Liquid-crystal photoalignment using low-molecular-weight photo-cross-linkable composites

O. Yaroshchuk

Institute of Physics of the National Academy of Science of the Ukraine, Prospect Nauki 46, 0028 Kyiv, Ukraine

L. G. Cada, M. Sonpatki, and L.-C. Chien^{a)}

Chemical Physics Program and Liquid Crystal Institute, Kent State University, Kent, Ohio 44242

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A liquid-crystal (LC) photoalignment method, based on the use of low-molecular-weight photo-cross-linkable (LMWPC) composites is proposed. The basic idea of this method is that cross linking or both cross linking and polymerization of LMWPC composites are realized immediately on the substrate simultaneously with the photoalignment or as a stage of the backing process. Providing the advantages of a conventional photoalignment method, the use of LMWPC composites simplifies the synthesis and alignment procedure, makes possible wide range control of pretilt angles, and enhances the thermal stability of the LC alignment. The abilities of this method are demonstrated using a series of cinnamate-containing monomers. © 2001 American Institute of Physics. [DOI: 10.1063/1.1381567]

Liquid-crystal (LC) photoalignment, a nonrubbing liquid-crystal alignment method, is a promising technology for manufacturing a variety of liquid-crystal displays (LCDs) including the liquid-crystal-on-silicon displays where the substrates are sensitive to rubbing. This technique avoids many drawbacks of the traditional rubbing technique for LC alignment, such as sample contamination and static charge generation. The LC photoalignment typically uses films of photo-cross-linkable polymers where photosensitive side groups are dimerized via illumination with linearly polarized UV light.¹ Several types of photo-cross-linkable polymers have been used for LC photoalignment. Among them, polymers containing cinnamate¹ and coumarin² photo-crosslinkable groups are the most widely studied. Photodimerization, appearing in such polymer films upon illumination with linearly polarized UV light, leads to the generation of surface anisotropy and unidirectional LC alignment. Simultaneously, this process increases the rigidity of the films.

One can anticipate that alignment films prepared from low-molecular-weight photo-cross-linkable (LMWPC) materials can also be solidified and used for LC alignment after irradiating the films with linearly polarized UV light. Moreover, multifunctional materials containing various crosslinkable and polymerizable groups may serve equally well for the same purpose.³

The aim of this letter is to demonstrate a type of LC photoalignment based on LMWPC multifunctional materials containing a photo-cross-linkable and a photopolymerizable group. Our approach to producing a liquid-crystal alignment film utilizes a series of cinnamate-containing monomers for which the molecular structures are as follows:



All prepared monomers are highly soluble in common organic solvents. The LC photoalignment composites were prepared as mixtures of monomer (monomers) and 10 wt % Irgacure 369 photoinitiator [or 20 wt % AIBN, bis-(azoisobutylnitrile)] thermal initiator. These compositions were solved in dichloroethane or 2- butanone with a concentration of 1%-5% by weight. The filtrated solutions were spin coated on glass substrates covered by ITO coatings as well as on the substrates covered by rubbed layers of polyimide PI 2555. The coated monomer films were kept at 60 °C for 10 min in order to remove all of the solvent. Then, films containing a thermal initiator were baked at 180 °C for 10-90 min for polymerization. The polymerization of the films containing the photoinitiator was achieved through irradiation with nonpolarized polychromatic UV light of a Xe lamp $(10 \text{ mW/cm}^2, 15 \text{ min})$ or with the polarized light of intensity $5-10 \text{ mW/cm}^2$ simultaneously with induction of the anisotropy. The anisotropy in the aligning substrates was induced in two steps; the films were irradiated with the nonpolarized light (30 mW/cm², 1 min), followed by polarized light $(10 \text{ mW/cm}^2, 4 \text{ min})$. The incident angle of the light was 45°. Oblique irradiation with nonpolarized light was needed to remove the pretilt degeneracy. This process brings asymmetry in the orientational distribution of cinnamate fragments in the light incidence plane. The maximal concentration of the cinnamate units remaining after irradiation should be in the direction of the light propagation, since the cross-linking efficiency in this direction is minimized. So, the direction of the LC pretilt is given by the inclination direction of the exciting light. Two types of cells were produced: (a) symmetrical cells, consisting of two ITO-coated

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^{a)}Author to whom correspondence should be addressed; electronic mail: lcchien@lci.kent.edu

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TABLE I. LC alignment on the studied LMWPC (p, planar; h, homeotropic).

(a)

| No. | Material | E7 | ZLI 2293 |
|-----|----------|--------------------|--------------------|
| 1 | M1 | p/h^{a} | р |
| 2 | M2 | р | р |
| 3 | M3 | h | р |
| 4 | M4 | h | p/h^{a} |

^aHomeotropic alignment obtained either under photopolymerization at room temperature or short-term backing (180 °C, 10 min).

glass slides with LMWPC overlayers; and (b) combined cells, with one substrate covered by LMWPC, and the second one by rubbed PI 2555. Nematic mixtures E7 and ZLI 2293 (both from Merck) were filled at the isotropic state into the cells with a 5–50 μ m cell gap. An azimuthal anchoring energy was calculated through measurement of the twist angle in the combined cells.⁴ A polar anchoring energy was estimated using the electro-optical method developed in Ref. 5. The pretilt angle in the cells was measured by the crystal rotation method.⁶

The studied LMWPC materials provide various types of alignment for the chosen LCs. The results are presented in Table I. Some materials provide both planar and homeotropic alignment depending on the curing conditions. The homeotropic alignment is usually achieved when backing time τ_{h} $\leq 15 \text{ min}$, whereas at $\tau_b > 30 \text{ min}$ planar alignment is observed.

Materials M1 and M2 provide planar alignment for both LCs. A typical symmetrical cell with planar alignment is presented in Fig. 1(a). Figure 1(b) illustrates a three-domain LC cell combined from a rubbed PI 2555 substrate (bottom) and photoaligned M2 substrate (top) viewed between a pair of crossed polarizers. The PI rubbing direction is parallel to the polarizer. The quality of the LC alignment is the same as that of the best photoaligning polymer [Figs. 1(a), 2(a), and 2(b)]. Figure 1(b) demonstrates that the direction of the easy axis of the LC alignment is induced perpendicularly to the light polarization direction **E** and could be easily controlled by changing the direction of E. The pretilt angle of the LC alignment on materials M1 and M2 measured in both symmetrical and combined cells is $1^{\circ}-2^{\circ}$. The value of polar anchoring energy W_p estimated for E7 aligned on M1 and M2 was within $(0.8-1.5) \times 10^{-4}$ J/m². This value is close to the values obtained earlier with the same method for rubbed PI substrates.⁴

LMWPC materials M3 and M4 provide homeotropic alignment for LC E7 [see Fig. 1(c)]. The pretilt angle estimated in the symmetrical cells is 88°-88.5°. This shows that LMWPC materials can be useful for vertically aligned displays. The LC alignment on all studied LMWPC materials is thermally stable; a sample kept at 120 °C for 0.5 h did not damage the LC alignment.

Figure 2 shows the dependence of the azimuthal anchoring energy W_a on the UV illumination dose for the M1 and M2 layers backed at 180 °C over 60 min. For comparison, in Fig. 2 we present data the for photoaligning polymer, poly-(vinyl cinnamate) (PVCN). The maximal values of W_a for M1 and M2 are the same as that for PVCN. Significantly, M1 and M2 require less irradiation dosage in induction of maximum W_a .



FIG. 1. Photographs of LC cells fabricated by the LC photoalignment method using LMWPC materials. (a) A LC cell consisting of ITO-coated glass slides with M2 alignment layers is viewed between a pair of crossed polarizers as indicated by the double arrows. The LC molecules have a homogeneous alignment and a 1.5° pretilt angle with the director parallel to the polarizer. (b) A three-domain homogeneously aligned LC cell combined with M2 and rubbed PI 2555 aligning layers viewed between paired polarizers with the LC optic axis aligned 0°, 45°, and 90° with respect to one of the polarizers. (c) A homeotropically aligned LC cell with M4 layers viewed through a pair of crossed polarizers with an 88° pretilt angle.

In the case of photoinduced polymerization, we also obtained samples with planar and homeotropic alignment with the alignment quality achieved for the case of thermal polymerization. If a LMWPC film is first irradiated with nonpolarized light, subsequent irradiation with polarized light induces the easy axis of the LC alignment perpendicularly to the direction of the light polarization. The dependence of W_a on the exposure dosage for the M2 aligning film is presented in Fig. 3 (filled circles). This curve is similar to the corresponding curve for the baked film (Fig. 2, filled circles), except the maximal values of W_a are one order of magnitude lower. Interestingly, the curve corresponding to the M2 film irradiated only with polarized light (open circles in Fig. 3) shows a nonmonotonic behavior. For the low irradiation dosage (less then 2 J/cm^2), the easy axis is induced parallel to

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FIG. 2. Illumination dosage dependence of the azimuthal anchoring energy of E7 LC on baked M1 (open circles), M2 (close circles), and PVCN (triangles) substrates.

the polarization direction **E**, while for the higher dosage the easy axis is induced perpendicular to **E**. This phenomenon allows us to modulate the direction of the LC alignment by changing the irradiation dosage. This method, comprising simultaneous solidification and alignment induced with polarized light, simplifies the synthesis of the photoaligning materials and reduces the number of curing steps of the aligning substrates. It is especially useful for applications requiring low-temperature curing processes. Since the photoinduced solidification occurs at ambient temperature, this technique is indispensable for preparing LCDs on plastic substrates.

To summarize the peculiarities of the in-plane photoalignment, two types of curing conditions should be selected: (1) LMWPC layers are thermally or photopolymerized before photoalignment. (2) Phototopolymerization proceeds simultaneously with photoalignment. In the first case, the easy axis of the LC alignment appears in the direction perpendicular to vector **E**. This is in full agreement with the results obtained for cinnamate-containing polymers.¹ The surface anisotropy is caused by the angularly selective photo-crosslinking of cinnamate groups. In the second case, two LC alignment states with the easy axis parallel and perpendicular to **E** are observed. We explain the orientational transition of



FIG. 3. Illumination dosage dependence of the azimuthal anchoring energy of E7 LC on the photopolymerized M2 substrate; closed circles, substrate irradiated with nonpolarized light (10 mW/cm^2 , 15 min), followed by polarized light (5 mW/cm^2); open circles, substrate irradiated only with polarized light (5 mW/cm^2).

the easy axis with the increasing irradiation dose as the competition of two aligning mechanisms associated with the processes of photodimerization and photopolymerization providing LC alignment perpendicularly and parallel to vector **E**, respectively.

It is possible to realize different LC alignment parameters (pretilt and twist angle, anchoring strength) using mixtures of LMWPC materials to achieve different LC alignment. As listed in Table I, M2 and M3 provide planar and homeotropic alignment for the E7 LC, respectively. We prepared symmetrical cells with various ratios of M2 and M3 in the photoalignment layer. A sudden decrease in the pretilt angle (from homeotropic to planar alignment) is observed when a ratio of M3 and M2 in the composition reaches 1:4. The pretilt angle of planar alignment can be tuned from 4.5° to 1° by further increasing the M2 concentration in the mixture.

The LMWPC films spin coated on the rubbed PI substrates modify the LC alignment caused by these PI substrates. The LMWPC overlayers solidified through baking or irradiation with nonpolarized UV light provide LC alignment in the rubbing direction of the PI films. However, the LMWPC overlayers change the pretilt angle produced by rubbing. For instance, the pretilt angle for LC E7 on the rubbed PI substrates covered with M2 is 1°, while for the bare PI substrates the corresponding value is 3°. Irradiation of the LMWPC overlayers with polarized light, having the polarization direction not perpendicular to the direction of rubbing, induces LC alignment in a direction different from the rubbing direction. In general, the combined alignment layer technique provides flexibility in the LC alignment design and good alignment quality.

To conclude, we have demonstrated the use of a noncontact LC photoalignment method based on LMWPC composites in fabricating liquid-crystal displays. Indeed, the evidence suggests that the LC photoalignment obtained from LMWPC films has the same quality, anchoring parameters, and the stability of alignment, as those of the best photoalignment polymers. In addition, we explored the advantages of LMWPC composites such as ease of synthesis, reduced preparation of the aligning film, and low-temperature curing. The LMWPC materials are capable of providing LC photoalignment with a wide range of pretilt (ranging from planar to homeotropic) as well as patterned alignment.

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