

Effect of a Chiral Dopant on the Electro-Optical Properties of Polymer-Dispersed Liquid-Crystal Films

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Received 17 December 2006; accepted 24 January 2007

DOI 10.1002/app.26201

Published online 26 April 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Polymer-dispersed liquid crystal (PDLC) films were prepared by the ultraviolet-light-induced polymerization of photopolymerizable monomers in nematic liquid crystal/monomer/chiral dopant composites, and the effect of the chiral dopant on the electro-optical properties of the PDLC films was studied. It was demonstrated that the addition of a small amount of the chiral dopant increased the driving voltage somewhat but decreased the turn-off time significantly. Furthermore, the transmittance of ultraviolet,

visible, and near-infrared light of the off state of PDLC films showing light scattering increased with increasing content of the chiral dopant, and the optimum electro-optical properties of the PDLC films were obtained when the content of the chiral dopant was not more than 2 wt %. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2185–2189, 2007

Key words: chiral; films; light scattering; optics; photopolymerization

INTRODUCTION

Polymer-dispersed liquid crystal (PDLC) films consist of a liquid-crystal (LC) material dispersed within a semicontinuous polymer matrix,¹ and they are potentially useful for a variety of electro-optical applications, including switchable windows, flexible large-area displays, and other devices.² The films show transparent and light scattering states in the electric field-on and field-off states, respectively. In the electric field-off state, the refractive-index mismatch between the polymer matrix and the LC material ($n_p \neq n_{LC}$) gives rise to the light scattering of incident light. When the LC molecules are aligned in the electric field-on state, the films become transparent because of the matching of the ordinary LC refractive index with that of the polymer matrix.³ The switching properties of the LC molecules within the domains depend on some variables, such as the size and shape of the domains and the molecular interactions between the LC material and the polymer matrix. The application of an electric field of sufficient strength can overcome the elastic forces anchoring the LC molecules at the interface. Once the electric field is removed, the turn-off time for the molecules to revert back to the equilibrium distribution is also dictated by the strength of these forces. For PDLC films with a low driving voltage, the turn-off time is usually long.⁴

In this study, PDLC films were prepared by the ultraviolet (UV)-light-induced polymerization of photopolymerizable monomers in nematic LC/photopolymerizable monomer/chiral dopant composites, and the effects of the chiral dopant on the electro-optical properties of the PDLC films were studied. It was expected that the turn-off time could be decreased by the addition of the chiral dopant. Meanwhile, the variation of other electro-optical properties with the addition of the chiral dopant was investigated.

EXPERIMENTAL

Materials

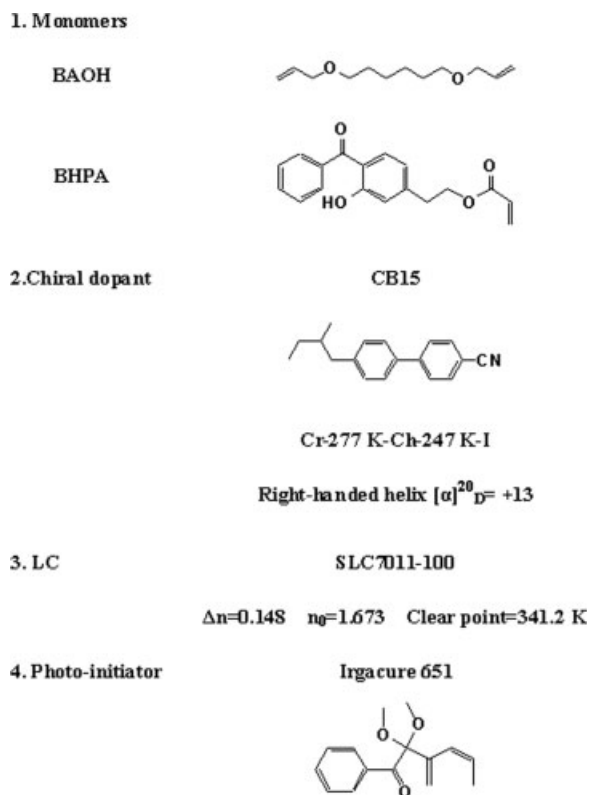
The nematic LC was SLC 7011-100 (Shijiazhuang Yongsheng Huatsing Liquid Crystal Co., Ltd., Shijiazhuang City, Hebei Province, China), the chiral dopant was CB15 (Merck Co., Ltd., Whitehouse Station, NJ), the monomers were 1,6-bis(allyloxy)hexane (BAOH) and 4-benzoyl-3-hydroxyphenethylacrylate (BHPA; Aldrich Chemical Co., St. Louis, MO), and the photoinitiator was Irgacure 651 (Shijiazhuang Yongsheng Huatsing Liquid Crystal). The chemical structures and some physical properties of the composite films are shown in Scheme 1.

Preparation of the PDLC films

The following method^{5–7} was used for the sample preparation. At first, an SLC 7011-100/BAOH/BHPA/CB15/photoinitiator composite was prepared. Then, the composite was sandwiched between two pieces of indium tin oxide (ITO), conductive plastic films. After the composite was irradiated by UV

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Contract grant sponsor: Science and Technology Program of Beijing; contract grant number: Y0405004040121.



Scheme 1 Chemical structures and some physical properties of the materials.

light (35-W Hg lamp, PS135, UV Flood, Stockholm, Sweden) for 3 min at 293.2 K, a polymer network (polymer matrix) was formed in the composite from the crosslinking between the molecules of the photopolymerizable monomers. Thus, PDLC films were prepared. The compositions of the composites from which the samples of the PDLC films were prepared are listed in Table I.

Observation of the polymer matrix in the PDLC films

The observation of the microstructure of the polymer matrix in the films was carried out with scanning electron microscopy (SEM; S360, Cambridge, England). To do that, the PDLC films were separated, and then the ITO film with PDLC material was dipped in *n*-hexane for about 24 h at room tempera-

ture so that the LC molecules were extracted, and the ITO film with the polymer matrix was dried *in vacuo*. The weight loss upon extraction was used to determine the continuity of the LC domains in the polymer matrix. After the polymer matrix was sputtered with gold, the microstructure of the polymer matrix was observed under SEM.

Electro-optic measurements

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

Measurements of the UV, visible (VIS), and near-infrared (NIR) spectra

The transmittance of the PDLC film in the wavelength range from the UV region to the NIR region was measured with a UV-VIS-NIR spectrophotometer (V-570, Jasco Corp., Tokyo, Japan).

RESULTS AND DISCUSSION

Observation of the polymer matrix in the PDLC films

Figure 1 shows the SEM micrographs of the polymer networks of the PDLC films prepared from samples A–D. It can be clearly seen that the LC domain increased in size with decreasing contents of the photopolymerizable monomers (and increasing CB15 content). This can be explained by the mechanism of the polymerization-induced phase-separation method.⁸ The solubility of the LC decreases in the stiffening polymers until the LC phase-separates, forming droplets during the UV curing. The droplet size is controlled by the relative contents of the photopolymerizable monomers and LC, the rate of polymerization, and some physical parameters such as the vis-

TABLE I
Compositions of the Samples

| Sample | Monomers (wt %) | | LC (wt %) | CB15 (wt %) | Photoinitiator (wt %) |
|--------|-----------------|-----------|-----------|-------------|-----------------------|
| | Total | BAOH/BHPA | | | |
| A | 28.0 | 8.4/19.6 | 70.0 | 0.0 | 2.0 |
| B | 26.0 | 7.8/18.2 | 70.0 | 2.0 | 2.0 |
| C | 24.0 | 7.2/16.8 | 70.0 | 4.0 | 2.0 |
| D | 22.0 | 6.6/15.4 | 70.0 | 6.0 | 2.0 |

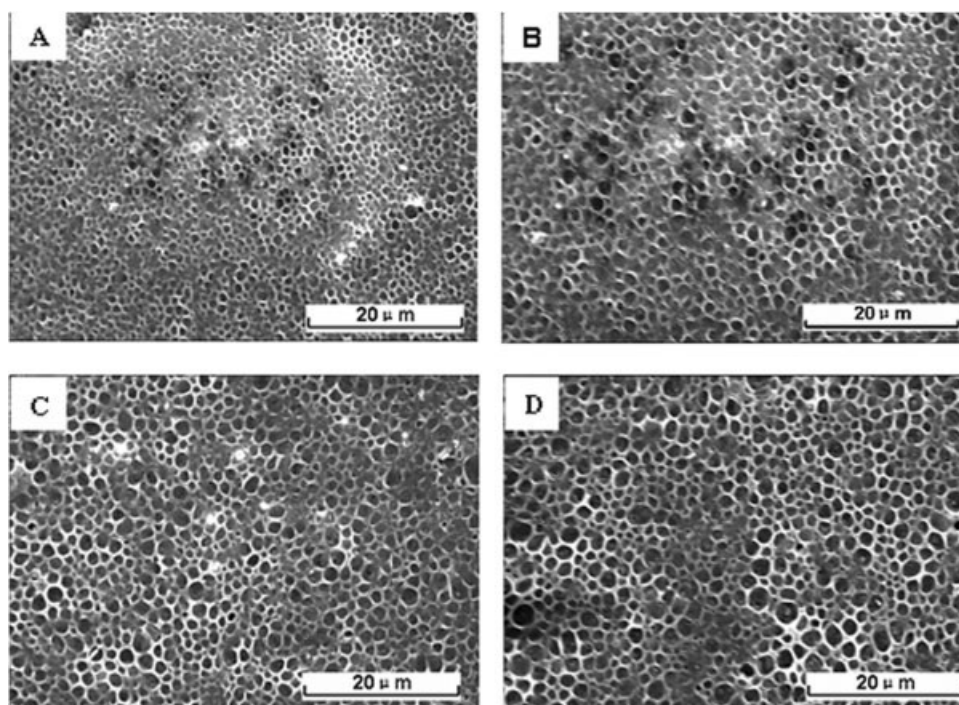


Figure 1 SEM micrographs of the polymer matrices of samples A–D.

cosity, rate of diffusion, and solubility of the LC in the polymer.⁹ For a definite system, the relative contents of the photopolymerizable monomers and LC have a great effect on the morphology of the polymer matrix. Therefore, the size of the LC domains increased with decreasing contents of the photopolymerizable monomers, as shown in Figure 1.

Electro-optical properties of the PDLC films

Figure 2 shows the voltage dependence of the transmittance of samples A–D. It is possible to observe a change in the off-state transmittance, the threshold

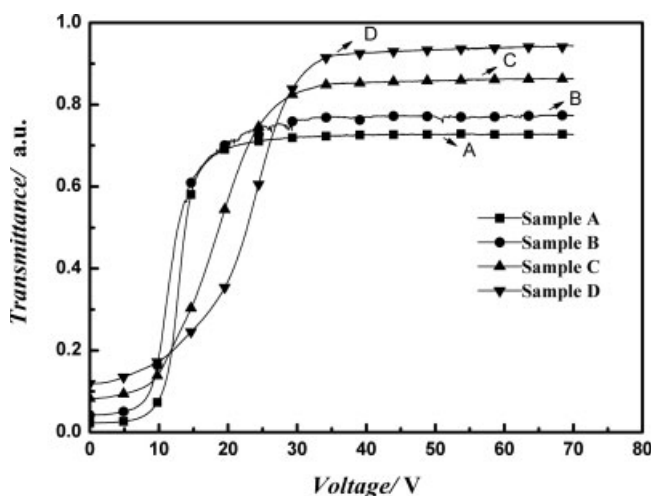


Figure 2 Applied electric field (100 Hz) dependence of the transmittance of samples A–D.

voltage (V_{th}), and the driving voltage (V_{dr}), where V_{th} and V_{dr} are defined as the electric fields required for the optical response to reach 10 and 90% of its maximum value, respectively. V_{th} changed little for CB15 contents up to 4 wt % but increased slightly at a content of 6 wt %. V_{dr} increased slowly when the CB15 content was less than 2 wt % and increased from 17.6 to about 27.2 V for contents up to 6 wt %. These behaviors are more evident in Figure 3, which shows the CB15 content dependences of V_{th} and V_{dr} . Generally, V_{th} and V_{dr} decrease with the increasing size of the LC droplet because the anchoring effect of the polymer matrix on the LC molecules decreases

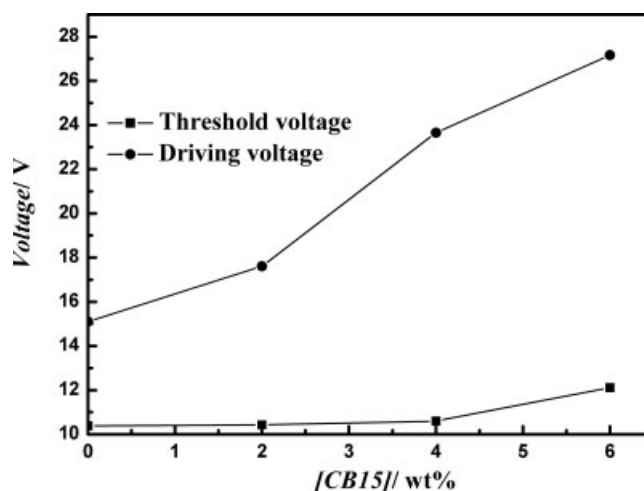


Figure 3 CB15 concentration dependence of V_{th} and V_{dr} .

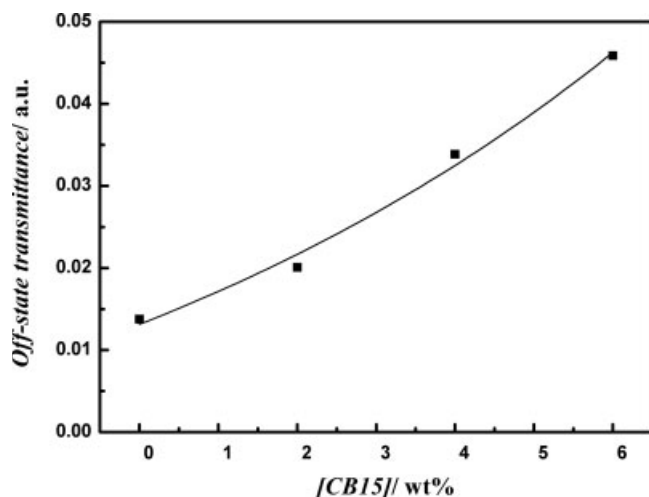


Figure 4 CB15 concentration dependence of the off-state transmittance.

as the size increases. However, V_{th} and V_{dr} of the samples increased with increasing size. Obviously, CB15 played a key role in the change of the values of V_{th} and V_{dr} . It is known that the configuration of the LC droplet will be bipolar when the droplet diameter (D) is smaller than the helical pitch (P). Reversely, if $P < D$, a twisted bipolar configuration will be formed. When the CB15 concentration is increased, P is decreased as P (μm) = $0.13/[\text{CB15}]$.^{4,10} Consequently, the twist elastic energy in the free energy of bipolar droplets is increased, and it needs a larger electric field to reorient droplets; that is, the greater the CB15 content is, the larger V_{th} and V_{dr} are.

Figures 4 and 5 show the CB15 content dependence of the off-state transmittance and the CB15 content dependence of the contrast ratio of the samples, respectively. It is shown in Figures 4 and 5 that the

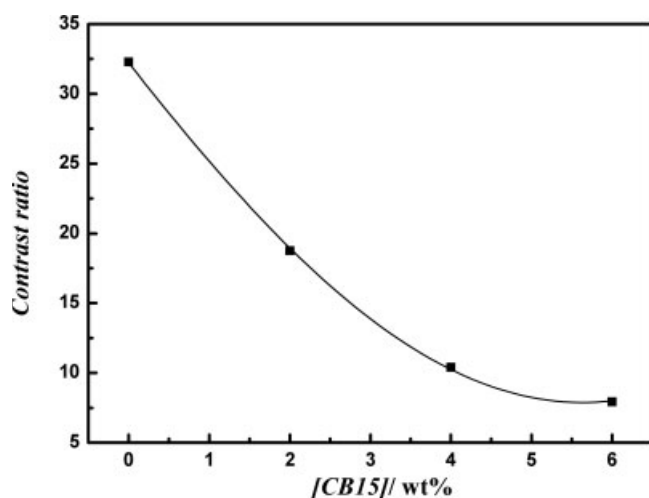


Figure 5 CB15 concentration dependence of the contrast ratio.

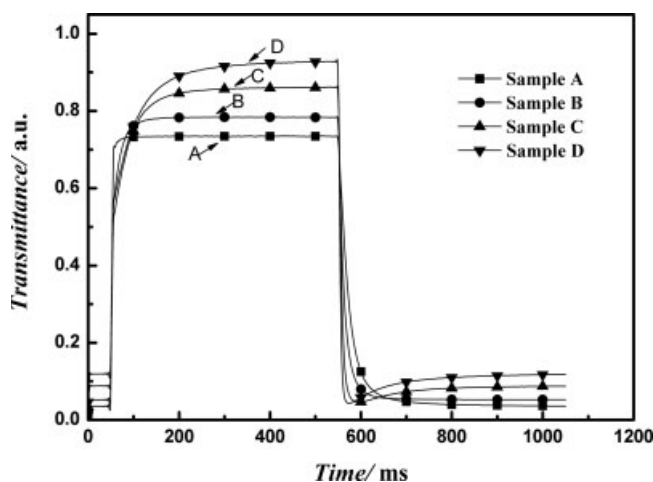


Figure 6 Electro-optical response of samples A–D.

addition of CB15 resulted in an increase in the off-state transmittance and a decrease in the contrast ratio. One generally approved explanation is that the transmittance increases with the increasing size of the LC droplet because the larger LC domain size results in an insufficient number of scattering centers.^{9,11} Therefore, the transmittance of the samples increased with the increasing size of the LC droplet, that is, with increasing CB15 content (as shown in Fig. 1). Meanwhile, the increase in the transmittance resulted in the decrease in the contrast ratio. Another possible explanation is that the LC molecules easily tend to form the alignment of a planar structure,¹² which is the most stable as the free energy needed is lowest when the chiral dopant is added, which will also increase the transmittance and decrease the contrast ratio of the samples. This will be discussed in a near-future report.

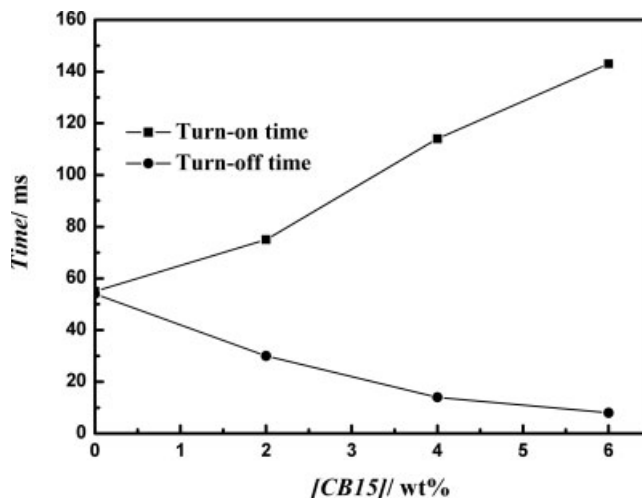


Figure 7 CB15 concentration dependence of the turn-on time and turn-off time.

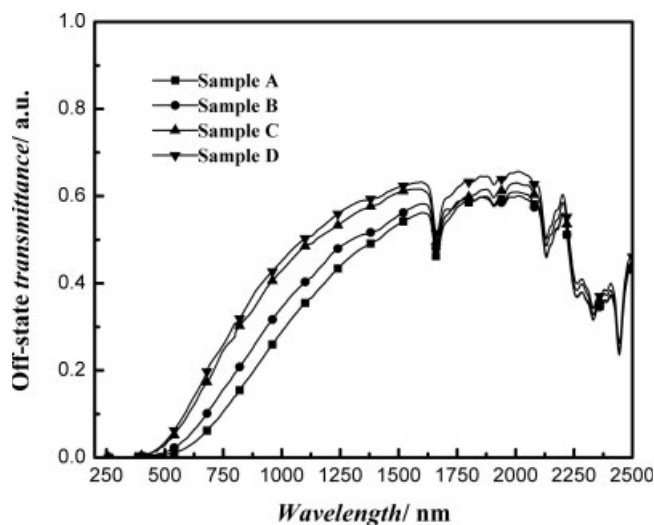


Figure 8 Wavelength dependence of the off-state transmittance of samples A–D.

Figure 6 shows the electro-optical response of the switchable samples to an applied driving field (70 V, 100 Hz), and Figure 7 shows the CB15 content dependence of the turn-on and turn-off time. The turn-off time decreased dramatically whereas the turn-on time increased synchronously with increasing CB15 content. The phenomena can be explained by the twisting effect of CB15. A competition among the applied field, the elastic forces anchoring the LC molecules at the interface, and the helically twisting power of CB15 governs the response time. As a result, the samples needed a longer turn-on time to overcome the helically twisting power of CB15, and once the electrical field was removed, the turn-off time for the molecules to revert back to the equilibrium distribution decreased because of the existence of the helically twisting power of CB15.

Effect of the wavelength

Figure 8 shows the wavelength (λ) dependence of the off-state transmittance for the samples. The transmittances of all the samples tended to increase and decrease with the wavelength increasing in the wavelength range of 190–2000 nm and in the range of 2000–2500 nm, respectively. Meanwhile, the transmittance increased with increasing CB15 content, and this was in good agreement with the results of the electro-optical properties of the samples, as shown in Figure 4.

The off-state light scattering intensity of PDLC films is basically caused by the mismatches in the refractive indices of the polymer and LC. For a single

LC droplet, Zumer and Doane¹³ using a Rayleigh–Gans approximation showed that the intensity follows a Rayleigh λ^{-4} dependence when $k \leq R$ ($k = 2\pi/\lambda$, and R is the radius of the LC droplet). According to this theory, it can be explained that the light scattering intensity of the samples in the range of UV and VIS light was stronger than that of the samples in the range of the NIR light. Meanwhile, the light scattering intensity decrease with increasing CB15 content was due to the increasing size of the LC droplets.^{14,15} Because of the reflecting effect of the surface of ITO films,¹² the light scattering intensity of the all the samples began to decrease with increasing wavelength from 2000 nm, and this also was demonstrated by our experiments.

CONCLUSIONS

For a PDLC film with doped CB15, the turn-off time decreased but V_{th} , V_{dr} , and the turn-on time increased with increasing CB15 content as the helically twisting power of CB15. Therefore, by the adjustment of the CB15 content, the electro-optical properties of the film could be optimized. However, it should be noted that CB15 affected the off-state transmittances of the incident UV, VIS, and NIR light because the microstructure of the polymer matrix changed with the CB15 content somewhat.

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