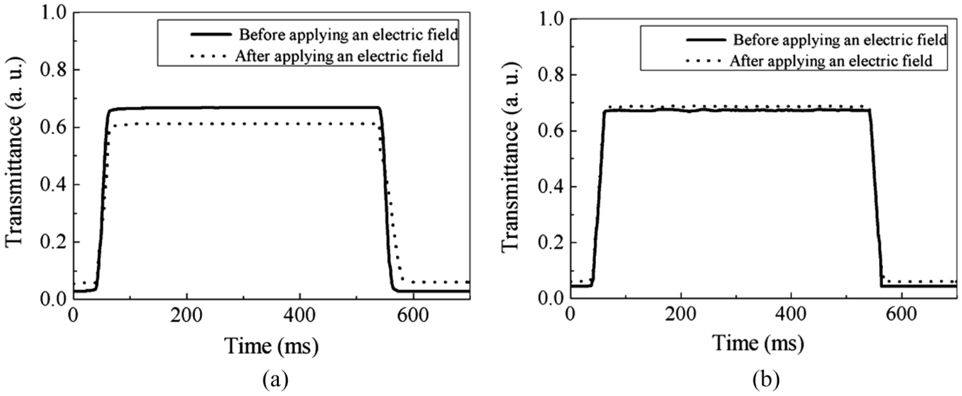


Figure 4. The electro-optical properties of samples 1 (a) and 2 (b) before and after applying an electric field 500 times.

one is due to a strong adherence to the ITO film substrates, and the other is the fine mechanical properties of the polymer network.

Adherence and Elasticity of the PDLC Films

The adhesion strength of samples 1 and 2 is measured to be 274 and 325 MPa, respectively. It reveals that the adhesion strength of polymer matrix to the ITO film substrates for sample 2 is larger than that for sample 1. Figure 5 shows what was experimentally observed when the PDLC films sandwiching between the two ITO substrates are torn open. After pulled by an applying force, the polymer of sample 1 adheres to only one of the ITO films, whereas that of sample 2 adheres to both. This indicates that the conglutination of the polymer and the ITO films for sample 2 is much stronger than for sample 1. It also suggests that adding HPA monomer enhances the adherence force between the ITO film and the polymer network. For the HPA-containing sample, the formation of hydrogen bonds between the –OH in the polymer and the oxygen of ITO increases the conglutination force. On the other hand, the coherence of the HPA-containing film is lower to some extent because its cross-linking density is much lower than that of the other [18]. The stronger conglutination might therefore be assigned to the fact that the adherence between

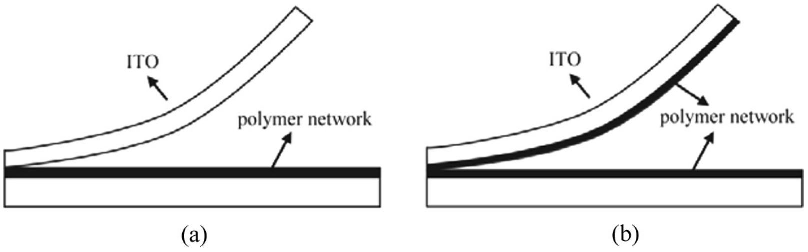


Figure 5. Schematic tearing illustrations of the HPA-free PDLC (a) and HPA-containing PDLC (b) films sandwiching between the two ITO substrates by an applying force.

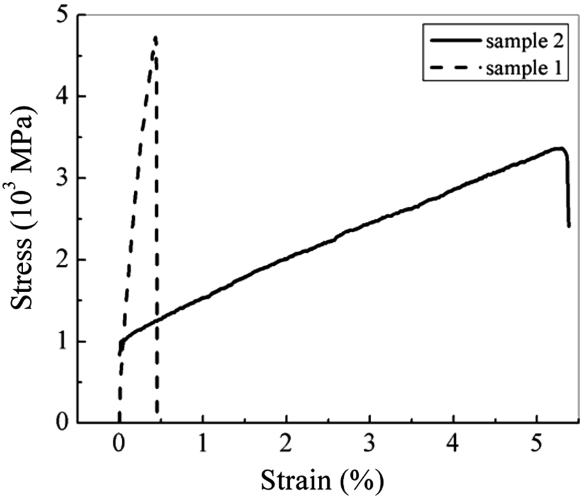


Figure 6. The tensile curves of the polymer for samples 1 and 2.

the polymer and ITO is larger than the coherence of the polymer network in the HPA-containing film.

The mechanical properties of the polymer in the two samples were tested as shown in Fig. 6. The tensile strength needed to pull the polymer apart for sample 1 is much higher than that for sample 2, whereas the tensile elongation of the polymer for sample 2 is much greater than that for sample 1. Therefore, the polymer matrix of sample 2 has a better elasticity, which is helpful to maintain the electro-optical properties of the PDLC films. When applying an electric field, the LC droplets will change their tropism followed by the distortion of the holes in the polymer network. In the case of the polymer network with a larger elasticity, the holes can be resilient when removing the electric field. This characteristic increases the stability of polymer network and enhances the electro-optical properties of the HPA-containing PDLC film.

Conclusion

Two PDLC films were fabricated by light-induced polymerization of acrylate monomers in nematic LC/monomers composites. The thermal properties and elasticity of the PDLC films can be significantly improved by adding the HPA monomer. Compared with the PDLC film using BDDA and BMA monomers, the polymer film using BDDA, BMA, and HPA exhibits larger and more uniform polymer network holes, resulting in reducing the threshold and saturation voltages and improving the steepness. Meanwhile, adding HPA to the monomers also enhances the stability of the electro-optical properties with a relatively reduced contrast ratio.

Acknowledgment

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