Control of nematic director orientation by exposing rubbed polyimide films to linearly polarized ultraviolet light

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The delicate interplay between the effects of mechanical rubbing and subsequent photo-induced chemical reactions on polyimide films has been studied for aligning liquid crystals. Exposure to linearly polarized ultraviolet (LPUV) light was found to profoundly alter the direction and the degree of molecular orientations obtained by rubbing. A simple model is presented to describe the observed changes in the director orientation. The results show that LPUV exposure can be very effectively used to control and fine-tune liquid crystal alignment. © *1997 American Institute of Physics.* [S0003-6951(97)02447-9]

Substrates with obliquely evaporated SiO layers, Langmuir–Blodgett films, rubbed polymer films, and linearly photopolymerized films possess anisotropic surface potential and have been successfully used to align liquid crystals (LCs).[1–4]

Among the various methods, rubbed polyimide (PI) films are most commonly used in mass production of LC displays (LCDs) because of the simplicity of making them and their good thermal stability. Several PIs currently in use exhibit sensitivity to ultraviolet (UV) light.[5,6] It is believed that irreversible anisotropic chemical reactions induced by linearly polarized UV (LPUV) light cause changes in the alignment of LC molecules.[7] Presumably, polymer aggregates in a PI layer, which are anisotropically oriented by rubbing,[8–10] can be modified by LPUV. We have studied the surface morphology of rubbed PI films before and after LPUV exposure with atomic force microscopy (AFM) and measured their optical birefringence. In this letter, we report the results of our study of the interplay between the effects of mechanical rubbing and LPUV exposure of PI films. The main features of the experimental results are described by a simple model.

In our studies, we use the PI SE610 (Nissan Chemical Co.) and the nematic LC E48 (British Drug House). PI films are prepared by spin-coating and soft baking at 100 °C for 15 min, followed by hard baking at 220 °C for 1 h. These films are rubbed two and four times, for comparison, using a velvet cloth wrapped cylinder with a surface velocity of 1.1 m/min. The rubbed PI films are subsequently exposed to the LPUV light. The intensity of the polarized UV light from a Xe lamp is approximately 6 mW/cm^2. A Nanoscope III from Digital Instruments, operated in the contact mode with a constant force, is used for the AFM work. The optical birefringence is measured using a He–Ne laser and a photoelastic modulator (PEM 90, Hinds Instruments).

As shown in Fig. 1(a), the polarization direction of LPUV makes an angle $\phi_0 = 40°$ with respect to the rubbing direction. Figure 1(b) shows the microscopic texture of a sample which is rubbed two times. Only one half of the substrate is exposed to LPUV light for 20 min. The rubbing direction, R, coincides with the axis of one of the cross polarizers and minimum transmittance is obtained in the unexposed region (marked as I), as expected. The exposed region (region II) appears bright. Minimum transmission for this region is obtained upon rotation of the LC cell by 50° clockwise or 40° counter clockwise showing that the LC alignment direction has changed by 40° and become perpendicular to the polarization direction of UV.

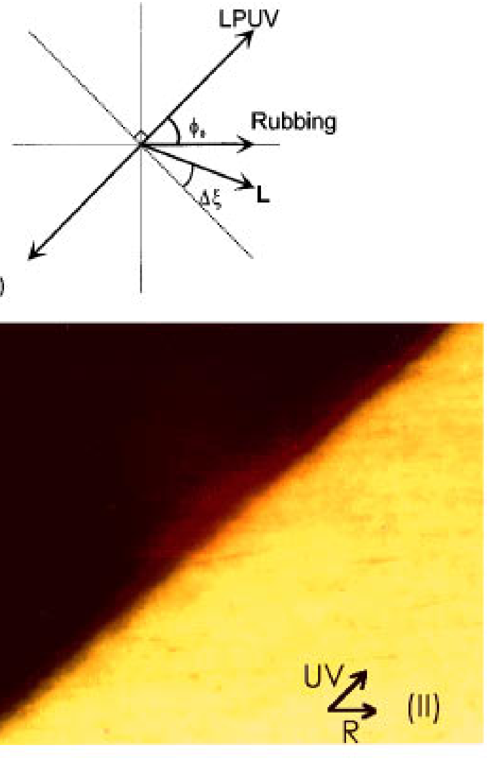

FIG. 1. (a) Relationship between the rubbing direction and the direction of polarization of LPUV. **L** is the easy axis and $\Delta\xi$ represents deviation of alignment direction from the direction perpendicular (the dotted line) to the polarization of LPUV. (b) A homogeneously aligned cell between crossed polarizers. Cell's rubbing direction coincides, R, with the axis of one of the crossed polarizers. Dark (bright) regions marked as I (II) are without (with) LPUV exposure.

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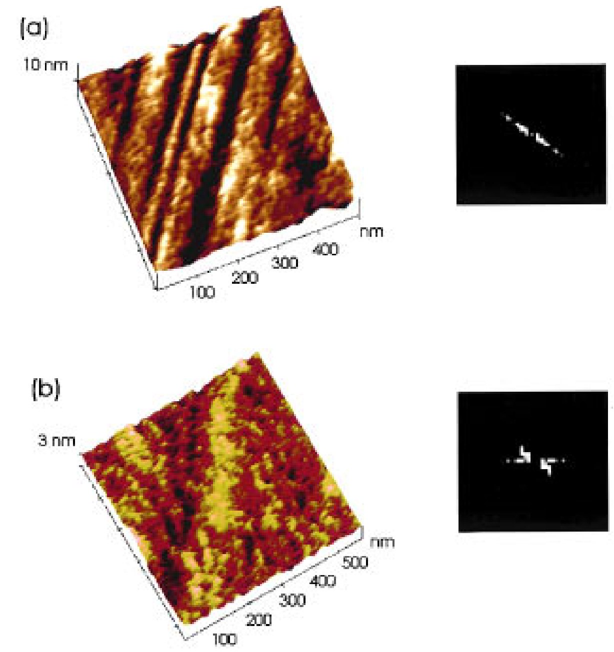

FIG. 2. Surface morphologies obtained by AFM and their power spectra for a rubbed PI film (a) without and (b) with LPUV exposure.

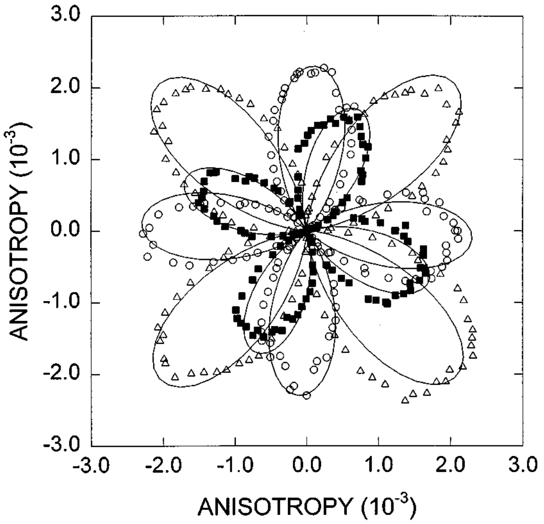

FIG. 3. The angular dependences of optical anisotropy for a two times rubbed film. The open circles, filled squares, and open triangles represent exposures of 0, 5, and 20 min, respectively.

To further understand the LPUV induced changes, we determine the changes in surface morphology with AFM. Prior to LPUV exposure, micro-scratches and PI clusters extending in the direction of rubbing are clearly visible in Fig. 2(a). Anisotropy in film's morphology, seen in the accompanying power spectrum, is believed to be responsible for LC alignment.[8–10] After LPUV exposure, the prominence of these scratches and hence the anisotropy is diminished, [Fig. 2(b)]. Interestingly, the PI micro-clusters now appear to be elongated in the direction perpendicular to the polarization. It is believed that the photoreaction process is responsible for their formation. The power spectrum shows a new branch at an angle of ~40° with respect to the rubbing direction. This albeit subtle change in surface morphology profoundly changes the LC alignment direction as shown in Fig. 1(b).

Since the easy axis of LC alignment coincides with the fast optical axis of the PI films, the deviation $\Delta\xi$ of the alignment direction, L, from the direction normal to the polarization of LPUV [Fig. 1(a)] can be determined from the film birefringence. Figure 3 shows the time dependence of the measured optical anisotropy (birefringence), in polar coordinates, for the twice rubbed PI film with LPUV exposures of 0 min (circles), 5 min (squares), and 20 min (triangles). After 20 min, the fast optical axis is rotated by 40°. Also, it is evident from Fig. 4 that $\Delta\xi \rightarrow 0$ with increasing exposure time, i.e., alignment direction rotates by 50°. It should be noted that unrubbed PI films, when exposed to LPUV, also align LCs perpendicular to the polarization direction.[5] With the help of the model presented below, it should be possible to control and fine-tune the LC alignment.

We believe that the LC alignment depends on the orientational distribution of photosensitive C(O)=N bonds in the PI film including those in the imide ring. The average direction of C(O)=N bonds in PI is nearly parallel to the polymer chain. Without rubbing or UV exposure, the angular distribution of these bonds can be assumed to be azimuthally isotropic (i.e., independent of ϕ).[7] The orientational distribution that polymer chains and C(O)=N bonds acquired during rubbing can be assumed to be a Gaussian peaked in the direction of rubbing. Consequently, the LC director becomes parallel to the rubbing direction.

However, as a previous Fourier transform infrared study[11] has confirmed, the UV irradiation selectively dissociates photosensitive bonds that are parallel to the polarization direction. This decreases the polarizability of PI molecules along that direction and reduces the dispersive (van der Waals) interactions between the LC and PI molecules. The azimuthal distribution of (remaining) photosensitive bonds becomes anisotropic. The LC director, which orients along the extremum value of the distribution of photosensitive bonds, becomes strongly dependent on angle ϕ. Assuming that the azimuthal and polar distributions are independent

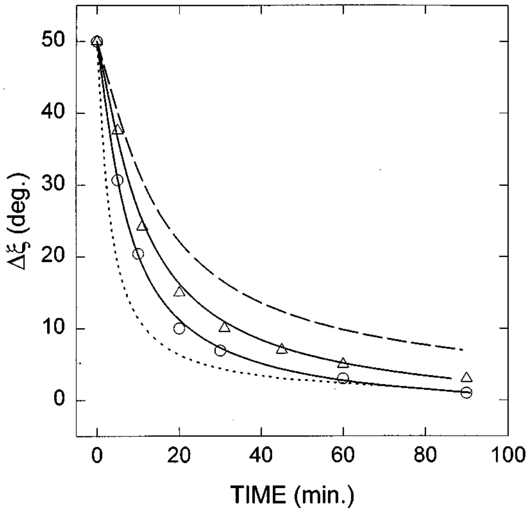

FIG. 4. Dependence of the angle of deviation, $\Delta\xi$, on LPUV exposure time. The circles and triangles denote the experimental results for two and four times rubbed films, respectively. The solid lines represent best fits to Eq. (2). The dashed and dotted lines are the calculated curves for $A = 0.1$ and 0.5 min/deg, respectively.

of each other, the resultant distribution of C(O)=N bonds can be written as

$$N(\theta,\phi,t)=N_0(\theta)\exp\left[-\frac{1}{2}\left(\frac{\phi-\phi_b}{w}\right)^2\right]\times\exp[-\alpha t\ \cos^2(\phi_0-\phi)\cos^2\ \theta],\qquad(1)$$

where ϕ and θ denote azimuthal and polar angles of the direction of transition moment of the photosensitive bonds with respect to the LPUV's electric field. $N_0(\theta)$ is the initial angular distribution of photosensitive bonds and w represents the width of ϕ distribution. The exposure time is t and the parameter α depends on the UV intensity. Here, ϕ_b and ϕ_0 denote the azimuthal angles for the rubbing and LPUV directions, respectively. For $\phi_b=0$, the LC alignment direction ϕ_s induced by the LPUV exposure satisfies the equation

$$t\ \sin 2(\phi_0-\phi_s)+A\phi_s=0,\qquad(2)$$

where $A=(1/w)/(2\alpha\ \cos^2\theta)$.

Solid lines in Fig. 4 represent a fit of experimental data to Eq. (2) for $\phi_0=40°$ and $\Delta\xi=\phi_s+50°$. From these fits, we obtain $A=0.24\pm0.01$ and 0.36 ± 0.01 min/deg for the two and four times rubbed films, respectively. For intermediate values of t, there is competition between the effects of rubbing and LPUV exposure. The angle of rotation lies between 0° and 50° and the birefringence is reduced from its initial value. With increasing t, the easy axis rotates towards the alignment direction preferred by LPUV, i.e., $\Delta\xi\rightarrow0$ and the birefringence increases as LPUV begins to affect the distribution of bonds deeper in the film. The width of the Gaussian distribution, w, is related to the surface anchoring energy in such a way that w decreases with increasing rubbing strength. For stronger anchoring, i.e., smaller w, it will take longer exposures to rotate the easy axis. The dashed and dotted lines in Fig. 4 are the calculated results for $A=0.5$ and 0.1 min/deg, respectively. Clearly, it appears possible to fine-tune the direction of alignment of the nematic LC director by adjusting the exposure time and the direction of polarization.

In conclusion, we have studied the competition between the effects of mechanical rubbing and photo-induced chemical reaction in Nissan SE610 PI films on the director orientation of a nematic LC. It is concluded that LC alignment can be controlled by combining rubbing and controlled LPUV exposure of PI films. This technique can be used to build LCDs with improved viewing angle characteristics. Future studies of other substrates with different anchoring properties are planned and should result in complete understanding and use of this technique.

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[1] J. Cognard, *Alignment of Nematic Liquid Crystals and Their Mixtures*, Mol. Cryst. Liq. Cryst. Suppl. 1 (Gordon and Breach, London, 1982).

[2] A. Dyadyusha, T. Marnsii, Y. Resnikov, A. Khizhnyak, and V. Reshetnyak, Pis'ma Zh. Éksp. Teor. Fiz. **56**, 18 (1992) [JETP Lett. **56**, 17 (1992)].

[3] M. Schadt, K. Schmitt, V. Kozinkov, and V. Chigrinov, Jpn. J. Appl. Phys., Part 1 **31**, 2155 (1992).

[4] E. Guyon and W. Urbach, *Nonemissive Electro-optic Displays*, edited by A. R. Kmetz and F. K. von Willsen (Plenum, New York, 1976).

[5] M. Hasegawa and Y. Taira, Proceedings of the International Display Research Conference, 1994, p. 213.

[6] J. L. West, X. Wang, Y. Li, and J. R. Kelly, SID Dig. **XXVI**, 703 (1995).

[7] J. Chen, D. L. Johnson, P. J. Bos, X. Wang, and J. L. West, Phys. Rev. E **54**, 1599 (1966).

[8] J. M. Geary, J. W. Goodby, A. R. Kmetz, and J. S. Patel, J. Appl. Phys. **62**, 4100 (1987).

[9] Y.-M. Zhu, L. Wang, Z.-H. Lu, Y. Wei, X. X. Chen, and J. H. Tang, Appl. Phys. Lett. **65**, 49 (1994).

[10] Y. B. Kim, H. Olin, S. Y. Park, J. W. Choi, L. Komitov, M. Matuszczyk, and S. T. Lagerwall, Appl. Phys. Lett. **66**, 2218 (1995).

[11] K. Ha (unpublished results).