

# Studies on Electro-Optical Properties of Polymer Matrix/LC/SiO<sub>2</sub> Nanoparticles Composites

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**ABSTRACT:** Polymer-dispersed liquid crystal (PDLC) films were prepared by ultraviolet light-induced polymerization of photopolymerizable monomers in nematic liquid crystal (LC)/monomers/SiO<sub>2</sub> nanoparticles composites, and the effect of SiO<sub>2</sub> nanoparticles on the electro-optical properties of PDLC films was studied. The observed effect showed that by the adjustment of the SiO<sub>2</sub> nanoparticles content, the refractive index

ratio of the LC and polymer could be modulated, and the electro-optical properties of the polymer matrix/LC/SiO<sub>2</sub> nanoparticles composites could be optimized. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1449–1453, 2009

**Key words:** liquid crystal; SiO<sub>2</sub> nanoparticles; light scattering; optics; photopolymerization

## INTRODUCTION

Polymer-dispersed liquid crystal (PDLC) films consist of a liquid crystal (LC) material dispersed within a semicontinuous polymer matrix<sup>1</sup> exciting great application interests.<sup>2–4</sup> The films show transparent and light scattering states in the electric field-on and field-off states, respectively, which is decided by whether the refractive indices match between the polymer matrix and the LC material.<sup>5–7</sup> The switching properties of the LC molecules within the domains depend on many variables including the size and shape of the LC domain, molecular interactions between the LC material and the polymer matrix. The application of a sufficient strength electric field can overcome the anchoring energy on the LC molecules at the interface. When the electric field is removed, the turn-off time ( $T_{\text{off}}$ ) for the molecules to revert to the equilibrium distribution is usually long.<sup>8</sup>

In our previous research,<sup>9</sup> the addition of a small amount of chiral dopant in PDLC films decreased  $T_{\text{off}}$  significantly, but decreased the light scattering intensity in field-off state and contrast ratio (CR) simultaneously. In this study, PDLC films were prepared by ultraviolet light-induced polymerization of photopolymerizable monomers in nematic LC/photopolymerizable monomers/SiO<sub>2</sub> nanoparticles composites, and the effect of SiO<sub>2</sub> nanoparticles on the electro-optical properties of PDLC films was studied. This interest was also caused by recent achievements of modern nanotechnologies suggesting that a huge number of nanoscale objects could be potentially used as filling materials for PDLC films. Yaroshchuk and coworkers<sup>10,11</sup> investigated the electro-optical properties of filled nematic LC with added inorganic nanoparticles. They made the exhaustive explanation about the variety of the off-state transmittance ( $T_o$ ) and the saturation transmittance ( $T_s$ ), and did present some of the experimental results on the switching times and the voltages measured as a function of Sb<sub>2</sub>O<sub>5</sub> nanoparticles content. However, little work was investigated about the mechanism of the changes in the switching times and the voltages. Their studies may be more reasonable if they had considered this situation.

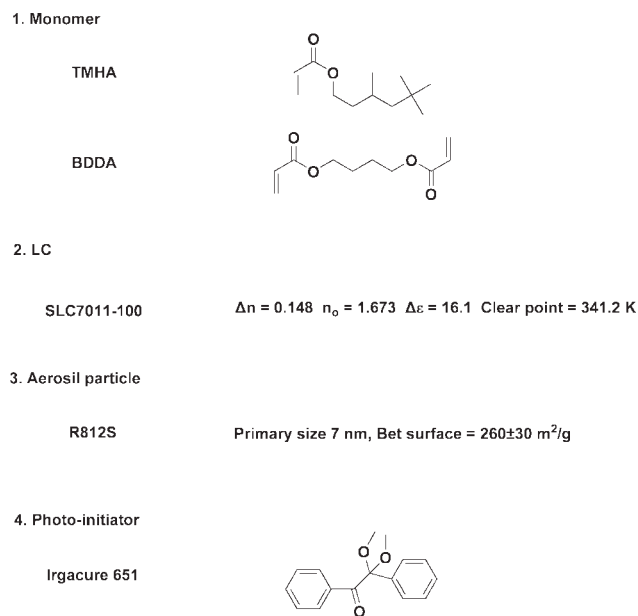
Therefore, in this article, we aimed to investigate the electro-optical properties of the PDLC materials with added organic SiO<sub>2</sub> nanoparticles, and present a reasonable explanation on the changes in the switching times and the voltages in detail. In addition, it was expected that  $T_{\text{off}}$  would be decreased whereas turn-on time ( $T_{\text{on}}$ ) and CR would be

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

increased simultaneously by the adjustment of the SiO<sub>2</sub> nanoparticles content.

## EXPERIMENTAL

### Materials

The nematic LC was SLC 7011-100 (Shijiazhuang Yongsheng Huatsing Liquid Crystal, Shijiazhuang City, Hebei Province, China), and the monomers were 3,5,5-trimethylhexylacrylate (TMHA) (Aldrich Chemical, St. Louis, MO) and 1,4-butanedioldiacrylate (BDDA) (Aldrich Chemical). SiO<sub>2</sub> nanoparticles were hydrophobic silica nanoparticles aerosil R812S (primary size 7 nm, Degussa-Huis, Essen, Germany). The photoinitiator was irgacure 651 (Shijiazhuang Yongsheng Huatsing Liquid Crystal). The chemical structures and some physical properties of these raw materials are shown in Scheme 1.

### Preparation of the PDLC cell

The polymerization-induced phase-separation (PIPS) method<sup>12–14</sup> was used for the sample preparation. At first, SLC 7011-100/TMHA/BDDA/SiO<sub>2</sub> nanoparticles composites were prepared (LC/monomers = 4/1 wt %, TMHA/BDDA = 4/1 wt %), 2.0 wt % of irgacure 651 was added as a UV-curing photoinitiator. Then, the composites were vigorously stirred until a homogeneous mixture had formed. After that the composites were filled into the indium tin oxide (ITO)-coated glass substrates by capillary action. The cell thickness was adjusted to 40 μm by using glass fiber spacers. The composites were irradiated by UV

light (35-W Hg lamp, PS135, UV Flood, Stockholm, Sweden) for 5 min at 273.15 K, thus PDLC cell was prepared. The samples A–E are doped with 0.0, 0.5, 1.0, 1.5, and 2.0 wt % of SiO<sub>2</sub> nanoparticles, respectively.

### Electro-optical measurements

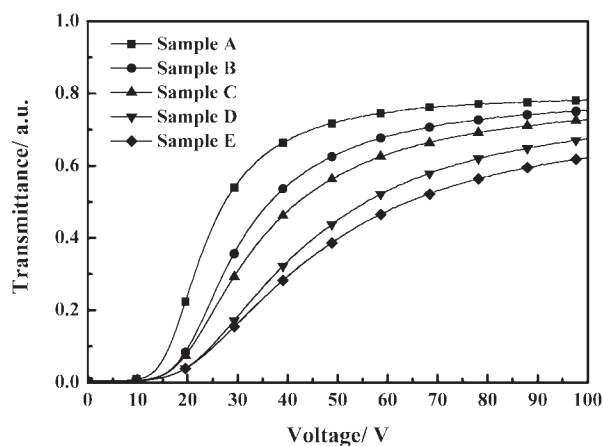
The electro-optical properties of the PDLC films were measured by LCD parameters tester (LCT-5016C, Changchun Liancheng Instrument, Changchun City, Jilin Province, China). A halogen laser beam was used as an incident light source (5 mW power at wavelength 632.8 nm). The transmittance of the PDLC films was recoded with a photodiode, and the response of the photodiode was monitored with a digital storage oscilloscope. The electric field square wave (1 kHz) was applied and the distance between the PDLC film and photodiode was 300 mm. The transmittance of air was normalized as 100%.

## RESULTS AND DISCUSSION

Generally, it is convenient to fix the contents of two components and investigate the electro-optical properties of the system by only changing the content of the third component. In our subsequent consideration of LC/photopolymerizable monomers/SiO<sub>2</sub> nanoparticles composites, the contents of the LC and photopolymerizable monomers are fixed, and the modification of the LC/photopolymerizable monomers composites by SiO<sub>2</sub> nanoparticles is taken into account. When the applied voltage increases, the transmittance of the samples reaches the saturation level  $T_s$ , and  $CR = T_s/T_o$  is commonly known as the switching contrast where  $T_o$  is the initial off-state transmittance. The threshold voltage ( $V_{th}$ ) and the driving voltage ( $V_{dr}$ ) are defined as the electric fields required for the transmittance to reach 10 and 90% of  $T_s$ , respectively.

Figure 1 shows the voltage dependence of the transmittance of samples A–E. As the SiO<sub>2</sub> nanoparticles content increased,  $T_s$  decreased obviously. Meanwhile,  $T_o$  decreased dramatically for the SiO<sub>2</sub> nanoparticles content up to 0.5 wt %, then decreased slightly for contents increasing from 1.0 to 2.0 wt %. These behaviors are more evident in Figure 2, which shows the content of the SiO<sub>2</sub> nanoparticles dependence of  $T_o$  and CR. CR increased at first for the SiO<sub>2</sub> nanoparticles content up to 1.0 wt %, because CR is strongly influenced by  $T_o$  which is the denominator of the fraction, and then decreased dramatically as  $T_s$  decreased fast.

One generally approved explanation is that more LC orientation defects are formed with doping SiO<sub>2</sub> nanoparticles in LC/photopolymerizable monomers



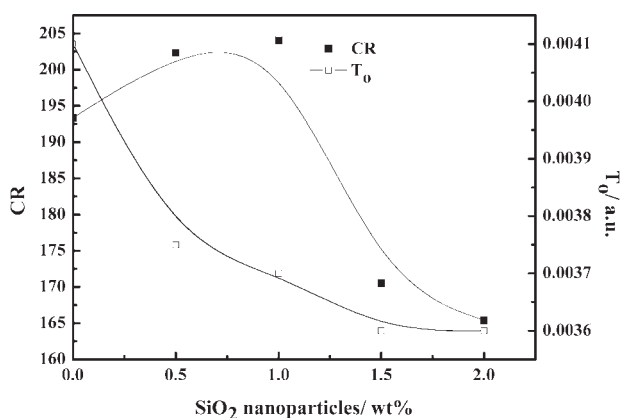
**Figure 1** The applied electric field (1 kHz) dependence of the transmittance of samples A–E.

composites.<sup>10,11,15</sup> The refractive index jump at the border separating LC and SiO<sub>2</sub> nanoparticles aggregates results in a stronger light scattering for samples. As a result,  $T_o$  decreased with increasing the SiO<sub>2</sub> nanoparticles content. When an electric field is applied to the samples, the light scattering caused by the refractive index mismatch of coexisting LC and the SiO<sub>2</sub> nanoparticles can be reasonably considered as a major factor for the samples in the transparent state, where the LC orientation defects disappear. Consequently,  $T_s$  decreased with doping the SiO<sub>2</sub> nanoparticles.

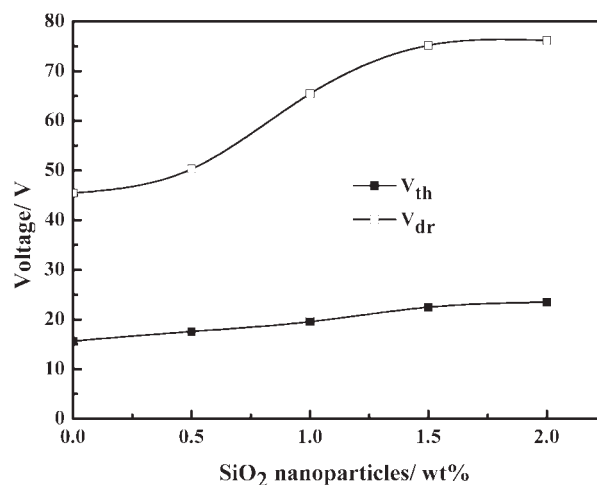
In addition, the refractive index of the modified polymer doped with SiO<sub>2</sub> nanoparticles ( $n_{mp}$ ) is a linear function of the content of SiO<sub>2</sub> nanoparticles<sup>10</sup>:

$$n_{mp} = n_p \phi_p + n_{np} \phi_{np}$$

where  $\phi_p$  and  $\phi_{np}$  are the volume fraction of polymer and SiO<sub>2</sub> nanoparticles,  $n_p$  is the refractive index of the polymer doped without SiO<sub>2</sub> nanoparticles. For PDLC composites, the modification of  $n_p$  may



**Figure 2** SiO<sub>2</sub> nanoparticles concentration dependence of CR and  $T_o$ , respectively.

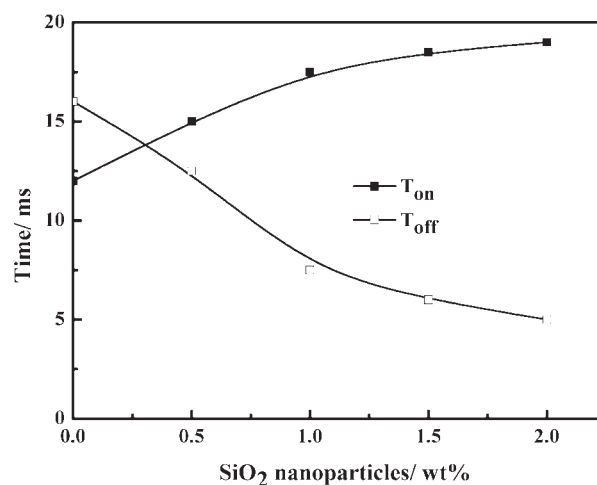


**Figure 3** SiO<sub>2</sub> nanoparticles concentration dependence of  $V_{th}$  and  $V_{dr}$ .

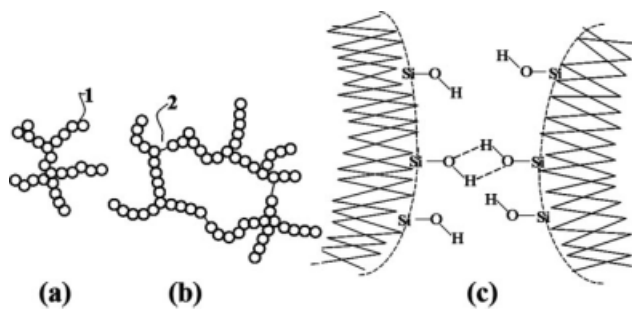
result in significant changes of light scattering characteristics caused by the refractive index mismatch of the coexisting phases.

Figure 3 shows the content of SiO<sub>2</sub> nanoparticles dependence of  $V_{th}$  and  $V_{dr}$ .  $V_{th}$  increased slightly with increasing the content of SiO<sub>2</sub> nanoparticles. Meanwhile,  $V_{dr}$  increased fast when the SiO<sub>2</sub> nanoparticles content was less than 1.5 wt %, and then changed a little for contents up to 2.0 wt %. In addition, it is shown in Figure 4 that  $T_{off}$  decreased dramatically whereas  $T_{on}$  increased simultaneously with increasing the SiO<sub>2</sub> nanoparticles content.

Obviously, SiO<sub>2</sub> nanoparticles played a key role in the variation of the parameters of electro-optical properties as mentioned earlier. Generally, modification can be brought about by the reaction of the  $\equiv\text{SiOH}$  groups on the surface of the silica with organosilicon compounds leading to silanized silica or with other organic compounds.<sup>16</sup>



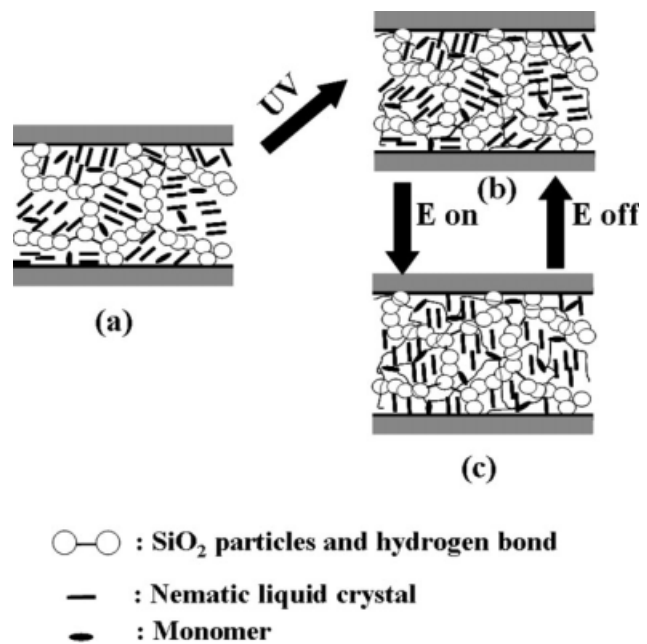
**Figure 4** SiO<sub>2</sub> nanoparticles concentration dependence of  $T_{on}$  and  $T_{off}$ .



**Figure 5** (a) A particle comprising an aggregate of primary particles 1 aggregated by covalent chemical bonds; (b) and (c) agglomeration of the particles by noncovalent bonds hydrogen bonds 2.

In our experiment, the  $\text{SiO}_2$  nanoparticles used were hydrophobic silica nanoparticles aerosil R812S, the surfaces of which were modified with hydrophobic polymethylsiloxane fragments<sup>17,18</sup> and contained a density of  $0.29 \text{ OH groups nm}^{-2}$ . Consequently, the  $\text{SiO}_2$  nanoparticles dispersed in a nematic LC phase could form aggregates through  $\equiv\text{Si}-\text{O}-\text{Si}\equiv$  covalent chemical bonds as shown in Figure 5(a), and then form larger agglomerates via hydrogen bonds as shown in Figure 5(b,c).<sup>19,20</sup>

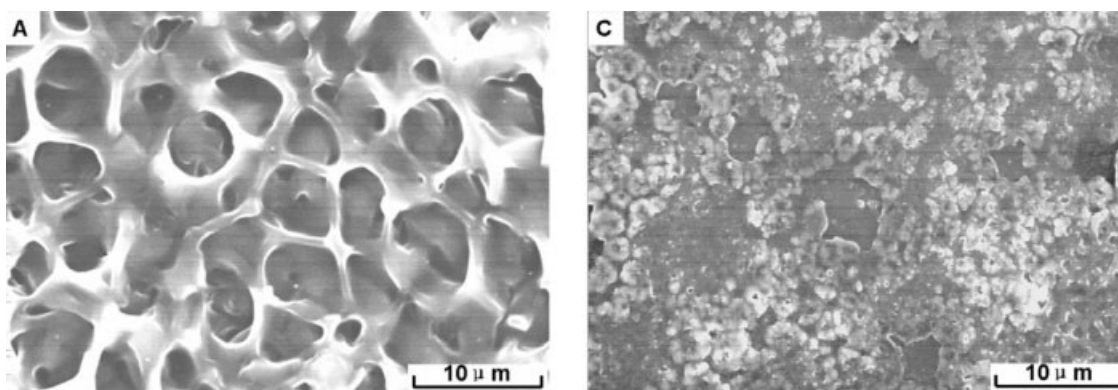
As a result, the agglomerates formed a rather strong network<sup>21,22</sup> in LC layers as shown in Figure 6, which shows the scheme of the inside structure of the sample in three different states. The hydrogen bonds between the  $\text{SiO}_2$  particles surface OH groups and the LC molecules<sup>14</sup> resulted in an effective interaction (a high anchoring strength) of the LC molecules with the  $\text{SiO}_2$  particle surface. Therefore, a larger electric field was required to reorient LC droplets along the direction of the applied electric field, which implied that the greater the  $\text{SiO}_2$  nanoparticles content, the larger were the  $V_{\text{th}}$  and  $V_{\text{dr}}$ . Moreover, longer  $T_{\text{on}}$  was required to overcome the anchoring effect of  $\text{SiO}_2$  nanoparticles agglomerates on the LC molecules. However, when the electrical field was removed,  $T_{\text{off}}$  for the molecules to revert to



**Figure 6** The scheme of the inside structure of the sample in different states: (a) the sample before UV curing; (b) the sample after UV curing in off-state; (c) the sample after UV curing in on-state.

the equilibrium distribution decreased because of the existence of the anchoring energy of the  $\text{SiO}_2$  nanoparticles agglomerates, and this was demonstrated by our experiments.

In addition, the observation of the microstructure of the polymer matrix in the PDLC films was carried out with scanning electron microscopy (SEM; S360, Cambridge, England). The glass substrates were carefully removed and the remaining composite layer was dipped in hexane for about 24 h at room temperature so that the LC molecules were extracted, and the ITO film with the polymer matrix was dried in vacuum. Then, the microstructure of the polymer matrix was observed under SEM after the polymer matrix was sputtered with gold. Figure 7



**Figure 7** (a) and (b) SEM image of the polymer matrix of samples A and C, respectively.

shows the microstructures of the polymer matrix of sample A without SiO<sub>2</sub> nanoparticles [Fig. 7(a)] and sample C with doped 1.0 wt % SiO<sub>2</sub> nanoparticles [Fig. 7(b)]. The formation of the smooth polymer matrix can be seen in Figure 7(a), whereas the formation of the coarse polymer matrix with the particle aggregation can be seen in Figure 7(b). That means the addition of the SiO<sub>2</sub> nanoparticles affected the microstructure of PDLC films significantly because of the formed agglomerates of SiO<sub>2</sub> nanoparticles. This result demonstrates that the above explanation is reasonable.

### CONCLUSIONS

For a PDLC film with optically transparent polymer matrix modified by SiO<sub>2</sub> nanoparticles,  $T_{or}$ ,  $T_{sr}$  and  $T_{off}$  decreased, but  $V_{th}$ ,  $V_{dr}$  and  $T_{on}$  increased with increasing the SiO<sub>2</sub> nanoparticles content due to the anchoring effect of SiO<sub>2</sub> nanoparticles agglomerates on the LC molecules. The observed results show that nematic LC/photopolymerizable monomers/SiO<sub>2</sub> nanoparticles composites are promising for LCD and other electro-optical applications. Further research to optimize these devices and to better understand the mechanism of physics is in progress.

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