Communications to the Editor

Liquid Crystal Alignment on Photoreactive Side-Chain Liquid-Crystalline Polymer Generated by Linearly Polarized UV Light

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Recent progress in liquid crystal displays (LCD) requires a precise aligning control of the low molecular weight liquid crystal (LC) director **ñ**, which is conventionally achieved by confining LC between mechanically rubbed surfaces.[1−4] However, the mechanical rubbing process is apt to produce dust during the process and generates uniform alignment over an entire substrate. In addition, for the high-grade LCDs, a multialignment of the LC director is required to increase a viewing angle of the LCDs,[5−8] and to fabricate patterned birefringent LC films,[9,10] etc. The photoaligning method promises the dust-free process and a possibility of a photopatterning of the LC alignment. Recently, several types of polarized-light-induced LC aligning techniques have been presented.[7−20] One is based on photoisomerization of azo compounds doped in polymeric materials.[10,14−18] The others are anisotropic photoreactions of poly(vinyl cinnamate) (PVCi) derivatives[7−9,11−13] and polyimide thin films[19,20] by a linearly polarized (LP) UV light. However, all of these materials so far can induce a unidirectional LC alignment in only one direction, which is perpendicular or parallel to the direction of the electric field vector **Ê** of the incident LP-UV radiation. Therefore, it is necessary to change the direction of **Ê** of the incident LP light in order to establish the multialigned LC pattern using these materials.[11] In addition, a bias-tilt angle between the LC director **ñ** and the substrate is needed for practical LCDs.

In this paper we describe a novel type of photoreactive side-chain liquid-crystalline polymers that can align the LC director both parallel and perpendicular to **Ê**, depending on the degree of the photoreaction of the polymers. Our polymer can afford a multiphotoaligned LC pattern without a change of the direction of the LP-UV light. Furthermore, the bias-tilt angle between the LC director and the photoreacted polymer substrate is also presented.

The chemical structure of the aligning polymer in this paper is depicted in Figure 1. They exhibit a nematic LC phase in the temperature range between 47 and 75 °C for **1a** and between 82 and 108 °C for **1b**, respectively. Their syntheses are described in the literature.[21] A Hg-UV lamp with glan-taylar polarizing prisms with a cut filter under 290 nm is used for the LP-UV photoreaction at room temperature. The photo-cross-linking reaction of **1** is known to undergo a [2 + 2] reaction of the cinnamoyl group.[21] The film was prepared by the spin-coating method from a methylene chloride solution on a quartz substrate, resulting in a 200 nm thick film.

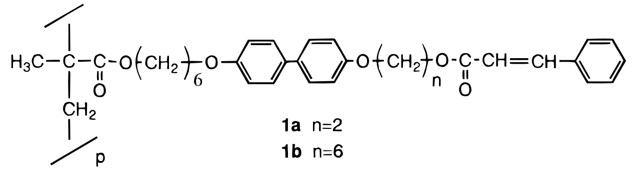

Figure 1. Chemical structures of **1a** and **1b**.

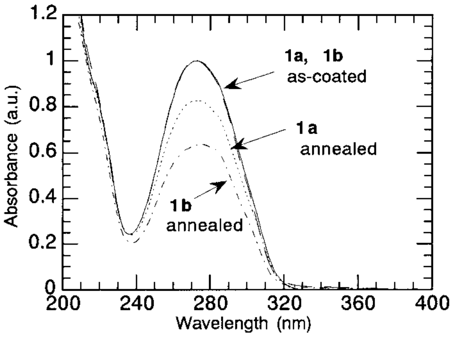

Figure 2. UV−vis spectra change of **1a** and **1b** thin films on a quartz substrate before and after annealing. The λ_{max} (ϵ) of the as-coated films are 272 nm (6.5/μm) for **1a** and 272 nm (6.9/μm) for **1b**.

Because of the LC characteristics of polymer **1**, thin film properties will be changed by a heat-and-cool treatment.[22,23] Figure 2 shows UV−vis spectra of as-coated and annealed thin films of polymers **1a** and **1b**.[24] Before heating, as-coated films should exhibit an amorphous nature and the arrangement of biphenyl and cinnamoyl groups is random since the methylene spacer is located between them. After annealing, the absorption decreased due to the aggregation of the chromophore and fixation of the LC phase of the polymer, as shown in Figure 2, where biphenyl and cinnamoyl groups were liable to be in a straight line through the methylene spacer. In addition, the decrease of the absorption intensity was smaller for **1a** than for **1b**. This is because the arrangement of biphenyl and cinnamoyl groups might be partially in a straight line for polymer **1a** due to the short methylene spacer before annealing, and the change of the molecular arrangement is small after annealing.

To observe the aligning ability and the director of the low-molecular-weight LC on the polymer film, a parallel LC cell was made by using two substrates that were coated with linearly photocross-linked **1a** or **1b** films. The cell was filled with a nematic LC mixture (E7: Merck Japan) doped with 0.3 wt % disperse blue 14 (Aldrich Co.) at 63 °C and then cooled slowly. Utilizing

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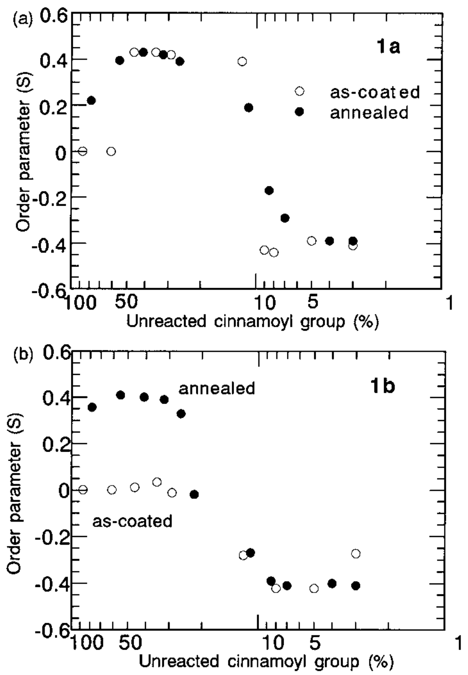

Figure 3. Order parameter of the parallel LC cell as a function of the unreacted cinnamoyl group: (a) **1a**; (b) **1b**; The amount of unreacted cinnamoyl group was determined by FT-IR. (○) as-coated film, (●) annealed film. *S* was determined by the absorbance at 653 nm.

the guest–host effect, the orientational order can be evaluated from absorption measurements. The order parameter *S* is expressed in the form of eq 1; where $A_{\|}$

$$S = \frac{A_{\|} - A_{\perp}}{A(\text{large}) - 2A(\text{small})} \tag{1}$$

and $A_{\perp}$ are the absorbances parallel and perpendicular to $\hat{\mathbf{E}}$, respectively, $A_{(\text{large})}$ means the larger of $A_{\|}$ and $A_{\perp}$, and $A_{(\text{small})}$ means the smaller. This equation expresses that the LC director $\tilde{\mathbf{n}}$ is parallel to $\hat{\mathbf{E}}$ for $S > 0$ and perpendicular for $S < 0$. Parts a and b of Figure 3 plot *S* of the cell as a function of the unreacted cinnamoyl group, which is determined by monitoring the decreasing –C=C– bond of the cinnamoyl group by FT-IR.[25] In the case of as-coated substrate, the LC did not align until 90% of the cinnamoyl group had reacted for **1b**, while the LC aligned parallel to $\hat{\mathbf{E}}$ for **1a** when the unreacted cinnamoyl group became between 50 and 10%. For both polymers, the LC director $\tilde{\mathbf{n}}$ became perpendicular to $\hat{\mathbf{E}}$ when the remaining cinnamoyl group was less than 10%. On the other hand, in the case of the annealed substrate of both polymers, the LC director was parallel to $\hat{\mathbf{E}}$ until the unreacted cinnamoyl group became 10%. This case also required that the remaining cinnamoyl group be less than 10% to align the LC director perpendicular to $\hat{\mathbf{E}}$.

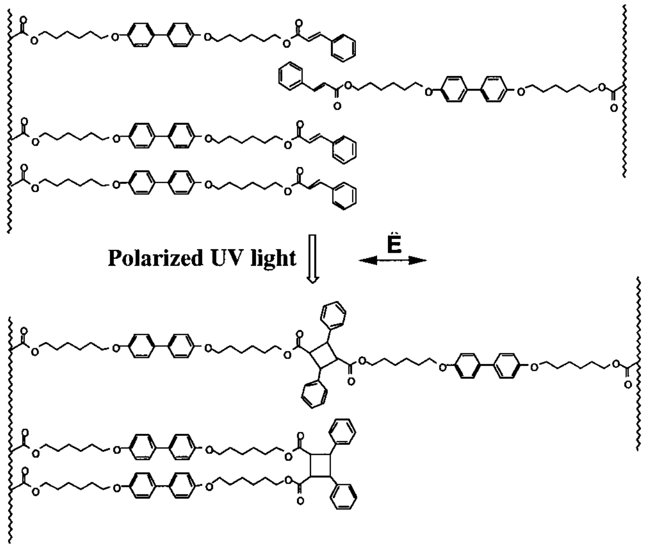

Figure 4. Anisotropic photo-cross-linking reaction of the annealed **1b** under LP-UV irradiation.

In view of the earlier work for PVCi[11] and a coumarin-based prepolymer,[7] the LC alignment on our polymer surface is caused by anisotropic interactions between the LC and the biphenyl group and/or the cinnamoyl group, which is anisotropically photo-cross-linked. Figure 4 shows the possible anisotropic photo-cross-linking reaction of **1b** under LP-UV radiation. In the case of the annealed polymer film, anisotropic Van der Waals or steric interactions between the biphenyl group and the LC will increase after the photo-cross-linking, where the direction of the long axis of the biphenyl group is parallel to $\hat{\mathbf{E}}$, resulting in the parallel LC alignment (Figure 4). Therefore, as-coated **1b** film cannot align LC parallel to $\hat{\mathbf{E}}$ since the direction of the biphenyl group and the cinnamoyl group are random. Because biphenyl and cinnamoyl groups are partially in a straight line due to a short methylene spacer, parallel LC alignment occurs for the as-coated substrate of **1a**. On the other hand, the interaction between the LC and the photo-cross-linked cinnamoyl group increases with the increasing photoreacted cinnamoyl group, resulting a perpendicular LC alignment. A large amount of photo-cross-linked cinnamoyl groups could align the LC director perpendicular to $\hat{\mathbf{E}}$, in which the long axis of the reacted molecule is perpendicular to $\hat{\mathbf{E}}$, as reported by Schadt et. al.[11]

Since polymers **1a** and **1b** can align LC both parallel and perpendicular to $\hat{\mathbf{E}}$, an optically patterned LC alignment becomes feasible by controlling the LP-UV irradiation time. An annealed **1b**-coated substrate was irradiated without a photomask for 30 s and with it for 20 min by a LP-UV lamp without change of the direction $\hat{\mathbf{E}}$, where the amounts of the reacted cinnamoyl group were about 30% for 30 s and 95% for 20 min irradiation, respectively. The LC cell was made up of this patterned **1b**-coated one and a conventionally rubbed polyimide substrate. Parts a and b of Figure 5 show a patterned LC cell as seen through crossed and parallel polarizers, respectively. The resolution bars are a homogeneous parallel alignment (30 s LP-UV irradiated region), and the background has a 90° twisted alignment (20 min LP-UV region). Since the LC alignment direction can be controlled by the irradiation time, this polymer system has the following advantages: (1) Only one kind of photomask is needed. (2) Alignment of the photomask for the patterning process is not necessary.

Finally, a bias tilt angle of the aligned LC, which is very important for stable electro-optical characteristics of LCDs, is realized by exposing the LP-UV light obliquely to the substrate. To demonstrate a large pretilt angle using a photoaligned technique, it is necessary that the photopolymer can regulate $\tilde{\mathbf{n}}$ parallel to the $\hat{\mathbf{E}}$ direction.[7] At present we used annealed **1b**-coated substrates. The films were irradiated at the angles between $\hat{\mathbf{E}}$ and the film surface from 0 to 30°.[26] An antiparallel LC cell was prepared using a nematic LC mixture (ZLI-2061: Merck Japan) and the photoreacted substrates. In this condition, the projected

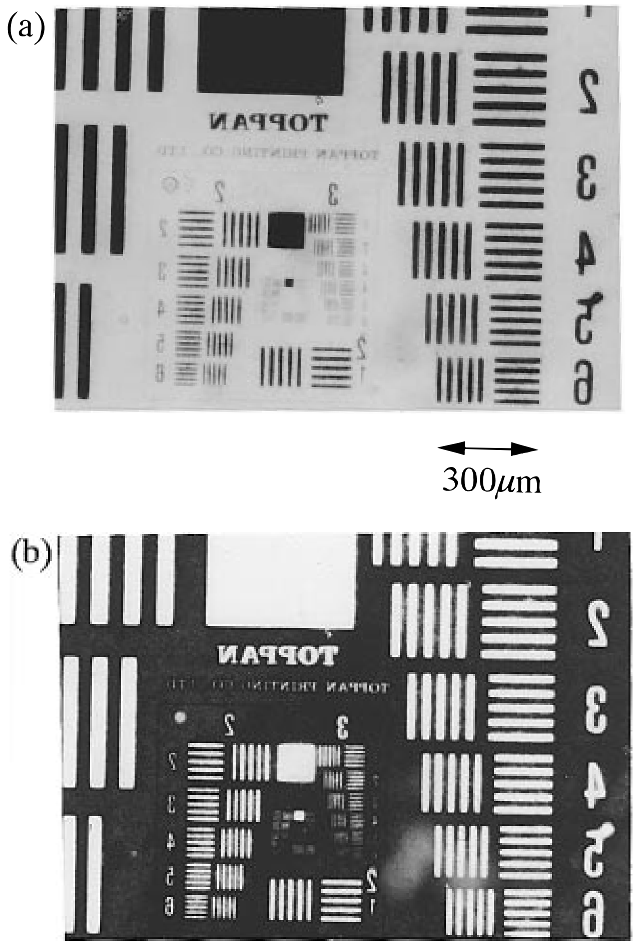

Figure 5. Photograph between parallel (a) and crossed (b) polarizers of the LC cell. The resolution bars are a homogeneous alignment, and the background has a 90° twisted alignment. The cell thickness was 12.5 μm, and E7 was used.

Table 1. Bias Tilt Angle for the Antiparallel LC Cell[a]

irradiation angle (deg)	0	10	20	25	30
tilt angle (deg)	0	0.5	1.4	2.3	3.6

[a] Nematic LC mixture of ZLI2061 (Merck Japan) was used.

direction of $\tilde{\mathbf{n}}$ on to the film surface is parallel to the projected direction of $\hat{\mathbf{E}}$ on to the substrate. The LC pretilt angles θ were measured by the crystal rotation methods,[27] and the results are shown in Table 1. θ increased with increasing the irradiation angle. This is also the consequence of the LC molecules interacting with the slanting biphenyl group, whereas the cinnamoyl group photoreacts anisotropically at a slant in the film.

In conclusion, we at first demonstrate that the LC aligns both parallel and perpendicular to the incident $\hat{\mathbf{E}}$ direction on the photo-cross-linked polymer film by changing the degree of the reacted cinnamoyl group, which can be controlled by the LP-UV irradiation time. A bias-tilt angle between the LC director and the substrate is also realized by controlling the irradiation angle of the LP-UV light. The direction of the interactive group of the polymer with the LC plays an important role for the LC alignment. Further studies on the photo-cross-linking conditions and the effect of the spacer length of the polymer side chain to the LC alignment are still underway.

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(24) As-coated film: Each film was stored at room temperature after spin-coating and no heat treatment was carried out on the film. Annealed film: Each film was annealed for 10 min at 74 °C for **1a** and at 107 °C for **1b**, respectively, and then cooled to room temperature at the rate of −10 °C/min.
(25) The amount of unreacted cinnamoyl group was determined by FT-IR monitoring, utilizing the vibrations at 1635 cm^{-1} for the −C=C− of the cinnamoyl group and at 2950 cm^{-1} for the C−H bonds. *S* was 0.42 with conventional rubbed polyimide substrates.
(26) About 30% of the cinnamoyl group was linearly photo-cross-linked at the angle 0° for 30 s of irradiation.
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