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Effects of surface modification with reactive mesogen on the anchoring strength of liquid crystals

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We studied the effects of polymer chain ordering in the alignment layer and resulting molecular interactions on the surface anchoring energy by introducing a reactive mesogen (RM) coating to the alignment layer. Directionally polymerized RMs on the rubbed alignment layer decrease the steric repulsion and increase the electronic interaction with liquid crystal molecules, and, as a result, the surface anchoring energy is enhanced in both the out-of plane and in-plane directions. We also demonstrated that this enhanced surface anchoring energy can be used to improve the response time characteristics of liquid crystal displays. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4809746]

I. INTRODUCTION

Surface anchoring of liquid crystals (LCs) on substrates is important to the understanding of a wide variety of interfacial phenomena, such as surface ordering, surface transitions, and surface wetting.[1–4] Technologically, a reliable procedure is crucial that permits good alignment control to produce high-quality alignment of LCs used in electro-optic devices, such as LC displays. Alignment layers prepared by different techniques, or processed differently using a specific technique, result in different anchoring properties. A good understanding of the anchoring properties of the involved surfaces is essential to being able to control the LC alignment. A number of methods based on the Rapini-Papoular phenomenological model[5] for surface-free energy have been used to measure the polar and azimuthal anchoring energies.

Recently, a modified Rapini-Papoular model was suggested to explain the anchoring properties of rubbed polyimide films.[6] This model suggests that the surface anchoring energy depends on molecular interactions between the LC and the polymer chains, and/or it depends on the polymer chain distribution in the alignment layer. Since anchoring energy is closely related to the alignment stability of LCs in static conditions[7,8] and to switching behavior in dynamic conditions,[8–10] various studies have investigated methods to increase anchoring energies. In general, anchoring energies can be increased by increasing the rubbing strength for a given LC, but this effect is reduced after reaching a certain value, because the polymer chain distribution becomes diminished above a certain critical rubbing strength.

In this letter, we studied the effects of polymer chain ordering in the alignment layer and the resulting molecular interactions on the surface anchoring energy produced by introducing a reactive mesogen (RM) coating on the alignment layer. The directionally polymerized RMs on the rubbed alignment layer increase chain ordering and decrease steric repulsion, and, as a result, the surface anchoring energy is enhanced in both the out-of plane and in-plane directions. We also showed that response time characteristics of liquid crystal displays (LCDs) are improved by using the enhanced surface anchoring energy.

II. EXPERIMENTAL

Figure 1 shows the schematic diagrams of the proposed RM-coated system. As shown in Fig. 1(a), the polymer chains of the alignment layer have isotropic alignment before rubbing. The shear force created by rubbing aligns the polymer chains in the rubbing direction, as shown in Fig. 1(b). Since RMs are liquid crystalline monomers before UV exposure, the spin-coated RM molecules become aligned on the rubbed polyimide layer, as shown in Fig. 1(c). The RM is directionally polymerized in the rubbing direction and then permanently fixed on the polyimide layer by UV exposure [Fig. 1(d)]. Figure 1(e) shows the LC alignment on the polymerized RM layer in the cell. In our study, we use the planar alignment material AL-22620 (Japan Synthetic Rubber) and the RM mixture that consists of the proper amounts of RM monomer (BASF, RM 257) and a photo-initiator (Ciba Chemical, IRGACURE 651) that enhances the photo reactivity. We dissolve the RM mixture 0.5 wt. % in propylene glycol monomethyl ether acetate (PGMEA) solvent to coat it on the rubbed planar alignment layer. The planar alignment material was spin-coated and soft baked at 100 °C for 10 min, followed by curing for complete imidization at 210 °C for 2 h. After the polyimide (PI) coating step, we carried out the rubbing process to define the azimuthal direction. We coated the RM mixture dissolved in PGMEA solvent on the rubbed planar PI layer and then baked it at 60 °C for 90 s to evaporate the solvent. Then we exposed it to UV light for 30 min to polymerize the RM monomers. The intensity of 365 nm UV light from a mercury lamp is approximately 1 mW/cm^2. Figure 1(f) shows the optical anisotropy of the substrates coated with rubbed PI and RM-coated PI after UV exposure. We measured the optical anisotropy using a photoelastic

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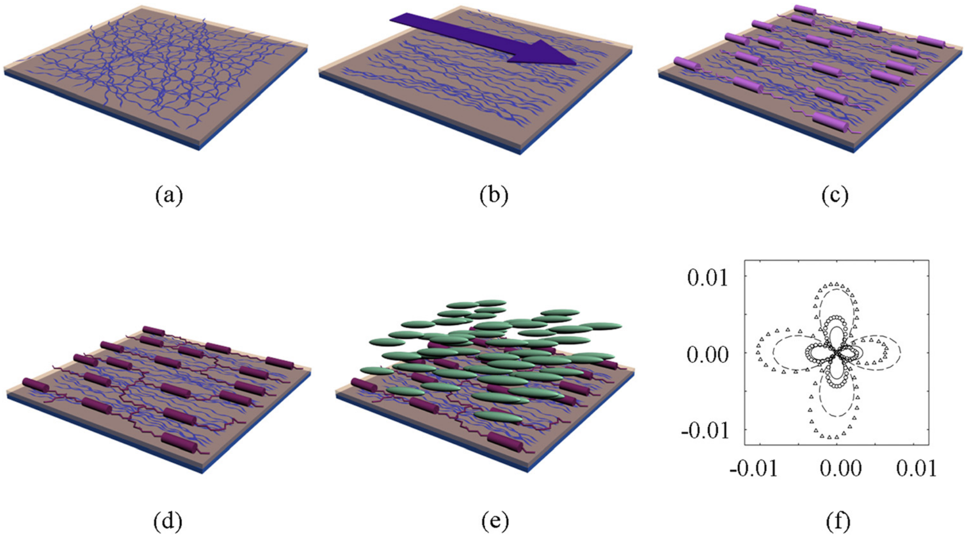

FIG. 1. The schematic diagrams of the proposed RM-coated system. (a) Isotropically aligned polymer chains before rubbing, (b) polymer chains aligned with rubbing direction after rubbing (the arrow indicates the azimuthal direction defined by the rubbing process.), (c) spin-coated RM molecules aligned in the rubbing direction, (d) RMs polymerized by UV exposure, (e) LC alignment on the polymerized RM layer, and (f) the angular dependence of optical anisotropy of rubbed PI film (open circles) and RM-coated PI film (open triangles).

modulator (PEM-100, HINDS Instruments). It is very clear that the optical anisotropy of the RM-coated PI film was notably increased in the rubbing direction. This means that the RMs are directionally polymerized along the azimuthal direction, which is defined as the direction of the rubbing process, as shown in Fig. 1(d). From the birefringence measurement,[11] we found that the thickness of the RM is about 5.23 nm. We confirmed this calculated thickness (d) of the RM layer by surface morphology observation using an atomic force microscope (Park Scientific).

III. RESULTS AND DISCUSSION

We measured the polar and azimuthal anchoring energies of the samples with and without RM coating, according to the number of rubbings, as shown in Fig. 2. We measured the polar anchoring energy using the high field method.[12] The thickness of the test cells was 20 μm. We injected a nematic LC (ZKC-5085XX from Chisso, $\Delta\varepsilon = 9.8$, $\Delta n = 0.151$, $K_{22} = 6.9$ pJ/m, $K_{33} = 16$ pJ/m) into the empty cell using the capillary method, and then we measured the capacitance with applied voltage using a capacitance meter (HP-4284A) with a sinusoidal voltage of 10 KHz. We measured the azimuthal anchoring energy using the torque balance method.[13] The test cells of thickness 6 μm filled with ZKC-5085XX, and the actual twist angle (φ_t) was obtained from the angle with the maximum transmittance when the analyzer was rotated 0.1° using the stage controller. The azimuthal anchoring energy (solid line with open circles in Fig. 2) slightly increased for each rubbing, until the 4th times, and it saturated after 5 rubbing times, as shown in Fig. 2. When we increased the number of rubbings to more than 7, the anchoring energy decreased due to the imperfect unidirectional rubbing procedure.[14] On the other hand, the polar anchoring energy (dashed line with open circles in Fig. 2) remained almost the same value with increasing rubbings. This is because the polar angle distribution of LC molecules at the surface is determined by the bonding between LC molecules and the surface and therefore is not influenced by rubbing strength.[15] Therefore, there is a limitation in the increase of anchoring energies achievable by increasing the rubbing strength for given LC and PI conditions. However, it is very clear that, with RM coating, the azimuthal and polar anchoring energies increased more than 20% and 28%, respectively. This means that the coated RMs have modified the surface conditions, such as polymer chain distribution and/or molecular interactions.

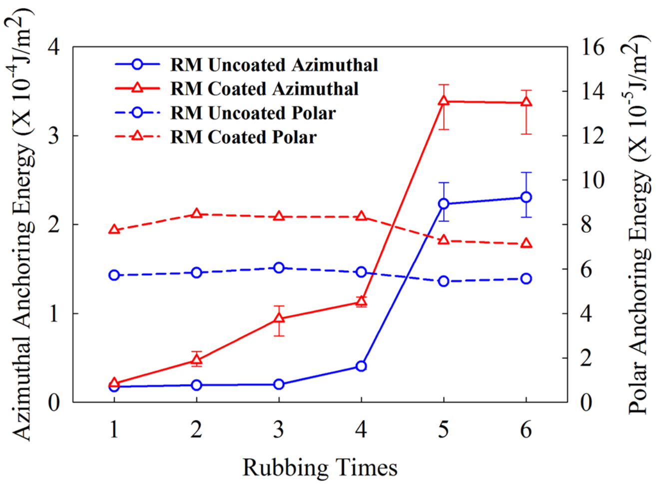

FIG. 2. Surface anchoring energies with rubbing times. (Solid lines and dashed lines represent azimuthal anchoring energy and polar anchoring energy, respectively.)

According to the modified Rapini-Papoular model,[6] the surface energy can be described as

$$F = \frac{1}{2}\int_0^{\pi} Cf(\theta,\varphi)\sin^2(\varphi - \varphi_t)d\varphi, \tag{1}$$

where C represents the average strength of intra-molecular interactions between the alignment layer and LC molecules, and $f(\theta, \varphi)$ is the distribution function of polymer chains, which is assumed to be a Gaussian distribution function,

$$f(\theta,\varphi) = \frac{e^{-(\varphi-\varphi_r)^2/2\omega^2}}{\displaystyle\int_0^{\pi} e^{-(\varphi-\varphi_r)^2/2\omega^2}d\varphi}. \tag{2}$$

Therefore, any microscopic modifications of the films' surface are reflected in the free energy through changes in the width ω of the polymer chain distribution and through interactions between the LC and the alignment layer, which determine C. Smaller ω and larger C lead to greater anchoring energy. We believe that the directionally polymerized RMs work by altering the values of ω and C to change the anchoring energy.

In order to determine the width ω of the polymer chain distributions before and after RM coating, we used polarized infrared (IR) absorption spectroscopy (FT/IR-620, JASCO Corp.) with rotating polarization.[16] Figure 3(a) shows the absorption spectra of the rubbed PI film before and after RM coating. We found three strong absorption bands: the $C=O$ asymmetric stretching vibration at $1724\,\mathrm{cm}^{-1}$, the aromatic $C=C$ stretching vibration at $1490\,\mathrm{cm}^{-1}$, and the C-N stretching vibration at $1375\,\mathrm{cm}^{-1}$. Since the $1490\,\mathrm{cm}^{-1}$ band is parallel to the RM and PI chain directions, we can obtain the orientational distribution of the RM and PI monomer units on the rubbed PI film by using the $1490\,\mathrm{cm}^{-1}$ band. Figure 3(b) shows the polarization angle dependence of the $1490\,\mathrm{cm}^{-1}$ band of the PI film before and after RM coating at normal incidence; we fitted the molecular orientation distributions using a Gaussian function. The widths are $\omega_{\mathrm{PI}} = 42.2$ and $\omega_{\mathrm{RM}} = 38.9$ for PI only and RM-coated PI, respectively. The smaller width for RM-coated PI means it has more ordered polymer chains than does PI only. It is well known that the LC molecules right on the alignment layer show a more ordered state than in the bulk. Since the RM monomers before UV exposure can be treated as LCs, we can expect that the RM monomers are well aligned on the rubbed PI and fixed by polymerization with UV exposure. However, these differences are not big enough to explain the increase in anchoring energy.

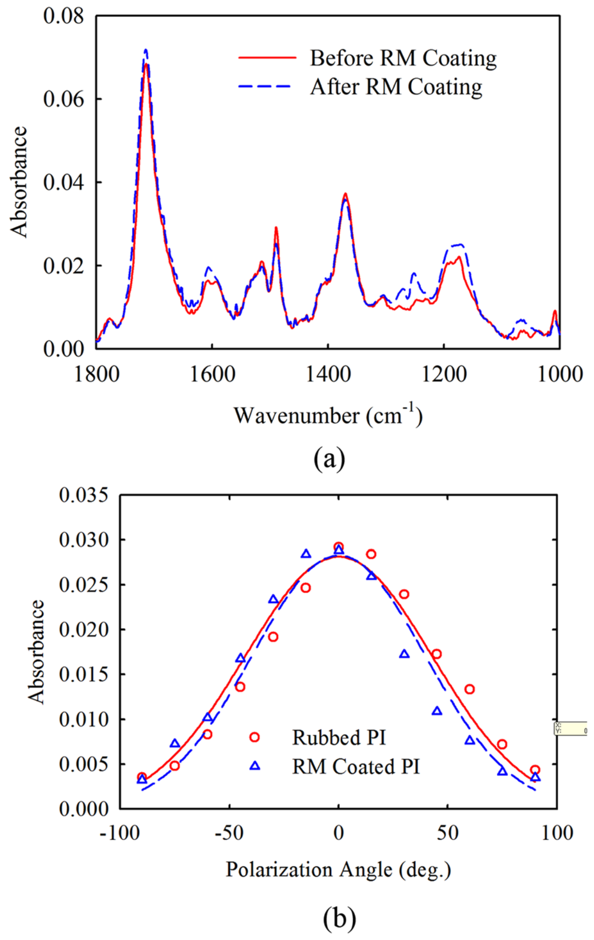

FIG. 3. (a) FTIR spectra of rubbed PI film (solid line) and RM-coated PI film (dashed line), (b) polarization angle dependence of IR absorption of rubbed PI film (solid line with open circles) and RM-coated PI film (dashed line with open triangles) at $1490\,\mathrm{cm}^{-1}$: curves are fitted using a Gaussian function.

Next, we measured intra-molecular interactions. Before RM coating, LC molecules interact with long and linear alkyl side chains or other non-polar groups on the alignment layer mainly via weak Van der Waals interactions (WDWI). But after RM coating, the RMs cover alkyl side chains and other non-polar groups on the alignment layer. As a result, the treatment induces LC molecules to have stronger types of interactions, including π-π stacking interactions and dipole-dipole interactions, with RMs in the alignment layer. To confirm our hypothesis, we measured the contact angle of a water droplet on the substrates. The changes in the surface properties with RM coating can be ascertained by measurement of the water contact angle, because the water contact angle represents the surface polarity. If the polymerized RM network covers the surface of the alignment layer, the polyimide film surface changes to a more-polar surface, and the water contact angle decreases. Figure 4 shows the water and NLC (5CB) contact angle, which decreased with increasing concentrations of RM coating. This indicates that the RM-coated surface became a more-polar surface, and the interaction between LC molecules and the alignment layer surface has been changed. Namely, the polymerized RM network allows relatively strong π-π staking interactions or dipole-dipole interactions instead of weak WDWI with the LC molecules. From these results, we conclude that the anchoring energy enhancement observed in the azimuthal and polar directions are caused by the conditions: $\omega_{\mathrm{PI}} > \omega_{\mathrm{RM}}$ and $C_{\mathrm{RM}} > C_{\mathrm{PI}}$.

The increased anchoring energies affect the dynamic behavior of LCs when we apply an electric field. Specially, since the relaxation time depends on the material parameters, such as elastic constants and rotational viscosities as well as

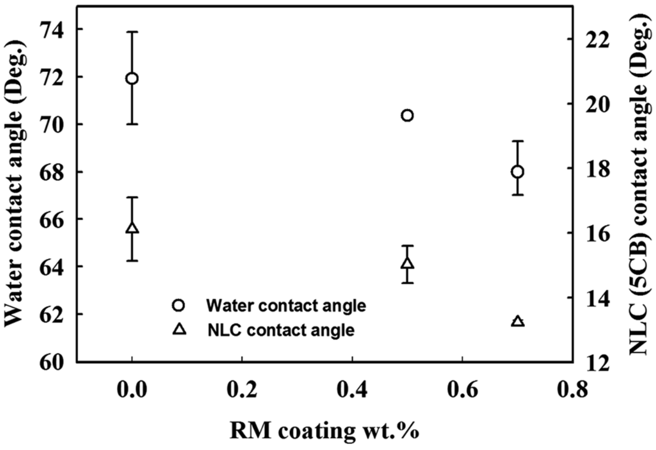

FIG. 4. The contact angle characteristics of water (open circles) and NLC (open triangles) with different RM concentrations.

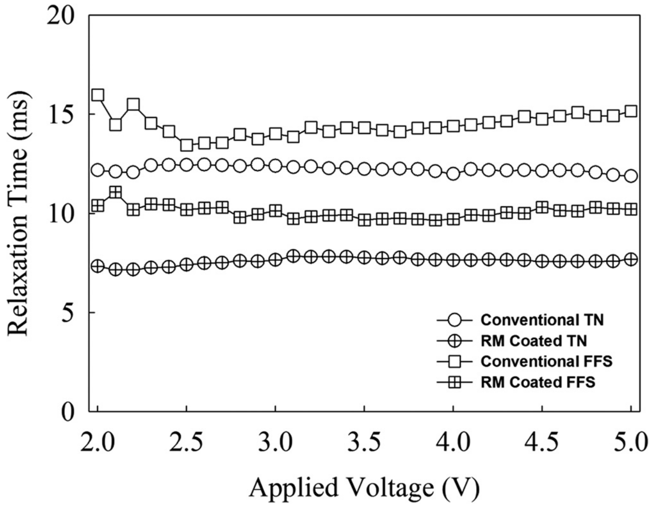

FIG. 5. The relaxation time characteristics of the conventional (empty symbols) and RM-coated (crossed symbols) cells. (Circle symbols and square symbols represent TN and FFS cells, respectively.)

anchoring energies, we expect faster relaxation in the sample with RM coating for given LCs. We compared the relaxation times of twisted nematic (TN) and fringe-field switching (FFS) modes with/without RM coating as a function of applied voltages, as shown in Fig. 5. The relaxation times decrease with increasing polar anchoring and azimuthal anchoring energies in the TN and FFS samples, respectively. As we expected, the relaxation time improved: 38.01% and 32.59%, compared with conventional PI-only TN and in-plane switching (IPS) samples, respectively. The relaxation time for electrically controlled birefringence (ECB) mode was improved 27.3%.[17] For vertically aligned (VA) mode, we used the RM mixing system, and that case, the response time characteristics was also improved.[18] These results are very important for LCD applications, because the material parameters affected with relaxation time are not easy to control.

IV. CONCLUSION

In summary, we proposed a new method to enhance surface anchoring energy using reactive mesogen (RM) materials on the planar alignment layer. The polymerized RM-coated PI layer shows more ordered alignment than does a PI-only layer. Moreover, the RM-coated PI film has lower steric repulsion and greater electronic attraction to LC molecules as well as more ordered alignment, and, as a result, the surface anchoring energy is enhanced. We also dramatically improved the response time characteristics of LCDs using the enhanced surface anchoring energy. We expect that this method will be very useful to improve LCDs characteristics, such as response time and photo-alignment stability.

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