Cholesteric liquid crystal devices with nanoparticle aggregation

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Abstract: A broadband cholesteric liquid crystal (CLC) device with a multi-domain structure is demonstrated by using an aggregation of polyhedral oligomeric silsesquioxane (POSS) nanoparticles in the CLC layer. The aggregation pattern of the self-assembled POSS nanoparticles depends on the concentration of POSS doped in the mixture of POSS/CLC and the cooling rate of the mixture from a temperature higher than the clear point. POSS-induced changes in the bulk and surface properties of the cholesteric cells, such as a promotion of homeotropic alignment, help to form a cholesteric structure with a broadband reflection of light; the latter can be used for improvement of bistable CLC devices. A higher POSS concentration and a higher cooling rate both improve the appearance of the black-white CLC device.

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1. Introduction

Bistable reflective cholesteric liquid crystal (CLC) displays have seen major development in the past few years in electronic paper applications due to their advantageous low power consumption and high reflectivity [1,2]. The CLC reflective displays have two bistable states at zero fields. One is a planar texture where the helical axis is perpendicular to the substrate surface and where the CLC reflects colored light centered at a wavelength given by $\lambda_0 = nP$, where n and P are the average reflective index and pitch of the CLC, respectively. Another state is the focal-conic texture in which the light scatters weakly, which can be applied as a dark state by using an absorption layer placed on the bottom substrate [3–6].

Because the mono-color display is not very desirable in electronic papers, where a black-white appearance is much preferred, extensive investigations of the black-white and broadband CLC display have been conducted and reported [5–10]. For example, a black-white CLC display was achieved by dissolving relatively high polymer concentrations in the CLC layer, which stabilizes the cholesteric texture (polymer-stabilized cholesteric texture, PSCT) [5]. However, the presence of a large amount of polymer at the interface between the liquid crystal and polymer caused strong scattering that prevented the dark state from being sufficiently black. Instead, the technique of doping a small amount of monomer into the CLC layer and then photo-polymerizing the monomer in the homeotropic state to form the polymer network was developed [6]. Thus the formed polymer network prevented the CLC helix of the planar structure from being perpendicular to the substrate surface, and generated the multi-domain structure.

In this paper, the proposed CLC broadening technique relied on an extremely different mechanism. A novel technique to achieve a broadband CLC display with a multi-domain structure was demonstrated by using an aggregation of polyhedral oligomeric silsesquioxane (POSS) nanoparticles in a CLC layer. POSS is a silica-based nanocomposite. Each POSS molecule contains covalently bonded reactive functionalities suitable for polymerization or for grafting POSS monomers to polymer chains and nonreactive organic functionalities for solubility and compatibility of the POSS segments with the various polymer systems [11–13]. The diameter of the POSS molecules is of the order of a few nanometers. The pattern of POSS aggregation depends on the POSS concentration in the POSS/CLC mixture and on the cooling rate of the mixture from a temperature higher than the clear point. The POSS nanoparticles also play a second role, in aligning LC molecules vertically. The vertical alignment capability induced by POSS is due to the adsorption of POSS on the inner surfaces of substrates and by the associated lowering of the corresponding surface energy [14,15]. Owing to the inherently strong aggregation property of POSS and the POSS-induced vertical alignment in the CLC layer, the existence of a POSS-cluster breaks the helix of the planar structure into a multi-domain structure and stabilizes the focal-conic texture.

2. Experimental

The broadband CLC cells were fabricated by using two ITO-glass substrates without using conventional alignment layers. The cell gap was maintained at around 9 μm by bead spacers. Here, 1,2-Propanediollsobutyl POSS (Aldrich) was used as the nanoparticle. The mixture of POSS and CLC ($\triangle$n = 0.179, $n_\parallel$ = 1.687, nP = 595nm, $T_{clearing}$ = 66°C) was prepared at concentration of 5, 10, 15 and 20 wt %, respectively. The POSS/CLC mixture was maintained in the isotropic phase and was injected into the empty LC cells by the capillary effect. During injection of the mixture, the sample was heated at a temperature above the clearing point to ensure that the POSS particles were dispersed uniformly in the cell and to avoid recrystallization–induced POSS-CLC demixing. After finishing the LC mixture injection and sealing the injection hole, all LC cells were first heated to the isotropic state and then cooled in a controlled cooling stage. During the cooling process, the POSS became aggregated and formed a random-cluster.

In order to evaluate the performance of the broadband CLC cells, the transmission spectra $T(\lambda)$ of the CLC cells were measured using diffused light produced by an integrating sphere. The cells were attached to one port of the integrating sphere and a spectrometer was placed behind the CLC cell as shown in Fig. 1. The apparatus was set up to measure transmission spectra rather than reflection spectra because the conventional reflection measurements are sensitive to apparatus geometry and a very careful measurement is required to obtain a reliable result [16]. Here the probing light source is nonpolarized white light, and the reflection spectra $R(\lambda)$ was determined by plotting $1-T(\lambda)$, assuming that energy is conserved $(T + R = 1)$. The electro-optic response of the CLC cell was determined by recording the reflection value at a wavelength of 590 nm. A 60 Hz square pulse with a width of 60 ms was applied to drive the CLC cell.
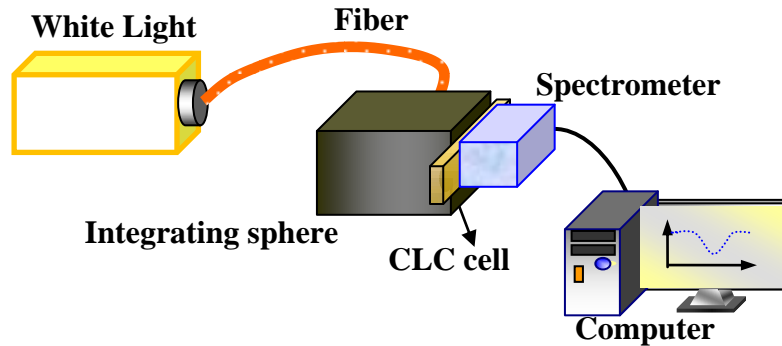

Fig. 1. The experimental setup for measuring the transmission spectrum of a CLC device.

3. Results and discussion

The structure of POSS nanoparticles used in this work is shown in Fig. 2. The POSS nanoparticles dispersed in the CLCs became aggregated to form a cluster due to the hydrogen bond formed between hydroxyl compounds in the side chains. The influences of the dispersed POSS concentration and cooling rate from a temperature higher than the clear point on the patterns of the POSS aggregates are shown in Fig. 3. The images were observed by polarized optical microscopy (POM) while the CLC cells were operated in the homeotropic state. As the POSS concentration is increased, more POSS nanoparticles aggregate to form denser and bigger clusters. Increasing the cooling rate reduces the size of the cluster and correspondingly the characteristic dimensions of the LC multi-domain unit.
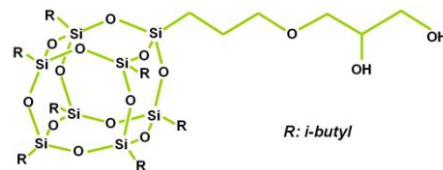

Fig. 2. The structure of 1,2-Propanediollsobutyl POSS.

The study of the aggregation of small particles to form clusters is a fundamental research topic in areas such as colloid physics. Two regimes of kinetic models, namely diffusion-limited and reaction-limited kinetics, have been developed to describe the growth dynamics of clusters [17]. The major differences in the aggregation patterns illustrated in Fig. 3 may be explained by the different growth kinetics, which depend on the cooling rate and POSS concentration.
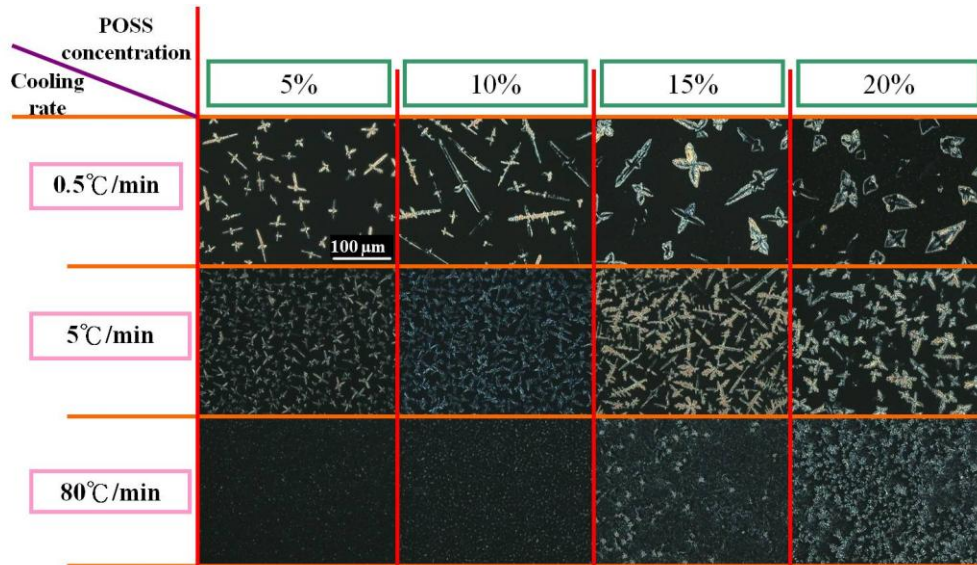
Fig. 3. The aggregation patterns of CLC cells doped with different POSS concentration (5 wt%, 10 wt%, 15 wt%, 20 wt%) and different cooling treatment (0.5 °C/min, 5°C/min, 80°C/min)observed by a polarizing optical microscopy.

The influence of POSS concentration on the reflection spectra of CLC cells is shown in Fig. 4, where the cooling rate is maintained at around 80°C/min. A Bragg reflection spectrum for a pure CLC cell (without POSS dopant) was measured and is shown in Fig. 4 for comparison. The randomly connected clustering induced by the POSS aggregation in the CLC was applied to disrupt the CLC's helical structure and break the planar texture into a multi-domain structure. The resulting observed broadband reflection spectrum is shown in Fig. 4. The high reflectance, of ~50%, for the CLC cells is mainly due to the contribution of surface reflection from the top and bottom glass substrates. The reflection at two interfaces of glass-air was measured by using a glass substrate as a test sample in Fig. 1, and the reflectance was determined as ~12%.

The influence of cooling rate of the CLC device on the reflection spectra of the CLC cells is shown in Fig. 5, where the POSS concentration was kept at 10 wt%. We found that the faster cooling rate did broaden the reflection spectrum of the CLC cell. In addition, the reflection of the CLC cells with a cooling rate of 80°C/min was higher than those with cooling rates of 5°C/min and 0.5°C/min. The higher reflection is mainly caused by the denser POSS clusters which contribute to the multi-domain planar structure in the CLC cell as shown in Fig. 3.

The appearance of a CLC cell operated in the multi-domain planar state and focal-conic state with 10 wt% POSS concentration and 80°C/min cooling rate is compared with a pure CLC cell without POSS in Fig. 6. Figure 6(a) and Fig. 6(b) illustrate that the existence of POSS clusters can contribute to the white appearance in the bright state (planar state) due to the broadband reflection spectrum and slight deterioration in the dark state (focal-conic state) due to the cluster-induced light scattering, as shown in Fig. 5(c) and Fig. 5(d).
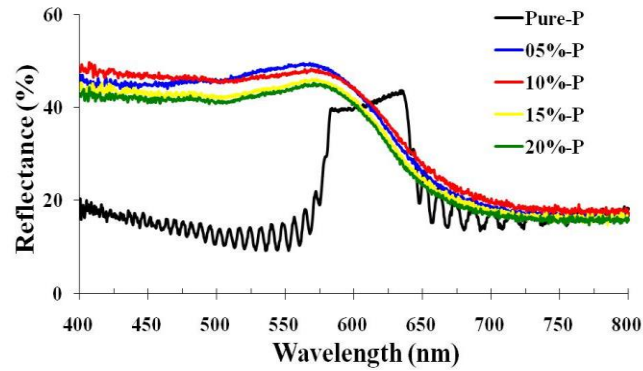
Fig. 4. The influence of POSS concentration on the reflection spectra of CLC cells operated in the multi-domain planar state.
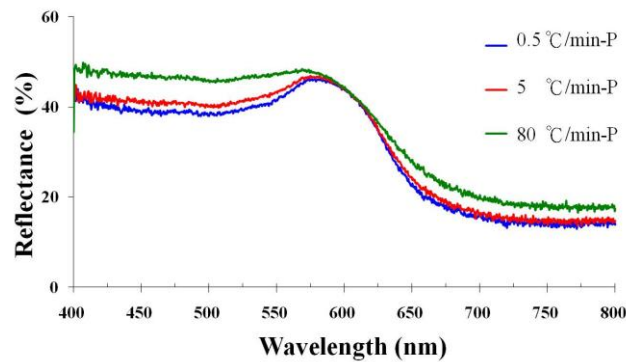

Fig. 5. The influence of cooling rate on the reflection spectra of CLC cells operated in the multi-domain planar state.
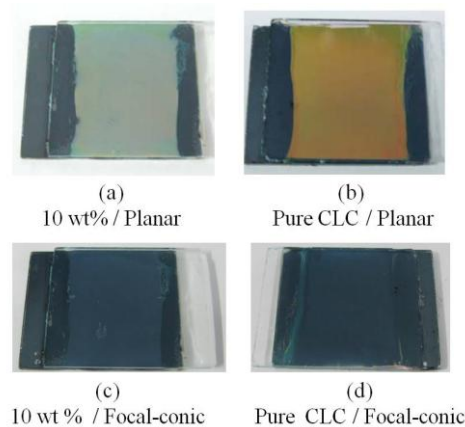

Fig. 6. The appearances of CLC cells operated in multi-domain planar state and focal-conic state with 10 wt% POSS concentration and 80°C/min cooling rate comparing with a pure CLC cell without POSS.

One typical electro-optical property of the CLC cell (80°C/min cooling rate, 5 wt% POSS) is shown in Fig. 7. The CLC cell was in the multi-domain planar state prior to the applied voltage. The reflectance decreased with increasing voltage when a driving voltage between 10 and 40 V was applied. The reflectance of the cell reached its original value when the driving

voltage was higher than 45 V. An applied voltage between 40 V and 45 V allows gray scale switching.
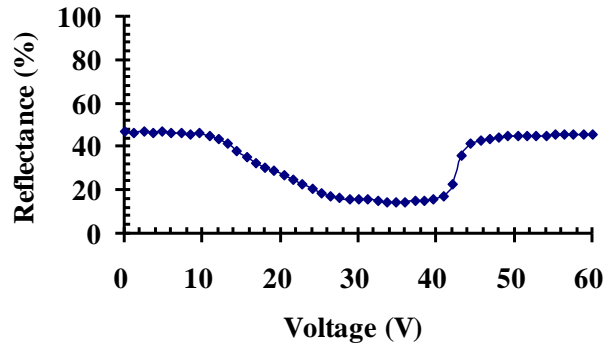

Fig. 7. Reflectance as a function of driving voltage for a CLC cell (10 wt% POSS concentration and 80°C/min cooling rate) operated in the multi-domain planar state prior to the driving voltage.

4. Conclusion

The adsorption of the POSS on the ITO glass substrate would anchor the LC molecules vertically, and the dispersed POSS will aggregate to form clusters with properties controlled by the cooling process and POSS concentration in the CLC cell. The presence of the POSS cluster would break the planar texture into a multi-domain structure and stabilize the focal-conic texture. As a result, the orientations of the CLC helical axes will have a wide distribution and a multi-domain planar texture is thus created. These POSS clusters cannot only be used to stabilize the bistable states of the CLC, but also to broaden the reflection spectrum of the planar texture to generate a white appearance.

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