Polymer stabilized vertical alignment liquid crystal display: effect of monomer structures and their stabilizing characteristics

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Abstract

A polymer-stabilized vertical alignment (PS-VA) mode using a new type of photoreactive monomer for polymer stabilization of the liquid crystal (LC) director was developed. Conventional reactive mesogens having a higher molecular weight than those of the host LC tend to aggregate and form large-sized polymer grains when exposed to ultraviolet (UV) light, subsequently deteriorating the quality of the dark state. To address these problems, bis(4-hydroxyphenyl) diacrylates were synthesized with four different linking groups as stabilizing monomers (SMs) which have molecular weights similar to that of the host LC. Their stabilizing characteristics with respect to the molecular size and polarity of SMs were evaluated by examining the electro-optic characteristics of LC cells after UV irradiation. The results showed that the SM containing a small linking group in size between biphenyls with high polarity was favored to achieve excellent polymer stabilization. The SM containing an ether linkage showed excellent electro-optic characteristics with no large-sized polymer grains even in the absence of a photo-initiator. Consequently, we anticipate that SMs, polar and smaller in size, can improve the electro-optic characteristics in PS-VA mode.

Keywords: vertical alignment, polymer stabilization, reactive mesogen, stabilizing monomer

(Some figures may appear in colour only in the online journal)

1. Introduction

Image quality of liquid crystal displays (LCDs) has been developed using many LC modes such as in-plane switching (IPS) [1], fringe-field switching (FFS) [2–7], and multi-domain vertical alignment (MVA) [8–11]. Among these, the MVA modes are rubbing free devices with high contrast ratio in normal directions compared to other modes. However, these modes have problems such as slow rising response times. In order to address this problem, vertical alignment with a slight tilt angle in four different azimuthal angles with the help of polymer stabilization has been developed [12–18]. In a polymer-stabilized vertical alignment (PS-VA) mode, a small amount of photoreactive stabilizing monomer (SM) is added into the host LC mixture. Figure 1(a) schematically shows the dispersion of LC and SM molecules in the filled cell before curing. When a
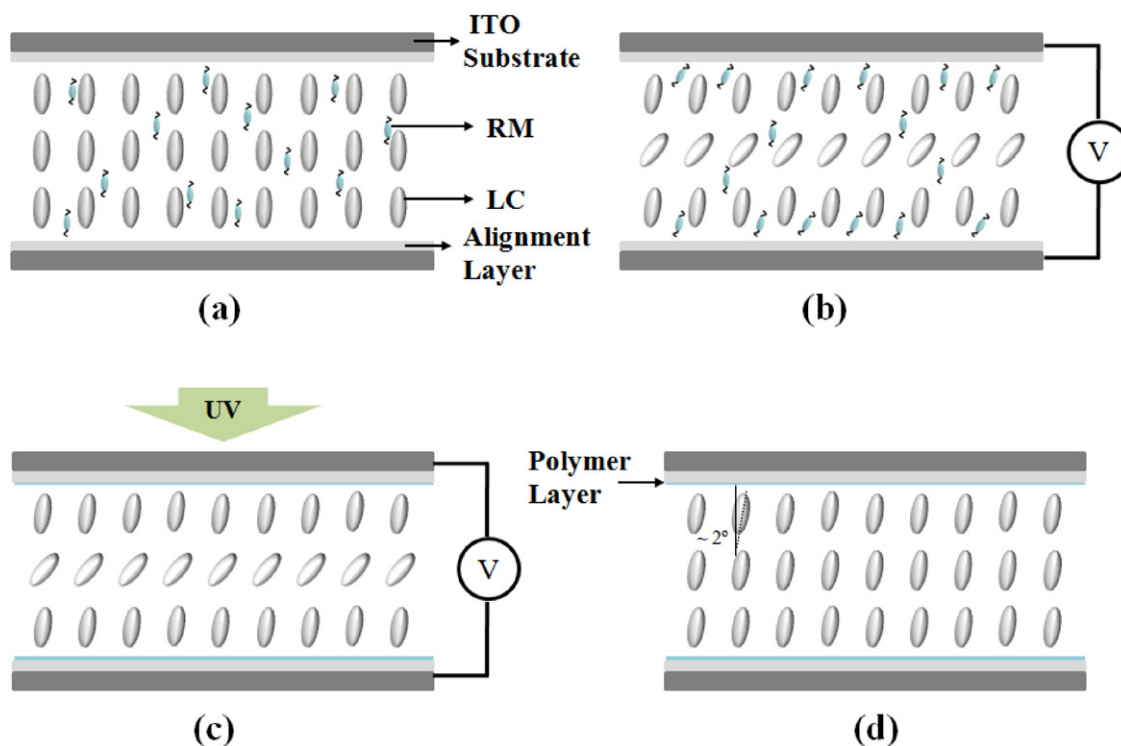
Figure 1. Schematic illustrations for the fabrication of the PS-VA mode: (a) the LC/SM mixture confined in the cell before photo-polymerization of SMs, (b) the reoriented LC molecules above the threshold electric field ($V > V_{th}$), (c) the UV photo-polymerization of SM above the electric field ($V > V_{th}$), (d) the near vertical alignment of the LC director with a predetermined tilt angle of about 2° without the electric field.

voltage larger than the threshold voltage (V_{th}) is applied to the cell, the LC directors are tilted down as shown in figure 1(b). When LC directors are in a stable state while forming a surface tilt angle, the UV light is exposed to the cell inducing photo-polymerization of SM, and subsequently, thin polymer layers are formed at both surfaces producing a surface tilt angle (see figure 1(c)). Finally, when the voltage is released, the LC director is relaxed to a vertical alignment except for a slight pretilt angle at both surfaces due to the polymerized SM layer (see figure 1(d)). Therefore, it is important for the SM to exhibit good diffusion in LC, appropriate phase separation and no large aggregation during UV exposure. If the size of aggregation is too large, it may cause a strong light leakage in the dark state [17]. It is also known in PS-VA mode that a tilt angle change can occur by voltage stress (which will appear as a image sticking problem in LCDs) and the level of change is strongly dependent on the chemical structure of the monomer, meaning that a monomer in which two polymerizable acrylate groups are bound directly to 1,1′-dihydroxybiphenyl is favored for a small tilt change [19]. In addition, fast polymerization of the RM with weak UV intensity is also important for reducing the processing time. Therefore, it is crucial to understand relationships between the molecular structure of SMs and their stabilizing characteristics of PS-VA LCDs.

In this work, we synthesized four SMs containing different linking groups between two 4-acryloxyphenyl groups, and investigated their stabilizing characteristics with respect to their molecular structures in VA cells with a fishbone shaped pixel electrode and plane shaped common electrode. As a result, we found that electro-optic characteristics of LC cells
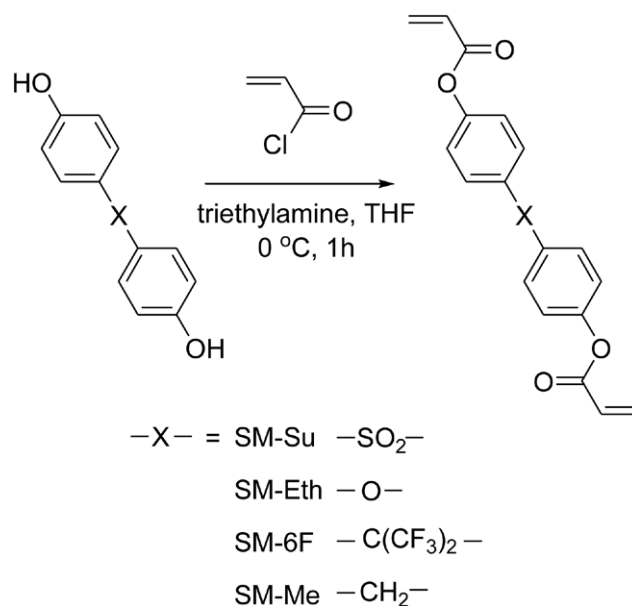

Figure 2. Chemical structures and general synthetic scheme of photoreactive SMs containing different linking groups.

strongly depend on the structure and properties of SMs such as polarity and molecular size.

2. Syntheses of reactive monomers and experimental conditions

We set up molecular dimension of SMs similar to LCs (around 300 g mol^{-1}), expecting fast diffusion and consequently less
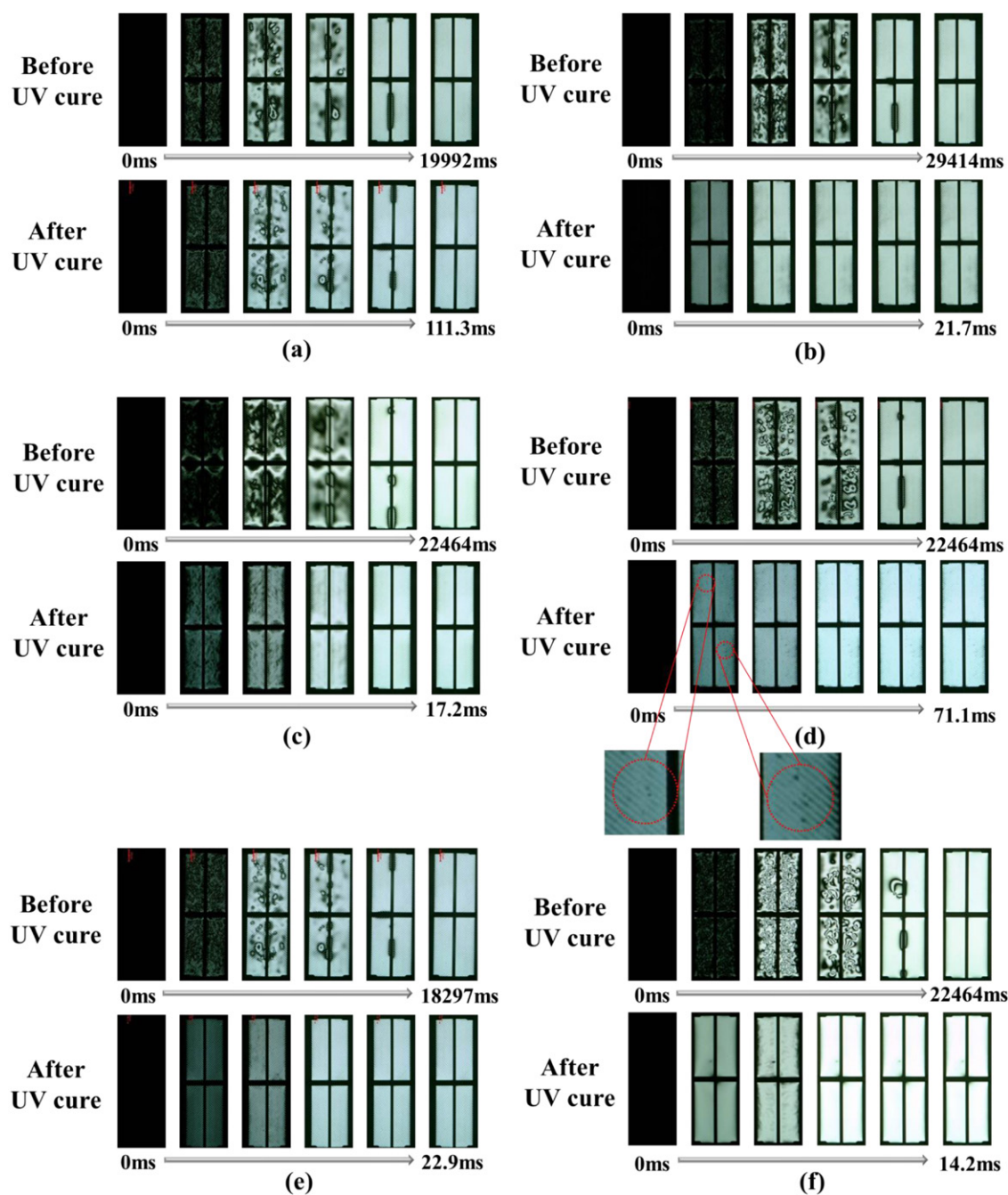
Figure 3. Time-resolved LC texture at V90 after UV exposure of 50 J: SM-Su (a) without and (b) with photo-initiator, SM-6F (c) without and (d) with photo-initiator, (e) SM-Eth without photo-initiator, and (f) SM-Me without photo-initiator. In the case of (f), a pixel structure with finer electrode pattern is used, which explains higher luminance in the on-state compared to other cells.

aggregation. Therefore, we synthesized four different monomers from the corresponding bis(4-hydroxyphenyl) derivatives and acryloyl chloride in the presence of trimethylamine in tetrahydrofuran (THF) as shown in figure 2. We chose acrylate instead of vinyl groups as a polymerizable moiety because of its high reactivity even in the absence of a photo-initiator [19, 20]. Four different linking groups (i.e. sulfone, ether, hexafluoroisopropylidene, and methylene) were chosen for bis(4-hydroxyphenyl) derivatives. They can be categorized into two groups depending on the size and polarity of SMs. Sulfonyl (SM-Su) and hexafluoroisopropylidenyl (SM-6F) derivatives are taken for bulky SMs, and ether (SM-Eth) and

methylene (SM-Me) derivatives are taken for non-bulky SMs. In terms of polarity, SM-Su and SM-Eth can be considered as more polar SMs, while SM-6F and SM-Me are less polar. All SMs were obtained in high yield (>85%) as a white solid after recrystallization.

We used a plane-shaped common electrode on the top substrate and a fine patterned fishbone pixel electrode on bottom substrates [12, 16] in which the width of the patterned electrode and its distance are 3 μm and 4 μm, respectively. The super-fluorinated LC with negative dielectric anisotropy $\Delta\varepsilon = -4$ and birefringence $\Delta n = 0.077$ at wavelength (λ) of 589.3 nm, 20 °C was used. The cell gap was 4.6 μm. The
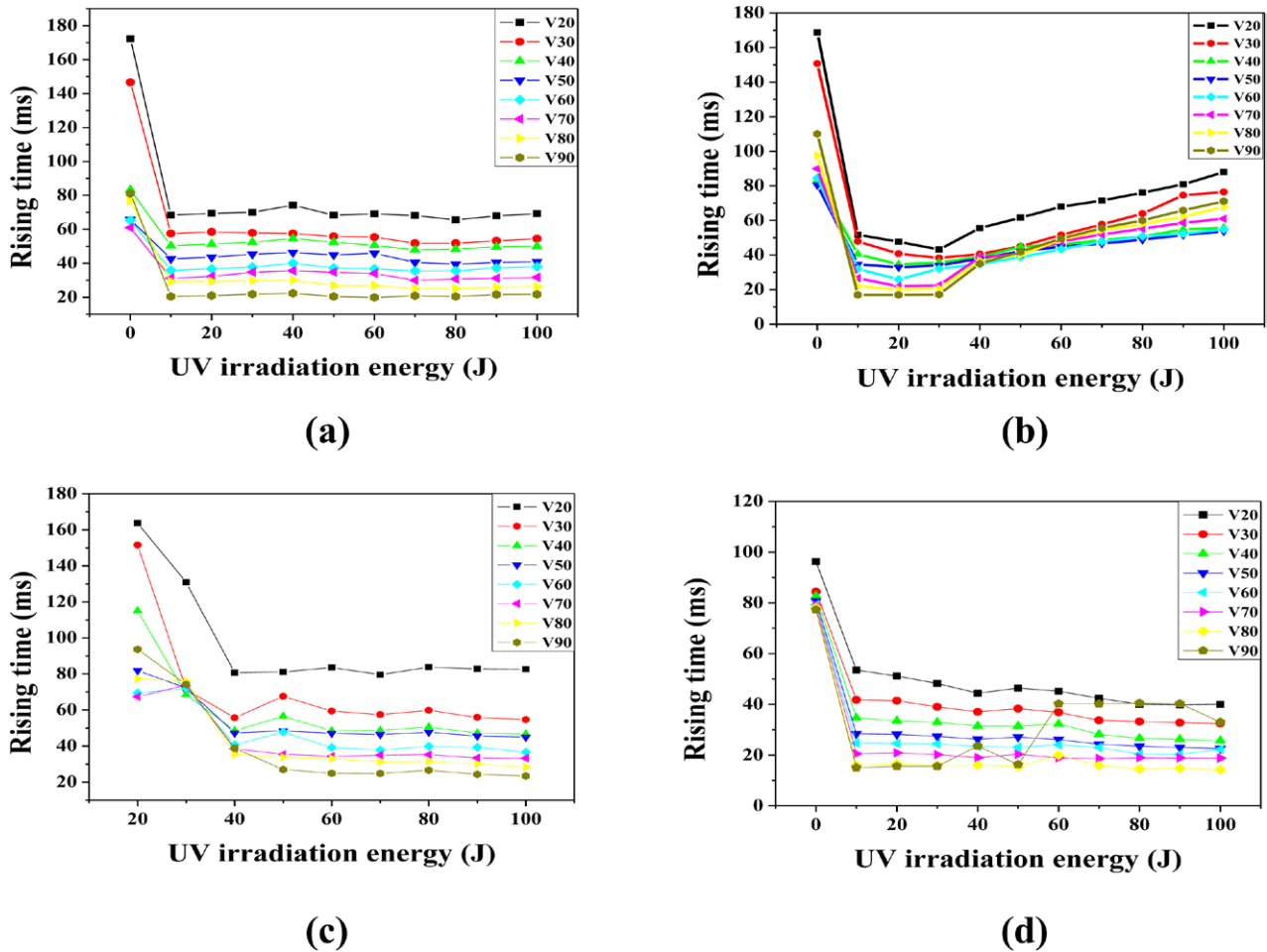
Figure 4. UV irradiation energy-dependent response time curves of the PS-VA LC cell as a function of grey scales: (a) SM-Su, (b) SM-6F, (c) SM-Eth and (d) SM-Me.

LC mixtures doped with 0.1 wt% of each SM were injected between the two substrates. In the preliminary test, no photo-initiator was used because the use of the photo-initiator in the PS-VA device may create image-sticking problems [21], and some of the acrylate monomers doped in the LC materials were reported to undergo self-initiated photo-polymerization [20]. However, some of the synthesized SMs containing electron-withdrawing linking groups such as sulfonyl or hexafluoroiso-propylidene did not undergo photo-polymerization without a photo-initiator. In this case, we added 1 wt% (relative to SM weight) of Irgacure 651 (from Merck) to the LC-SM mixture as a photo-initiator. In the device, the voltage at which 90% of maximum transmittance is induced was firstly applied to render the LC director to form four domains, and then the cell was exposed to UV light with intensity 35 mW cm^{-2} while the cell was held at that voltage. We evaluated electro-optic char-acteristics such as voltage-dependent transmittance curves and response times with increasing UV energy 10 J each time to confirm stabilization of the LC director.

3. Results and discussion

In the VA mode in which the LC is vertically aligned under crossed polarizers, the normalized transmittance is proportional to $\sin^2(2\psi)\sin^2(\pi d\Delta n_{\text{eff}}/\lambda)$ where ψ is a voltage-dependent angle between one of the transmittance axes of the crossed polarizers and the LC director, and Δn_{eff} is voltage-dependent effective birefringence of the LC layer. In the voltage-off state of the conventional PS-VA mode, the surface tilt angle of the LC is fixed by a polymer layer formed by SM and the LC directors have a slight tilt angle of about 88° in four different directions so that a good dark state, slightly less perfect than that with 90°, is achieved due to almost vertical alignment [22]. In voltage-on state, the LC directors tilt down in four different directions along the patterned electrode direc-tions satisfying $\psi = 45°$ to maximize transmittance. However, if there is no such fixed surface tilt angle, the LC director tilted down in a random azimuthal direction exhibiting a Schlieren texture instantaneously before the LC director reached a stable orientation. Therefore, time-resolved LC texture is a good tool to judge whether the LC directors tilt down in a predetermined azimuthal direction or not; that is, no observation of instant Schlieren texture during switching indicates the polymer layer formed by SM gives rise to a well-defined surface tilt angle.

To confirm the photo-induced polymerization of SMs and the generation of surface tilt angle induced by the resulting polymer layer, we observed time-resolved LC textures using a polarizing optical microscope (POM) before and after UV
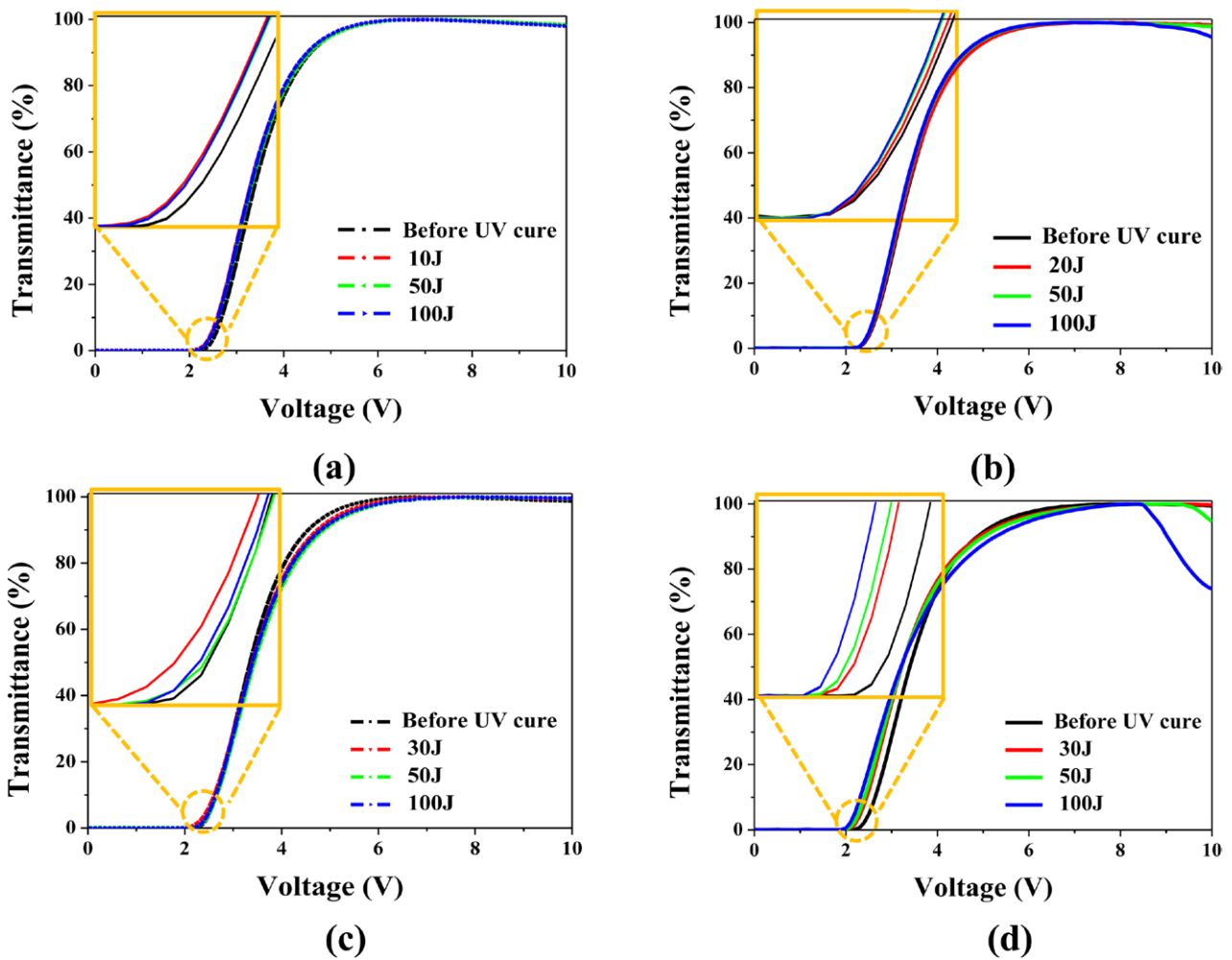
Figure 5. Voltage-dependent transmittance curves of the PS-VA LC cell as a function of UV irradiation energies: (a) SM-Su, (b) SM-6F, (c) SM-Eth and (d) SM-Me.

curing with 50 J while applying the voltage (V90) at which 90% of maximum transmittance of the cell was achieved, as shown in figure 3. Before UV irradiation, the surface tilt angle was 90° so that the collisions between LC directors were generated when the voltage was applied. Consequently, all of the cells exhibited relatively slow response times of about 2 s to reach a stable orientation of LC. After UV irradiation, we found that SM-Su and SM-6F did not show polymer stabilization for the surface tilt angle in the absence of the photo-initiator, which was evidenced by random Schlieren textures before reaching a stable four domain LC orientation (see figures 3(a) and (c)). In these cases, 1 wt% of photo-initiator (relative to SM weight) was added to the LC mixture to initiate photo-induced polymerization of SMs. Both of the cells exhibited no Schlieren texture after UV irradiation while exhibiting uniform transmittance over the whole area with a stable LC orientation within a few tens of milliseconds (see figures 3(b) and (d)). On the other hand, we confirmed that spots with a noticeable size larger than 1 μm^2 were formed in the case of SM-6F as marked in figure 3(d) by circles. These were identified as polymer grains of different sizes on the surface by optical microscopy. The large-sized polymer grains may hinder voltage-induced LC reorientation, resulting in a

much slower response time (71.1 ms) than that (21.7 ms) of SM-Su. The formation of large-sized and inhomogeneous aggregation of SM-6F could be attributed to the premature phase separation of polymeric materials from the LC host during polymerization. The low compatibility of SM-6F in the LC host mixture can be attributed to the low polarity of SM-6F as well as the bulky molecular structure with small aspect ratio compared to that of the LC mixture. In the case of SM-Su, polymeric materials produced during photo-polymerization, which are more compatible in the LC host mixture, may result in the slow and homogeneous formation of surface polymer layers.

On the other hand, in both cases of SM-Eth and SM-Me, the time-resolved textures did not show any Schlieren texture, i.e. uniform transmittance appeared in the pixel, and thus the rising time was greatly improved after UV curing as shown in figures 3(e) and (f). This indicates that the LC molecules on the surface area were uniformly fixed by the polymer layer with a determined tilt angle after UV irradiation. Interestingly, polymer stabilization was achieved without the photo-initiator in both SM-Eth and SM-Me. It is worth noting that Lee *et al* reported the self-initiated polymerization of acrylate monomers [20], in which self-initiated radical polymerization can
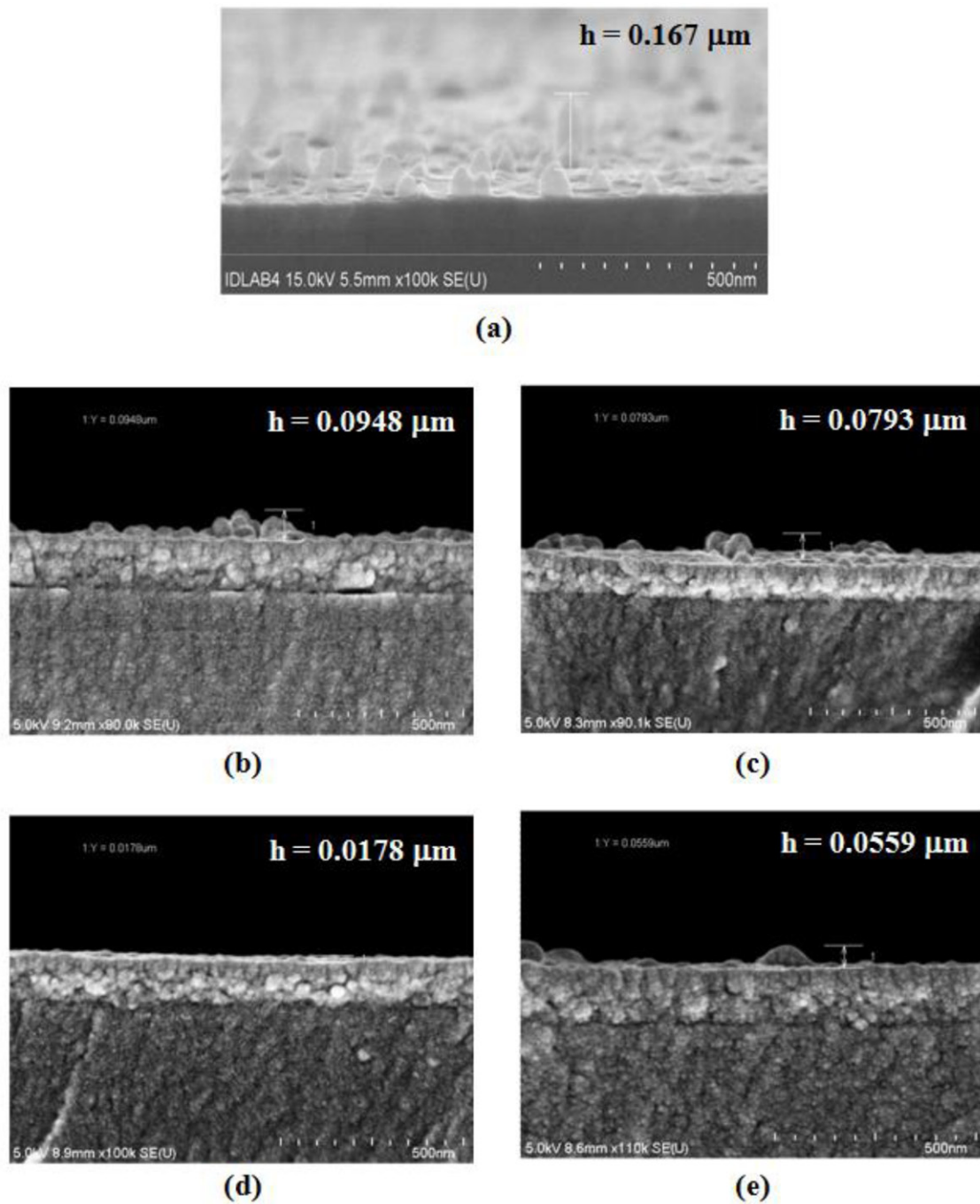
Figure 6. Side view of SEM images of the bottom substrates with the conventional RM257 (a) and synthesized RMs: (b) SM-Su, (c) SM-6F, (d) SM-Eth and (e) SM-Me.

be achieved most efficiently when the acrylate is substituted with an electron donating group such as vinyl ether. Based on their proposed mechanism, the alpha-cleavage between carbonyl carbon and oxygen on the ester group to generate the initiating radical could be more favorable when the ester group is more electron rich.

To confirm polymer stabilization of the surface tilt angle by photo-induced polymerization of SMs, response time and voltage-dependent transmittance (V–T) of the cells were measured with increasing UV energy by 10 J each time. In regard to response times, a rise in response time is measured according to grey levels by applying voltages

from V10 to V90. When the surface tilt angle is formed by polymerization of the SM as shown in figure 1(d), the rise time should be much shorter than that without the tilt angle. Therefore, a measure of rise time is a good indicator to confirm whether the tilt is formed or not by the SMs. In the cell with SM-Su and photo-initiator, the rise time in all greys became abruptly shorter just after UV irradiation of 10 J and then saturated even with further exposure, indicating that 10 J was enough to form the surface tilt angle (see figure 4(a)). In the cell with SM-6F and photo-initiator, the rise times in all greys became abruptly shorter just after UV irradiation of 10 J and then almost saturated up to 30 J
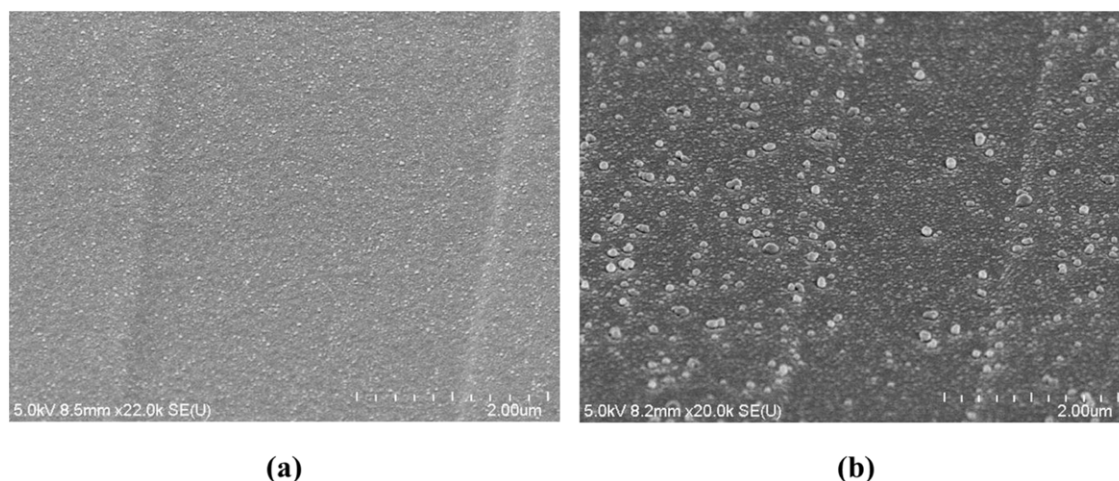
Figure 7. SEM top images of the bottom substrates in SM-Eth (a) and SM-Me (b).

(see figure 4(b)). However, further UV exposure after 30 J rendered rise times longer, which may come from the collision between LC molecules during the field-induced reorientation process. In figure 3(d), we already mentioned that polymer grains (>1 μm^2) were observed with irradiation energy of 50 J. From these, we can understand that further UV exposure continued polymerization of SM-6F, resulting in large-sized unwanted polymer grains which changed the predetermined tilting direction. In the cell with SM-Eth, the rise times became shorter and started to saturate after a UV irradiation energy of 40 J, which required higher energy than that in SM-Su because no photo-initiator was used (see figure 4(c)). In the cell with SM-Me, the rise times became greatly shorter with the irradiation energy of 10 J and those seemed to be slightly shorter in low greys with further UV exposure, implying that polymerization was still continuing even after the irradiation of 10 J (see figure 4(d)). Decay times were about the same as each other as long as the surface tilt angle formed by polymerization of SM remained the same, although it is not shown here.

In addition to the response times, *V–T* curves were investigated, as shown in figure 5. If a surface tilt angle was formed in the PS-VA cell, the threshold voltage V_{th} at which the LC orientation started to deform was lowered such that the *V–T* curve shifted to the left compared to the cell with vertical alignment without surface tilt angle. Figure 5(a) showed *V–T* curves of the cell using SM-Su with photo-initiator. We found that the V_{th} and operation voltage V_{op} at which maximum transmittance occurs were decreased after UV curing of 10 J compared to that before UV curing, confirming the existence of the surface tilt angle after curing. Further increase in the UV irradiation energy above 10 J did not shift *V–T* curves much, indicating that SM-Su with the photo-initiator was polymerized enough when UV light with 10 J was exposed to the cell. In the case of the cell with SM-6F, of which the substituent is nonpolar and relatively large in size compared with other cases, the *V–T* curve before UV cure shifted slightly to the left at a UV dose of 20 J. With further irradiation up to 100 J, *V–T* curves changed very little, indicating energy of 20 J was enough to polymerize the SM, even after over 50 J UV, as shown in figure 5(b). In

the case of the cell with SM-Eth in which the linking group is as polar as in SM-Su but smaller in size, we also confirmed that the V_{th} of the cell was lowered with UV dose of 30 J even without using the photo-initiator as shown in figure 5(c), although further UV exposure shifted the *V–T* curve very little to the right, indicating that the polymerization was almost done after the exposure of 30 J. In the case of the cell with SM-Me without the photo-initiator, we found that the V_{th} decreased when UV dose increased from 30 J to 100 J, as shown in figure 5(d). This behavior was also expected in the response time results such that even after a UV dose of 10 J, the rise time decreased slightly with increasing UV doses in several greys. In addition, the transmittance dropped rapidly above 8 V when the UV energy increased to 100 J. According to our observation of the cell under POM, the LC director reached stable state very fast (see figure 3(f)). However, we observed flow behavior of the LC director associated with electrohydrodynamic instability, which might come from impurity and charged particles in the LC cell associated with the uncured ones.

To examine the degree of aggregation of polymer grains on the surface, we observed scanning electron microscopy (SEM) images of the cell for all four cases. For these experiments, the top and bottom substrates were detached carefully and LC was carefully removed by washing with a mixed solvent of hexane and dichlorobenzene. Figure 6 shows the SEM images (side view) of the bottom substrates with the conventional RM (RM-257 from Merck) and other SMs [15, 23]. The height of polymer grains in SM-Su is slightly larger than those in SM-6F (see figures 6(b) and (c)). Nevertheless, large-sized polymer grains were not observed in SM-Su, implying that the size (area) of the polymer grains in SM-6F could be larger than those in SM-Su. The height of polymer grains formed by SM-Eth was very low (<17.8 nm) with relatively smooth surface compared with those of conventional RM-257 (167 nm) and other cases (>50 nm). This indicates that the degree of aggregation is low in SM-Eth, which can be attributed to the molecular properties of SM, polarity and relatively small size. We also compared polymer grains on the bottom substrate between the cells with SM-Eth and SM-Me to substantiate the effect of the polarity as shown

in figure 7. The average size of the polymer grains with the SM-Eth was much smaller (47.6 nm) and more uniform than those with the SM-Me (236 nm). This is probably because the polar SM can exhibit better dispersion without aggregation than the SM-Me. Consequently, we conclude that the more polar and smaller SM can fix a surface tilt angle more efficiently with very small polymer grains attributed to a better dispersion in LC during the photo-polymerization, which is favorable for a better dark state without giving rise to scattering [17]. The final question of how LC's molecular structure and its physical properties like dielectric anisotropy will affect the stabilization of the proposed monomers remains. In conventional PS-VA mode, the magnitude of dielectric anisotropy ranges from -2 to -4, implying that the effect of LC molecular structure on stabilization will not be so strong. However, it is worth proving this in a future work.

4. Summary

We synthesized a new type of SM and evaluated the electrooptic characteristic of the LC cell. When the size of the synthesized group of RM is smaller, it could be cured without the help of a photo-initiator. In addition, SMs with polarity have good dispersion. We expect the proposed RM with polar and smaller size molecules can contribute to improve the electrooptic characteristics in PS-VA mode.

Acknowledgments

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