

Surfactants Synergistically Contributes to Reduction of Driving Voltage of Reverse-Mode Polymer Network Liquid Crystals with UV-Curable Nanoparticles

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ABSTRACT

We demonstrate that combination of UV-curable silica nanoparticles (UVC-NPs) with polymerizable surfactants greatly reduce the threshold and saturation voltages of a reverse-mode polymer network liquid crystal (R-PNLC) device. Morphological observation reveals that surfactants contribute not only to reduction of the anchoring energy of LC at the interface between LC and polymer network but also to inhibition of aggregations of UVC-NPs and polymers.

1. INTRODUCTION

Light-scattering type devices based on the polymer-dispersed liquid crystal (PDLC) or polymer network liquid crystal (PNLC) that can control switching between the translucent and transparent states have been widely studied for one of advanced LC display applications because PDLC (PNLC) films can be fabricated by a cost-effective and simpler procedure, do not require additional optical element including polarizers, and find a variety of applications such as flexible displays, light shutters, smart windows, and so on [1].

Most of the PDLCs and PNLCs are formed by the polymer-induced phase separation (PIPS) process. Conventional PDLCs, referred to as normal-mode PDLCs, shows the translucent (light-scattering) states at no bias voltage, and becomes transparent under applied voltage because the LC director inside a droplet re-orient by electric field as resolving the mismatch of refractive index between LC droplets and surrounding polymer matrix. Contrary to this, reverse-mode PNLCs (R-PNLCs) have a transparent off state and a translucent on state. There are various methods for preparation of a R-PNLC film, among which forming anisotropic polymer network by photopolymerizing reactive mesogens (RMs) mixed with a low-molecular mass LC material is widely used [2].

In our previous study, we investigated the basic electro-optical properties of UV-curable silica nanoparticles (UVC-NPs) doped R-PNLC film [3]. The surface of UVC-NPs is covered with UV-curable functional groups such as acrylate. In Ref. [3], we reported that the threshold and saturation voltages of R-PNLCs incorporated with UVC-NPs are reduced, but contrast ratio

is deteriorated due to a small amount of aggregations of NANOBYK-3605 (UVC-NPs/HDDA dispersion) in the RMs/LC mixture. Thus, dissolving the aggregation of UVC-NPs is needed for high contrast ratio by realizing better transparent and translucent state of the R-PNLC with UVC-NPs.

In order to overcome this difficulty, we focus on the application of suitable polymerizable surfactants. It has been illustrated that (polymerizable) surfactants reduce the anchoring energy of LC in PDLCs and Holographic-PDLCs, thereby decreasing the driving voltage [4,5]. As motivated by prior research on application of surfactants to PDLCs, in the present study we investigate the combinational effect of UVC-NPs and polymerizable surfactants for R-PNLCs based on RMs/LC composites so as to improve the driving voltage as well as the contrast ratio by suppressing the aggregations of UVC-NPs. We evaluate the contribution of UVC-NPs and polymerizable surfactants to the performance of the R-PNLCs by measuring the basic electro-optical properties and observing the morphology by polarizing optical microscope (POM) and field emission-type scanning electron microscopy (FE-SEM).

2. EXPERIMENTAL

2.1 Materials

We used the commercial nematic LC mixtures MLC-2038 ($\Delta n = 0.103$ at $\lambda = 589.3\text{nm}$, $\Delta\epsilon = -5.0$ at $f = 1.0\text{kHz}$, and $\gamma = 179\text{mPa}\cdot\text{s}$ at 20°C , Merck) and MLC-2081 ($\Delta n = 0.201$ at $\lambda = 589.3\text{nm}$, $\Delta\epsilon = -4.2$ at $f = 1.0\text{kHz}$, and $\gamma = 400\text{mPa}\cdot\text{s}$ at 20°C , Merck) as host LC material which have a negative dielectric anisotropy. As for reactive mesogens (RMs), we purchased 1,4-Bis[4-(3-acryloyloxypropoxy)benzoyloxy]-2-methyl benzene (RM257, Tokyo Chemical Industry) which is a diacrylate monomer. As for photoinitiator, we used Irgacure 651 (BASF). In the present study, we used the same UV-curable silica nanoparticles (UVC-NPs), NANOBYK-3605 (BYK-Chemie GmbH), as used in our previous study to replace a part of RMs. NANOBYK-3605 is a dispersion of UVC-NPs whose surface is modified with acrylate groups in 1,6-Bis(acryloyloxy)hexane (HDDA) (carrier) with mixing ratio 1:1 by weight. HDDA is a non-liquid crystalline,

Table 1 Formulations of the R-PNLCs in weight ratio.

| Composite | RM257 | NANOBYK-3605 | LC |
|-----------|-------|--------------|----|
| A | 5 | 0 | 95 |
| B | 3.5 | 1.5 | 95 |

*We also prepare another set of composites in which 2% weight ratio of 10-Undecenoic acid was contained with respect to the above composites. We refer to them as A+10-UA and B+10-UA.

difunctional, and photopolymerizable monomer with relatively simple chemical structure. As for polymerizable surfactants, we applied 10-Undecenoic Acid (10-UA, Tokyo Chemical Industry) which has been used in Ref.[4].

2.2 Sample Cell Preparation

The sample preparation is as follows: first, RM257, NANOBYK-3605, and LC mixture were mixed with different weight ratios as shown Table 1. Next, a RM257/NANOBYK-3605/LC composite and 10-UA were mixed with 98:2 in weight ratio. Then, 3wt% (against the amount of reactive component, i.e., monomers and/or NPs) of Irgacure 651 was added to them. The uncured composite was first stirred by a magnetic stirrer over a sufficient period of time. In the case of the uncured composite containing UVC-NPs, it is additionally sonicated intensively to disperse UVC-NPs sufficiently. A small amount of the uncured composites was spread in an empty cell of gap of 10 μ m at +10°C above the clearing temperature, which has homeotropic alignment layers of polyimide SE-4811 (Nissan Chemical) without rubbing. As for the formation of alignment layer, the polyimide was dried at 90°C after spin-coating the varnish on the ITO glass substrates (E.H.C) and then baked at 210°C for 40min. Then the test cells were irradiated with a UV light of 365nm, 5mW/cm² for 60 min at room temperature in order to promote the polymerization-induced phase separation (PIPS) of mixtures. For the test cells containing UVC-NPs a voltage of around the threshold one (between 10V and 30V) with a square wave of 1kHz was applied before UV irradiation to disperse the aggregations. Finally, the cells were re-heated above +10°C of clearing temperature and gradually cooled down to room temperature.

2.3 Measurement

The electro-optical properties of these light-scattering films are measured with an LCD evaluation system LCD-5200 (Ohtsuka Electronics). During an electro-optical measurement, a square wave voltage of 1kHz was applied. For measuring a voltage-dependent transmittance, an applied voltage is varied from 0V to 150V by using a built-in function generator and an external high-speed voltage amplifier T-HVA02 (Turtle Industry). The rise time, t_{Rise} is defined as the time required reaching from $T_{\text{min}}+0.9(T_{\text{max}}-T_{\text{min}})$ to $T_{\text{min}}+0.1(T_{\text{max}} - T_{\text{min}})$ where T_{max} is the maximum transmittance at no applied voltage and T_{min} is the minimum transmittance reaching by applying a certain voltage for response time measurement

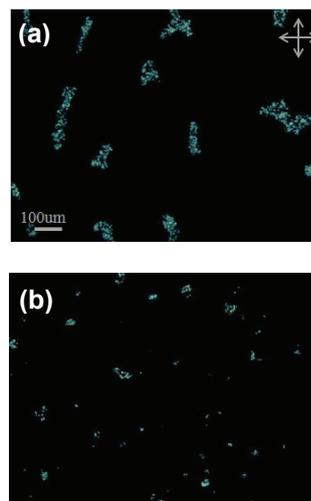


Figure 1 POM images of the cell (a) B (without surfactants) and (b) B+10-UA (with surfactants) after UV irradiation. The host LC material is MLC-2038. The bright spots correspond to lumps of UVC-NPs and polymer. The dark texture exhibits a vertical LC alignment. The bar is 100 μ m.

(which is usually not equal to a saturation voltage). The fall time, t_{Fall} is the time required to return to $T_{\text{min}}+0.9(T_{\text{max}}-T_{\text{min}})$ from $T_{\text{min}}+0.1(T_{\text{max}} - T_{\text{min}})$ after switching the voltage off. Here, the reference of light intensity is taken as a transmitted light without test cells. The measurement is done without any polarizer and at room temperature. For morphological observation, we used a polarized optical microscope (POM) BX-53 (Olympus) and a field-emission type scanning electron microscope (FE-SEM) S-4800 (Hitachi High-Tech).

3. RESULT

3.1 Morphological Observation

Figure 1 shows polarizing optical micrographs of the R-PNLC film with UVC-NPs (Composite B and B+10-UA) at no bias (initial) state after UV initiated polymerization under crossed polarizers. For the Composite B, several lumps are observed as large bright spots in Figure 1(a). These lumps are not observed in the R-PNLC films without UVC-NPs. Thus, it is inferred that UV irradiation causes the growth of lumps by photopolymerization from small aggregations of UVC-NPs which are present in the cell before UV irradiation (micrograph not presented). These large aggregations of UVC-NPs and polymers do not scatter light effectively and cause an upper shift of on-state transmittance of the R-PNLC at higher voltage region. It is the reason for lowering of the contrast ratio by incorporating UVC-NPs into the R-PNLC as was mentioned in the previous study [3]. On the other hand, it is clearly seen that adding the surfactants reduces apparent large lumps in the Composite B+10-UA as can be seen from Figure 1(b). That is, added 10-UA contribute to preventing the aggregation of UVC-NPs before UV irradiation as expected.

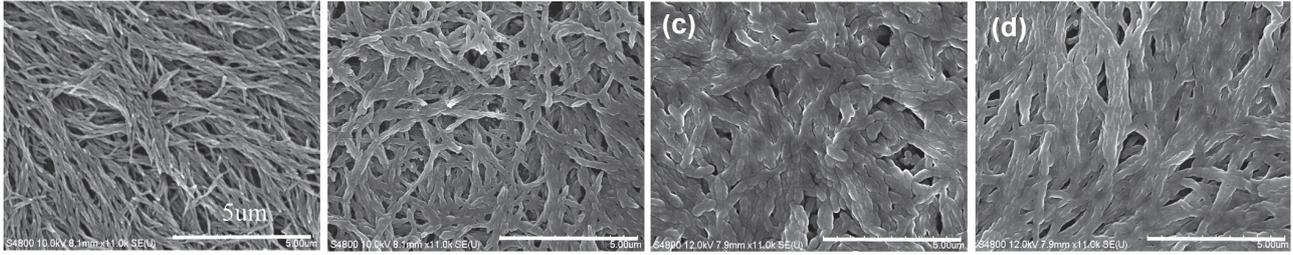


Figure 2 SEM images of polymer network formed inside the test cells (a) Composite A, (b) Composite A+10-UA (with surfactants), (c) Composite B (with UVC-NPs and without surfactants), (d) Composite B+10-UA (with UVC-NPs and surfactants). The host LC material is MLC-2081. The bar represents 5μm.

Figure 2 shows a series of SEM images of polymer network formed inside the R-PNLC cells. The host LC material used is MLC-2081. The morphology of polymer network made from RM257 only has an intermediate feature between the so-called “smooth” and “rice-grain like” one [6] as can be seen in Figure 2(a). The cross-sectional diameter of a distinguishable polymer bundle is around 50 nm. According to the fibril-bundle model of PNLC made from reactive mesogens [7], a small amount of LC molecules may be trapped inside a polymer bundle. Figure 2(b) shows a SEM image of polymer network formed with the presence of 10-UA. The cross-sectional diameter of a single polymer bundle increases about by two times as compared to that in Figure 2(a). A possible relevant factor of thickening the polymer bundles is hydrogen-bonding between carboxyl terminals of 10-UA, although clear evidence about this factor is lacked in the present stage. Figure 2(c) exhibit the morphology of polymer network incorporating the UVC-NPs without adding the 10-UA surfactant. Observed polymer bundles are much bloated and gnarled. Furthermore, the boundaries among bundles are not clear; It looks like a swollen blob rather than a meshed network. Figure 2(d) shows also the polymer network formed inside the UVC-NPs incorporated composite, as 10-UA was also added. Still the polymer bundles are very thick, but the cross-sectional diameter is smaller relative to the case of Figure 2(c). The morphological feature of polymer network is intermediate between those observed in Figure 2(b) and (c). As is clear from these SEM micrographs, both UVC-NPs and 10-UA largely affect the structure of polymer network formed inside the cells after photo-initiated polymerization. It is natural to think that the alternation of polymer network by addition of UVC-NPs and 10-UA inevitably cause the change in the electro-optical properties of the R-PNLC device. In the next section, we describe in detail the result obtained by the electro-optical measurement.

3.2 Electro-optical properties

Figure 3 shows the result and comparison of electro-optical properties of R-PNLC films of different host LC materials. Regarding on the overall voltage-dependent transmittance (V-T) curve, the cell whose host LC material is MLC-2081 works under lower voltage application and

becomes steeper than those based on MLC-2038. As represented by a dotted line in Figure 3(a)(b), addition of 10-UA leads to a small reduction of driving voltage. This voltage reduction is attributed to the decrease of anchoring energy at the interface between LC molecules and polymer network due to the exposition of hydrophilic part of 10-UA on the surface of polymer bundles [4,5]. When replacing a part of RMs with a dispersion of UVC-NPs with HDDA, the large shift of V-T curve to lower voltage region is obtained as is the same as our previous report [3]. It is also found that extra addition of 10-UA as a polymerizable surfactant leads to further reduction of driving voltage of the R-PNLC as summarized in Figure 3(c)(d). Before going to see the details of the result, we here give the definitions of V90 and V10 as important characteristic voltages. First for each V-T curve, T100 is defined as the maximum transmittance usually obtained at no bias voltage and T0 is the minimum transmittance (the highest haze state) usually obtained at saturation voltage. Then V90 is the voltage which gives the transmittance of $T_{90}=T_0+0.9(T_{100}-T_0)$ and it is a substitute of the threshold voltage. Similarly, V10 denotes the voltage which gives the transmittance of $T_{10}=T_0+0.1(T_{100}-T_0)$ and it is used as an applying voltage for response time measurement. The comparison of V90 and V10 for each composite is given in Figure 3(c)(d). The V90 of the R-PNLC incorporated with UVC-NPs (Composite B) marks 17.2% reduction for the composite of MLC-2038 and does 36.1% reduction for the case of MLC-2081 as compared to that the undoped R-PNLC (Composite A). Moreover, 35.3% and 46.3% reduction were obtained for the composite with extra addition of 10-UA for the composite based on MLC-2038 and MLC-2081 respectively (Composite B+10-UA). The voltage reduction tendency of V10 is almost the same as V90 except for the case of composites whose host LC is MLC-2081. Here it should be mentioned that the value of V10 of MLC-2081-based Composite B+10-UA is not too large but the V10 of Composite B is too small. This small V10 can be ascribed to the upper shift of T0 of the MLC-2081-based Composite B due to the presence of large aggregates as mentioned before and can be seen from a gray line in Figure 3(b). Concerned on the

response time measurement, both t_{Rise} and t_{Fall} increases as increasing the additives.

Now we are going to discuss the electro-optical properties of the R-PNLCs in conjunction with the morphological observation by FE-SEM. As discussed in our previous report, UVC-NP works as a big cross-linker during polymerization, and then largely contribute to the progress of PIPS. Consequently, UVC-NPs (and HDDA) are reacted intensely with the polymer bundles made from RM257, and then they are too much bloated. It may also lead to enlargement of mesh size of network in some places, resulting in the reduction of driving voltage and delay of response [7]. In addition, polymerized UVC-NPs and HDDA enclosing a polymer bundle of RMs may weaken the LC alignment ability of bare polymer bundle made from RMs only. On the other hand, 10-UA form a dimer in the uncured mixture, whose relatively long alkyl chain prevents aggregation of UVC-NPs as a surfactant. During UV irradiation, 10-UAs polymerize with RM257, UVC-NPs and HDDA, and then the hydrophilic carboxyl groups are exposed on the surface of polymer bundles. The presence of many hydrophilic groups on the surface of polymer bundle gives several effects. The one is the reduction of anchoring strength of LC molecules which leads to the lower shift of V-T curve and delay of response of the R-PNLC. And they restrain excessive bloating of polymer bundle, since carboxyl group of 10-UA is not a reactive one. These features of 10-UA synergistically contribute to the reduction of driving voltage of the R-PNLC implemented with UVC-NPs.

4. CONCLUSION

In this study, we investigate the synergetic effect of UVC-NPs and polymerizable surfactant on the morphological alteration of polymer network formed by UV irradiation as well as on the electro-optical properties of R-PNLC as a light-controlling device. It is found that the polymerizable surfactant plays an important role for realizing the better R-PNLCs.

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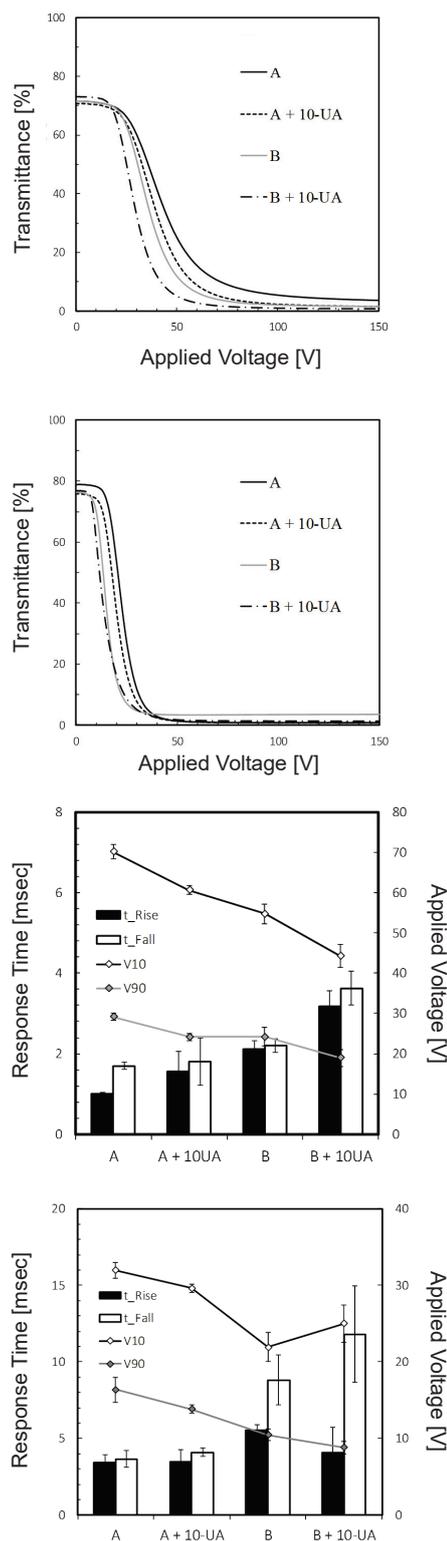


Figure 3 (a) (b) Applied voltage dependent transmittance of the R-PNLC films with different formulations. (c) (d) Comparison of the t_{Rise} and t_{Fall} response time of the samples. Line data corresponds to the threshold (V90) and saturation (V10) voltages. V10 is applied for response time measurements. The host LC material are (a) (c) MLC-2038, (b) (d) MLC-2081.