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Alignment mechanism of a nematic liquid crystal on a pre-rubbed polyimide film with laser-induced periodic surface structure

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A periodic surface structure was prepared on a pre-rubbed polyimide (PI) film surface with a pulsed UV laser polarized perpendicular to the rubbing direction. The experimental results demonstrate that the rubbing-induced molecular anisotropic orientation was relaxed by the pulsed laser irradiation, and the laser induced molecular orientation was perpendicular to the line of the laser-induced periodic structure. The dichroism of the anisotropy of molecular orientation increased with the increase of laser energy. Since the direction of the laser-induced molecular anisotropy was perpendicular to the surface groove direction of the pre-rubbed PI surface, the effects of surface microgroove and anisotropic molecular orientation of the PI chain on liquid crystal (LC) alignment can be distinguished from each other. LC alignment was investigated by evaluating the anchoring energy of the PI surface, which was calculated according to Berreman's theory using the twist angle of the LC in the cells. The experimental results demonstrate that the exact alignment direction of the LC molecules is determined by the relative strength of both factors.

1. Introduction

Liquid crystal (LC) alignment has a significant effect on the performance of LC devices; several methods have been used to align LC molecules, such as mechanical rubbing [1, 2], photoalignment [3, 4] and LB films [5]. There are two major models for the mechanism of LC alignment on treated substrates: (1) anisotropic intermolecular interaction between molecules of the alignment layer and LC molecules [6–9]; (2) surface microgroove interaction [10–13]. It would be very useful for fabricating multidomain LC devices to know the relative strengths of the surface microgroove effect and intermolecular interaction on LC alignment. Although it has already been reported that microgrooves and anisotropic intermolecular interactions lead to LC alignment [1, 2], the relative effect of each factor on LC alignment has not been reported, due to the coexistence, in the same direction, of both factors on the treated substrate surface.

A laser-induced periodic structure (LIPS) can be prepared on a polymer surface by irradiating the surface with a pulsed polarized UV laser whose energy is below the ablation threshold energy [14, 15]. In LIPS, the polymer chains orient partially perpendicular to the

resulting surface microgrooves [14–16]. This provides a simple method for measuring the relative effects of surface microgroove interaction and intermolecular interaction on LC alignment.

In the experiments described in this article we prepared a LIPS on a pre-rubbed PI surface and used this film to align LC molecules. The results provided a measure of the relative strengths of surface microgroove and intermolecular interactions on the LC alignment, which in our analysis was related to the anchoring energy on the LIPS surface. The competitive effect on LC alignment of simultaneously having surface microgrooves and anisotropic intermolecular interactions, on the rubbed PI surface, was also studied.

2. Experimental

PI films, with the chemical structure shown in figure 1 [17], were prepared by dissolving the PI material in *N*-methyl-2-pyrrolidone (10 wt%) and spin-coating onto clean glass substrates. After drying at 80°C for 30 min and 100°C for 2 h, films of about 1 μm thickness were obtained.

A 200 g poise packed by cloth was used to rub the PI films twice in the same direction. In order to ensure a uniform rubbing intensity for several cells, one

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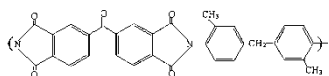
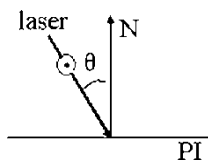


Figure 1. Chemical structure of the PI.

Figure 2. Sketch of the laser irradiation; $\theta = 20^\circ$.

substrate was cut into several parts after mechanical rubbing and then irradiated by a polarized UV laser.

Films for irradiation were fixed on an x - y stage whose speed was precisely controlled by a computer. The moving speeds of the station were 0.01 and 5 mm s^{-1} for the x and y directions, respectively. Detailed information of the optical set-up was provided in a previous paper [18]. A Nd:YAG laser source was used in this study, operated at its third harmonic frequency (355 nm). The repetition rate and pulse duration were 10 Hz and 5 ns , respectively. The angle of incidence of the plane-polarized pulse laser beam was 20° , as shown in figure 2.

The surface topology of the PI films was detected by atomic force microscopy (AFM, Nano Instruments Digital IIIa) in air using a contact mode. The orientation of PI chains on the surface was detected by FTIR spectroscopy (Bruker, Equinox55).

LC cells were assembled with one rubbed PI substrate (as reference substrate) and one laser-irradiated rubbed PI substrate. The reference substrate was rubbed strongly compared with the laser-irradiated rubbed PI substrate, on which the LC molecules align parallel to the rubbing direction. Polyethylene film of $10\text{ }\mu\text{m}$ thickness was used as a spacer, and the LC cell was sealed with epoxy resin. The nematic LC 5CB was injected by capillary action in its isotropic phase and then cooled to room temperature. The alignment behaviour and twist angle of the LC molecules were observed with polarizing optical microscopy (POM).

3. Results and discussion

3.1. Surface topology of a laser-irradiated rubbed polymer surface

Using polarized pulsed laser irradiation at 355 nm wavelength, a LIPS was obtained on the PI surface. The direction of the LIPS is parallel to the laser polarization [14]. In order to distinguish between the effects of surface microgroove and intermolecular interaction on LC alignment, the rubbing direction

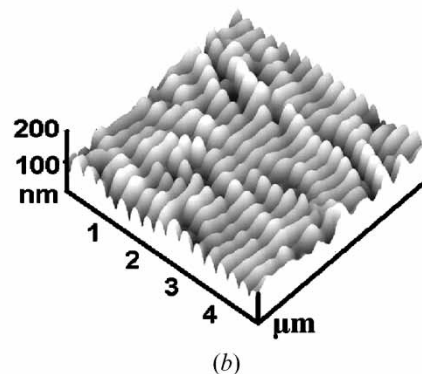
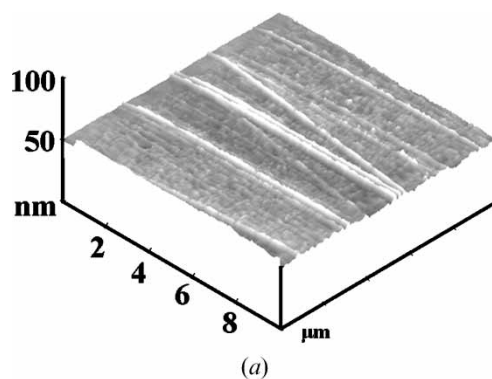


Figure 3. AFM images of a rubbed PI film (a) before and (b) after laser irradiation.

was limited to be perpendicular to the laser polarization. Figure 3 shows AFM images of a rubbed PI film before and after laser irradiation. The average depth of the rubbing-induced microgrooves was $7\text{--}10\text{ nm}$ in our experiment. After laser irradiation, a LIPS was obtained on the PI surface although a residual trace of rubbing-induced microgrooves could still be found on the PI surface of a newly formed LIPS. The amplitude (from peak to valley) of the LIPS increased with increase in laser energy in the range $7\text{--}16\text{ mJ cm}^{-2}$, as shown in figure 4. The LIPS period is in the range $290\text{--}310\text{ nm}$.

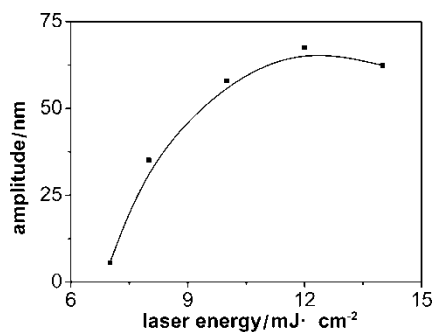


Figure 4. Relationship between laser energy and LIPS amplitude.

3.2. Molecular orientation in a laser-irradiated pre-rubbed PI surface

After rubbing treatment, a PI film shows IR dichroism between the directions perpendicular and parallel to the rubbing direction [14–16]. During laser irradiation, the PI surface may be softened or melted in the region receiving high energy [13]; this could lead to relaxation of the PI chain orientation induced by mechanical rubbing. But irradiation by the polarized pulsed laser also leads to PI chain orientation perpendicular to the LIPS [17, 18]. Therefore, it is necessary to investigate the molecular orientation of laser irradiated PI films.

Polarized FTIR spectroscopy was used to characterize the molecular orientation of the PI chains after laser irradiation. The pulsed laser polarization was always perpendicular to the rubbing direction in our experiments. In the IR dichroism experiments, angles were measured from an axis parallel to the rubbing axis. Because the vibration direction of the C–N bond is parallel to the direction of the PI main chains, the symmetrical C–N stretching vibration, 1370 cm^{-1} , can be used to characterize the orientation of PI chains. Figure 5 shows the absorption anisotropy of the C–N bond at varying incident IR light polarization. The absorption band reaches a maximum when the IR polarization is parallel to the rubbing direction, indicating that the PI chains are oriented partially parallel to the rubbing direction, i.e. perpendicular to the LIPS.

The absorptive ratio of the C–N bond, parallel and perpendicular to the rubbing direction (A_{\parallel}/A_{\perp}) was used to characterize the orientation dichroism of PI molecules. Before laser irradiation, the A_{\parallel}/A_{\perp} ratio induced by mechanical rubbing was about 1.08. The relationship between C–N bond dichroism and laser energy is shown in figure 6. The dichroism of the C–N bond increased with laser energy in the range $8\text{--}14\text{ mJ cm}^{-2}$. However, the PI dichroism was smaller than the rubbing-induced dichroism when the laser

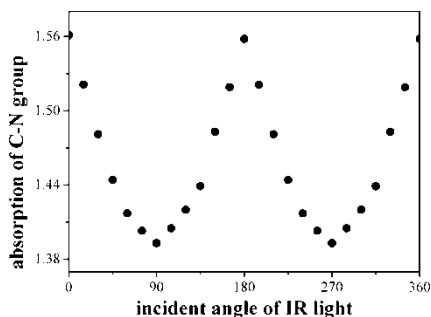


Figure 5. Anisotropy of orientation of the C–N bond in a PI film with LIPS.

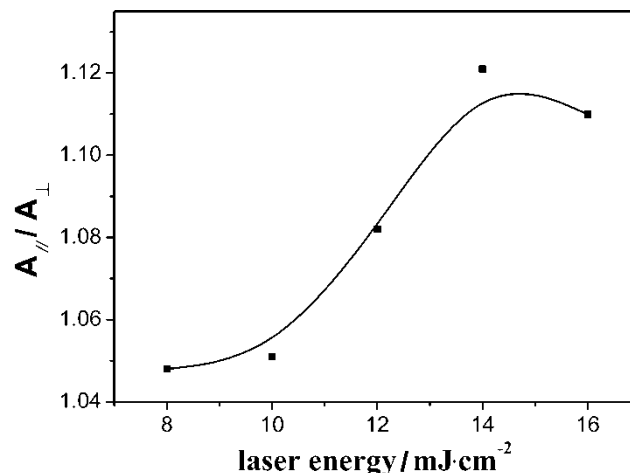


Figure 6. Relationship between dichroism of the C–N group and laser energy.

energy was below 12 mJ cm^{-2} . This result indicates that the orientation of the PI chain induced by mechanical rubbing was relaxed by the pulsed laser energy. The PI chain orientation in the newly formed LIPS was due mainly to the interaction of the polarized electric field of the laser with the main dipole of the PI chain [17]. The decrease of the dichroism at an energy of 16 mJ cm^{-2} was considered to be result of laser ablation.

3.3. LC alignment on a LIPS surface

LC alignment by LIPS was studied using a twist LC cell with one rubbed PI surface as reference substrate and one laser-irradiated pre-rubbed PI surface. The rubbing directions of the upper and lower substrates were perpendicular to each other. The polarizers were aligned so that rubbing-induced LC alignment led to a dark field. The POM images of such LC cells with varying incident laser energies are shown in figure 7. The lightness of the laser irradiated region increases with increase in laser energy, which indicates that the alignment direction of LC molecules on the laser-irradiated pre-rubbed surface (lower substrate) deviates from the rubbing direction gradually and tends to align nearly parallel to the LIPS direction.

Measurement of the twist angle in the LC cell enabled the study of the direction of the LC molecules on the LIPS surface [25]. In this experiment also, the LC cell was assembled with one strongly-rubbed PI substrate as reference and one laser-irradiated pre-rubbed PI substrate. The rubbing directions of the two LC cell substrates were parallel. The twist angle Φ of the LC molecules after exposure to different laser energies is shown in the table, with a measurement error of about $\pm 0.5^\circ$ in the LC cell. From the table, it

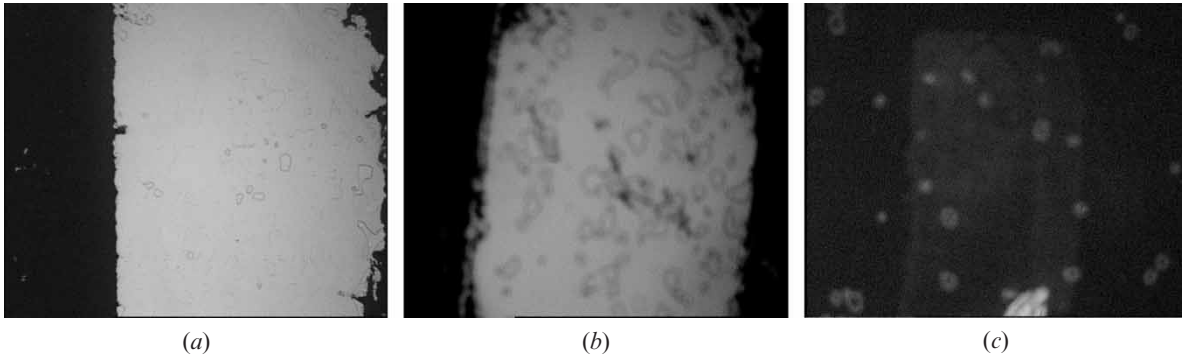


Figure 7. POM images of LC alignment in different LC cells with varying laser energy: (a) 7, (b) 10, (c) 14 mJ cm⁻².

Table. Anchoring energy of LC molecules on a PI surface with differing amplitude LIPS.

| Laser energy/mJ cm ⁻² | λ /nm | a /nm | $W_B/10^{-5} \text{ J m}^{-2}$ | $\Phi/^\circ$ | $W_\phi/10^{-7} \text{ J m}^{-2}$ |
|----------------------------------|---------------|---------|--------------------------------|---------------|-----------------------------------|
| 7 | 312.5 | 5.53 | 0.051 | 0.8 | 3.9 ± 0.1 |
| 8 | 289 | 35.1 | 2.30 | 2.5 | 3.9 ± 0.1 |
| 10 | 283.2 | 57.9 | 5.96 | 21.7 | 4.3 ± 0.2 |
| 12 | 306.6 | 67.5 | 8.10 | 57 | 8.5 ± 0.1 |
| 14 | 298.8 | 62.4 | 7.46 | 72.5 | 17.2 ± 0.5 |

can be seen that the twist angle of the LC molecules becomes larger with increase in laser energy. This also indicates that the LC molecules tend to align more closely to the LIPS direction when the LIPS amplitude increases.

3.4. Anchoring energy of LC alignment on a laser-irradiated pre-rubbed PI surface

The anchoring strength of LC molecules on the grooved surface can be calculated by measuring the twist angle of the LC. Assuming infinite anchoring energy at the reference PI surface, in the same LC cells that were used for measuring twist angles, the azimuthal anchoring energy of LC molecules on a grooved surface can be obtained from the following equation [25]:

$$W_\phi = \frac{2K_{22}\Phi}{d \sin 2\Phi} \quad (1)$$

where K_{22} is the twist elastic constant, Φ is the LC twist angle and d is the cell spacing. For the liquid crystal 5CB, K_{22} is about $3.9 \times 10^{-12} \text{ N}$. The value of the anchoring energy calculated according to equation (1) is shown in the table. Simultaneously, the LC anchoring energy on the grooved surface can be given by the following equation if we only consider the effect of surface microgrooves on LC alignment [10]:

$$W_B = \frac{2K\pi^3 a^2}{\lambda^3} \quad (2)$$

where K is the mean of bend and splay elastic constants

($K_{11} = 7.2 \times 10^{-12} \text{ N}$, $K_{33} = 9.5 \times 10^{-12} \text{ N}$), a is the LIPS amplitude and λ is the LIPS period. The anchoring energy on a LIPS surface irradiated by varying laser energy was calculated according to equation (2); the results are also shown in the table.

It can be seen from the table that the anchoring energy W_ϕ is much smaller than W_B . This is different from the alignment behaviour of LC molecules on excimer laser-ablated grooved surfaces [1]. The anchoring energies of excimer laser-ablated groove surfaces, obtained from twist angle measurement, agreed well (within experimental error) with the Berreman theory [10]. Newsome concluded that the alignment of LC molecules on excimer laser-ablated grooved surfaces was affected only by surface microgrooves.

It is widely known that only the effect of surface microgrooves on LC alignment is considered in the Berreman theory [10], and the measurement of W_ϕ is based on the consideration of the comprehensive effect of the surface on LC alignment [25]. In our experiments the surface microgrooves and anisotropic orientation of the PI chains coexisted on the film prepared with LIPS, and both of these can affect LC alignment. The surface microgroove effect leads the LC molecules to align along the microgrooves, to minimize the elastic distortion energy. But the effect of anisotropic molecular orientation leads the LC molecules to align perpendicular to the surface microgrooves. So these effects are competitive in controlling the LC alignment. If the surface microgroove effect is stronger than that of anisotropic molecular orientation, the LC molecules

will align closer to the surface microgroove; in the reverse situation, the LC molecules will align closer to the anisotropic molecular orientation. If the two effects are equal, the LC will align at an angle of 45° to the surface microgrooves.

According to equation (2), the surface microgroove effect on LC alignment is related to LIPS parameters such as amplitude and periodicity, which vary with laser energy as shown in figure 4. According to the W_ϕ measurement, the effect of anisotropic molecular orientation on LC alignment is related to its magnitude, which also varies with laser energy as shown in figure 6. So the effects of surface microgrooves and anisotropic molecular orientation on LC alignment also vary with the laser energy incident on the PI film surface. The exact direction of LC alignment depends on the relative strengths of the two effects.

When the PI film was laser-irradiated at 7 mJ cm^{-2} , the LIPS had an amplitude of 5.53 nm and a period of 312.5 nm, which corresponds to an anchoring energy of about $5.14 \times 10^{-7} \text{ J m}^{-2}$ according to equation (2). The anchoring effect of surface microgrooves on the LC molecules is very weak. Although the dichroism of the PI chains is rather small at this energy, the intermolecular interaction is stronger than the surface microgroove effect, so the LC director tends to align close to the PI chain orientation direction. But due to the competitive effect of surface microgrooves on LC alignment, the LC director deviates slightly from the PI chain orientation direction.

When the laser energy increases, the LIPS amplitude increases, and then the effect of surface microgrooves on LC alignment becomes stronger. The angle of deviation of LC directors from the PI orientation direction also increases. When the PI surface is irradiated at 12 mJ cm^{-2} , the LIPS has an amplitude of 67.5 nm and a period of 306.6 nm. The anchoring energy of LC molecules on this LIPS surface is about $8.10 \times 10^{-5} \text{ J m}^{-2}$ according to equation (2). On this film the LC alignment is closer to the surface microgrooves, indicating that the surface microgroove effect exceeds the intermolecular interaction effect, though the dichroism of molecular anisotropic orientation also increases with the increase in laser energy. But due to the competitive effect of the intermolecular interaction, the LC director does not lie completely among the LIPS direction.

As can be seen from the above results, LC alignment on the LIPS surface is controlled by the surface grooves and anisotropic orientation of PI chains. These effects are competitive in controlling the LC alignment. But on the rubbed PI surface used in our experiment, the two factors did not play the same role, due to the different contributions to LC alignment. The depth of

rubbing-induced microgrooves on a PI surface was about 7–10 nm as shown in figure 3(a), which is less than that of the microgrooves on a PI film irradiated at 8 mJ cm^{-2} . However, the dichroism of the PI chain on a rubbed PI surface is larger than that of a laser irradiated PI surface. On the PI surface with LIPS irradiated at 8 mJ cm^{-2} , LC molecules aligned in a direction close to the anisotropic molecular orientation. We thus conclude that LC alignment on the rubbed PI surface was controlled mainly by rubbing-induced anisotropic orientation.

4. Conclusion

A laser-induced periodic surface structure was prepared on a pre-rubbed PI film. The rubbing-induced molecular orientation was relaxed after laser irradiation and the anisotropy orientation of PI chains in the LIPS film resulted mainly from the polarized laser irradiation. The dichroism in the PI chain increases with the laser energy. LC molecules show homogeneous alignment on the LIPS surface, their alignment being affected by the competitive effects of surface microgroove interaction and intermolecular interaction. The direction of LC alignment lies in a direction between the surface groove and PI chain orientations.

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