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Stabilization of liquid crystal photoaligning layers by reactive mesogens

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Via passivation of liquid crystal (LC) photoaligning layers by thin layers of reactive mesogens, strong enhancement in LC alignment stability is achieved. Simultaneously, the passivation layers improve alignment uniformity and chemical stability of photoaligning layers and widely change pretilt angle of liquid crystal. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3168526]

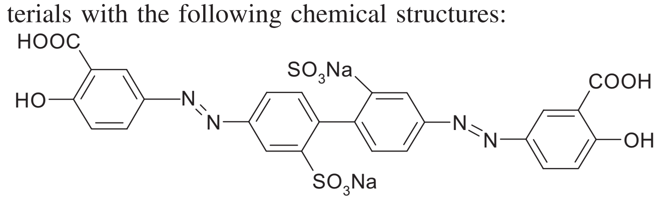
Nowadays, photoalignment[1] remains among the most promising candidates to replace rubbing procedure in liquid crystal (LC) devices. Avoiding mechanical contact with the aligning layer, the photoalignment technique minimizes mechanical damage and electric charging, provides excellent alignment uniformity, and an easy way for controlling LC alignment. It is irreplaceable in a number of new developments when LC alignment should be induced in closed volumes, on curved surfaces, and on the surfaces of microscopic scale used, for example, in optical communication devices.

Granting these advantages, photoalignment technique suffers from other problems such as insufficient alignment stability, relatively weak anchoring, and pronounced image sticking. The stability, to be implied here as a photostability, thermal stability, and aging stability, is a common issue of photoaligning materials. The best photostability gives photocrosslinkable materials like cinnamates and coumarines.[1,2] These materials, however, frequently demonstrate insufficient thermal stability and alignment aging understood as gradual alignment decay with a storage time of LC cell. On the other hand, one of the highest degrees of thermal stability of LC alignment provided photoaligning diazodyes.[3] But LC alignment induced by these dyes is not photostable. On the contrary, LC alignment in the filled cells can be easily controlled by light of proper spectral composition.[4] The attempt to strengthen the photostability of diazodyes was made[5] where molecules of the dyes were tailed with the reactive groups capable to crosslink. However, this idea was found not very efficient because the attached terminal groups worsen the LC alignment. This led us to the conclusion that some nonstandard approaches are needed for stabilization of LC alignment.

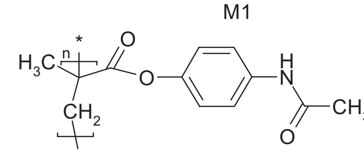
Our approach is based on so-named reactive mesogens (RMs).[6] These mesogenic compounds contain reactive groups capable to polymerize under irradiation or heating. The layers of these mesogens can be in a common way aligned and then solidified via polymerization. As a result, the orientational order of LC mesophase will be "frozen" in a formed polymer matrix. The RM are intensively studied as materials for passive optical films, such as retarders and polarizers. It was recently found that in-cell retarder (compensation film) can simultaneously be applied as an aligning film for LC filled in the cell.[7] However, the alignment direction provided by RM compensation film is frequently different from that one required in a certain display.

Our idea is to gain only the alignment function of RM films suppressing their retardation function. This can be realized by using thin RM films coated on photoaligning layers and subsequently polymerized. Below we demonstrate that RM films with a frozen LC order are excellent aligning layers providing high alignment stability. This means that the alignment function of photoaligning layer is important only for a short period of time needed to align and polymerize RM film.

To realize this approach we used two photoaligning materials with the following chemical structures:



M1



M2

These materials provide LC alignment of a very high quality, but insufficient alignment stability. Diazodye M1 gives alignment sensitive to visible light,[4] while polymer M2 shows alignment of poor thermal stability.[8] Both materials were dissolved in dimethylformamide at a concentration of 1 wt %. The filtered solutions were spin coated on indium tin oxide covered glass substrates preliminarily washed and treated in an ozone treatment machine. The obtained coatings were backed for 30 min at 140 °C and then exposed to UV light from a mercury lamp to impart the alignment function. To avoid a twofold degeneracy of pretilt angle, the irradiation was provided in two steps. First, 20 min with a polarized light at normal incidence, and then 3 min with a nonpolarized light at the incidence angle $\alpha=45°$ so that the light beam projection on the film was perpendicular to the light polarization direction in the first step. The light intensities in the emission line 365 nm were 3.3 and 9.2 mW/cm^2 in the first and second exposure steps, respectively. Some of these substrates were used to assemble reference cells, the other ones were first coated by RM layers. As RM, we used commercial RM mixtures RMM256C from Merck and UCL017

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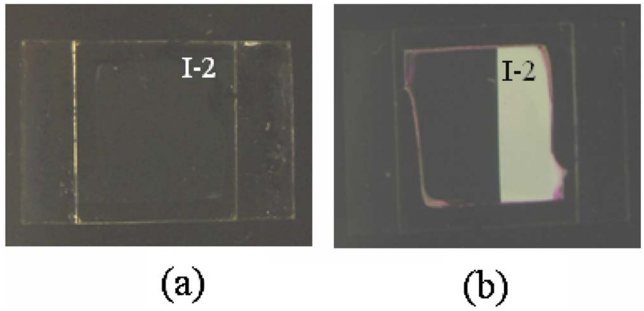

FIG. 1. (Color online) Photographs of LC cells based on (a) M1-RM256C and (b) bare M1 aligning layers placed between two crossed polarizers. All M1 layers are entirely irradiated with a polarized light over 20 min at normal incidence following with a nonpolarized light over 3 min at 45° incidence and then the layers of (a) cell are passivated with RM256C. After this a part of one M1 (M1-RM256C) layer in each cell (section I-2 in the photographs) was irradiated over 30 min with the UV light polarized in the direction parallel to the alignment direction induced in the first exposure step. The intensities of polarized and unpolarized light are 3.3 and 9.2 mW/cm^2, respectively. The cells are combined so that alignment directions of the opposite alignment layers induced in the first exposure step are antiparallel. The cell gap is 15 μm.

from DIC (Japan) designed for planar alignment. These RM were dissolved in toluene at a concentration of 1–3 wt %, filtered and spin coated on the photoaligning layers at 3000 rpm for 0.5 min. Subsequently, the films were photopolymerized with the unpolarized UV light (9.2 mW/cm^2, 3 min). A phase retardation of the obtained RM films was less than 10 nm.

Using these substrates, two kinds of cells were assembled with the exposure directions in the second irradiation step antiparallel or perpendicular each to other (antiparallel and twist cells, respectively). The cells were filled with nematic LC E7. The antiparallel cells were used to measure pretilt angle, while the twist cells were involved in the azimuthal anchoring energy tests.

The typical images of antiparallel and twist cells based on the photoaligning layers passivated by RM are presented in Fig. 1(a) and Figs. 2(a) and 2(b), respectively. There is evidence that passivated layers provide LC alignment of a high uniformity. Figure 3 demonstrates that, as in the case of nonpassivated photoaligning layers, this alignment can be easily patterned. The RM passivation eliminates reverse twist domains frequently observed in the photoaligning cells (Fig. 2). One can also see that the passivation layer prevents formation of colored defects near the contacts of photoaligning material with a glue. Since these defects appear only in the cells based on M1 layers, they are presumably caused by partial solution of this aligning dye in a photocurable adhesive used for gluing the cells.

The value of the azimuthal anchoring coefficient for M1/RMM256C aligning layers falls in the range $0.5-1.0\ 10^{-4}\ J/m^2$ and so is as high as for the bare M1 layers.[3] The polar anchoring coefficient is also high ranging from 1.0×10^{-3} to $1.4\times10^{-3}\ J/m^2$.

Influence of RM passivation layers on LC surface pretilt angle considerably depends on the kind and thickness of the RM coating. For M1/RMM256C binary layers the pretilt angle was in the range 2°–4°, i.e., practically equal to the range obtained for bare M1 layers. In turn, for M1/UCL017 layers the pretilt angle was 2°–5° and 84°–90°, for RM films obtained from 1 and 3 wt % solutions.

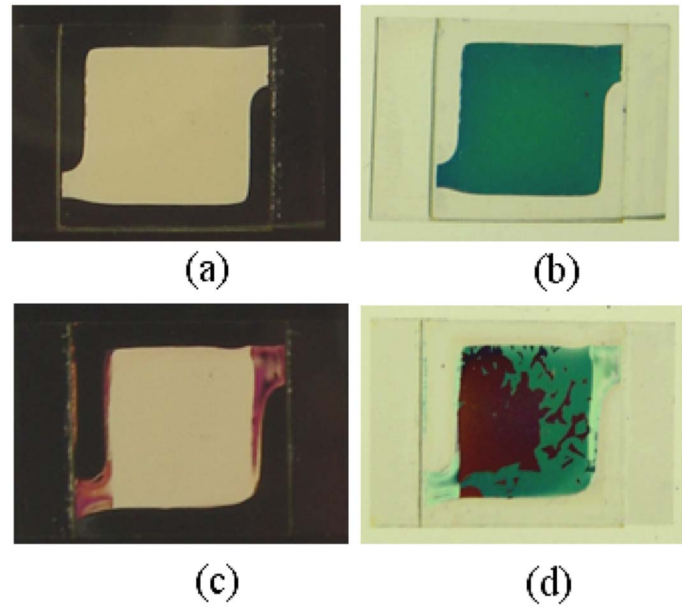

FIG. 2. (Color online) Photographs of twist LC cells based on (a) and (b) M1-RM256C and (c) and (d) M1 aligning layers placed between two polarizers. The angle between the polarizers is 90° in (a) and (c), and 10° in (b) and (d). The cell gap is 5 μm.

The pretilt angle in the antiparallel cells was periodically measured during the cell storage at ambient conditions. Figure 4 presents the pretilt angle versus storage time curves for the cells based on M1 and M1/RMM256C aligning layers. There is evidence that pretilt angle in the M1 based cell gradually decays. In parallel, for 90 days of aging azimuthal anchoring weakened by a factor of 2.4. This might be partially caused by hygroscopicity of the sulfuric dye M1 which is an organic salt. Humidity penetration in the cell may cause slow destruction of the aligning film becoming apparent in the pretilt angle decay. The other possible reason of the ob-

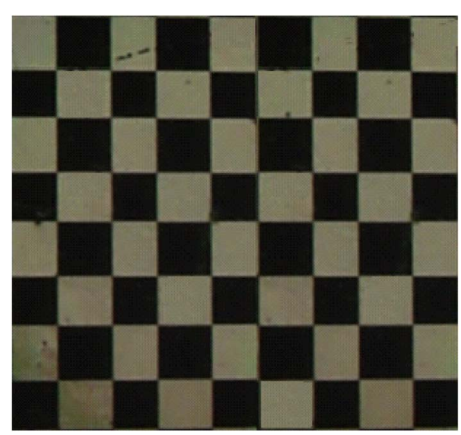

FIG. 3. (Color online) The chessboard type alignment pattern with a domain size of about 1 mm realized using M1/RMM256C aligning layers. The structure is viewed in polarizing microscope with crossed polarizer and analyzer. The M1 layers on the cell substrates are exposed to polarized light in the following manner. At first both M1 layers were entirely irradiated and then one M1 layer was irradiated through an aluminum mask with a light polarized in the direction parallel to the alignment direction induced in the first exposure step. Both irradiations are provided a normal incidence of the light. The light intensity was 3.3 mW/cm^{-2} and the exposure time in the 1st and 2nd exposure step was 15 and 30 min, respectively. The exposed M1 films were passivated by RMM256C layers and subsequently used as aligning layers in the cell. The cell gap is 15 μm.

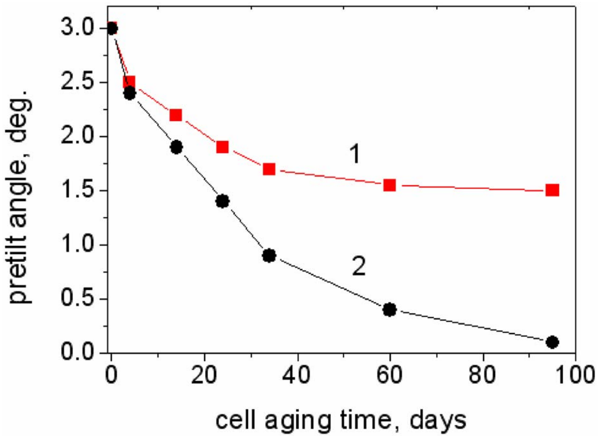

FIG. 4. (Color online) Pretilt angle vs aging time plots for the cells based on (a) M1-RM256C and (b) M1 aligning layers.

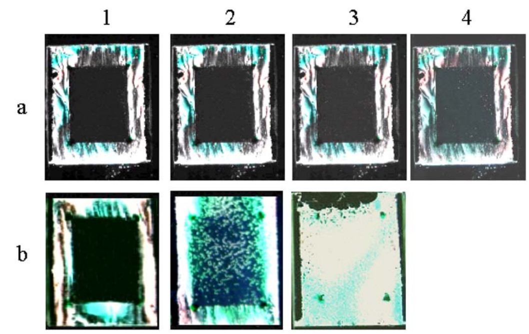

FIG. 5. (Color online) Photographs of two LC cells based on M2/RMM256C (a) and M2 (b) aligning layers after successive periods of backing at 150 °C. The backing time is 0, 15, 30, and 120 min in case 1, 2, 3, and 4, respectively. The aligned part is a rectangular area in the middle of the cell. The cells are viewed through a pair of crossed polarizers. The cell gap is 15 μm.

served aging might be destructive action of light resulting in appearance of free radicals on the aligning substrate capable to react with LC.[9] Compared with M1 cells, the LC pretilt angle stability in the M1/RMM256C cells is considerably higher. The pretilt angle shows stabilization trend (Fig. 4), while azimuthal anchoring keeps initial level. In parallel with stabilization of LC alignment, RM layers encapsulate M1 films preventing their degradation due to reactions with moisture, LC, and glue.

A photostability of passivated aligning layers was compared doubly. In the first experiment, half of M1 and M1/RMM256C photoaligning layers prepared as described above were illuminated with a polarized light so that polarization direction was perpendicular to that in the first illumination step. The cells were made by the combination of sectionally and entirely irradiated substrates. According to Fig. 1, a second irradiation easily changes LC alignment on the bare M1 layer but does not affect alignment on the passivated layer of M1. In the second experiment, the antiparallel cells with uniform LC alignment were partly exposed to visible polarized light (450 nm, 24 $\mathrm{mW/cm^2}$) so that polarization direction of the light formed an angle of 45° with the alignment direction in the cell. As in the first experiment, clear realignment in the M1 cell and no alignment change in the M1/RMM256C cell were observed.

Improvement of the thermal stability of LC alignment by RM passivation is especially strong for M2 aligning layers. LC alignment on these layers fully degrades after baking the cells at 150° for 30 min. At the same time, the alignment of the M2/RMM256C layers was practically intact even after 2 h curing of LC cells at this temperature (Fig. 5). Only the negligible changes in pretilt angle and coefficient of azimuthal anchoring were detected.

In summary, RM passivation layers dramatically improve the stability of LC alignment on the photoaligning layers. Simultaneously, it keeps advantages of photoalignment, such as high alignment uniformity, easiness of alignment control, and patterning.

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