

Liquid Crystal Alignment on Polyimide Surface with Laser Induced Periodic Surface Microgroove

Xue-min LU¹, Hong-jie Xu¹, Gang Li², Jie YIN¹, Zi-kang ZHU¹, Qing-hua LU*

¹ School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, 200240, Shanghai, China

² Instrumental Analysis Center, Shanghai Jiao Tong University, 200240, Shanghai, China

激光诱导聚酰亚胺表面形成的周期性微结构, 不仅具有纳米深度的表面沟槽, 同时聚酰亚胺分子链和链段具有垂直于纳米沟槽方向的排列趋势。我们研究了液晶分子在其上的定向行为。实验结果表明: 不仅聚酰亚胺表面沟槽对液晶分子具有定向功能, 而且取向的聚合物分子链对液晶分子也具有定向功能, 两者是一个竞争过程。当表面沟槽浅时, 液晶分子取向方向受衬底聚合物取向分子链底控制, 即“分子-分子相互作用理论”是液晶取向的主要机制; 当表面沟槽深时, 液晶分子的取向方向受沟槽方向的控制, 即“沟槽理论”成为主要因素。液晶分子从衬底聚合物分子链取向方向转变到沟槽方向过渡区的沟槽深度在 12-14 nm 范围。

1. Introduction

Rubbing technique has been widely used in manufacturing liquid crystal display for its simplicity and reliability for many years, but the exact mechanism of liquid crystal (LC) alignment was still a debated topic. The ability of rubbed polymer surface in controlling the alignment of LC molecules has been considered as the results of the induced alignment by the surface microgroove generated by the mechanical rubbing (“microgroove effect”)¹⁻⁶, or the anisotropic van der Waals interaction between the LC molecules and the oriented surface polymer molecules or segments (“molecule-molecule interaction”)⁷⁻¹². Since the microgroove and the orientation of polymer chains are generated simultaneously and have the identical direction in the rubbing process, it would be very difficult to clarify the mechanism of the LC alignment from the experimental results based on the rubbed polymer surface. Some researchers used laser-ablation polymer microrelief surface¹³⁻¹⁴, unidirectional stretching¹⁵ and Langmuir-Blodgett films¹⁶ to verify the effect of surface microgrooves or molecular orientation, respectively. But the surface of these treated polymer films has character of either molecular orientation or microgroove, or the two characters have the same direction. The real mechanism of liquid crystal alignment is far from clear.

The periodic microgroove structure on polymer surfaces induced by one polarized pulsed laser has recently been widely investigated¹⁷⁻²⁰. When the laser energy is smaller than the ablation threshold energy of the polymer (the minimal energy for polymer photodecomposition), periodic microgroove structure can be

obtained on the polymer surface. The periodicity of the microgroove structure (Γ) is decided by the wavelength of the laser (λ), the refractive index of the polymer (η) and the angle of incidence (θ) with the following relationship:

$$\Gamma = \lambda / (\eta \cdot \sin \theta) \quad (1)$$

It was also observed that the laser fluency would affect the depth but not the periodicity of the surface microgrooves.

In previous study on the laser induced periodic microgroove on polyimide surface, we reported that the polyimide chains or segments in the surface microgrooves tended to align in the direction perpendicular to the surface grooves¹⁷. We believe the observation would be very useful in the investigation of the alignment mechanism of liquid crystal molecules on the polymer surface, and therefore we studied the alignment behavior of LC molecules on the laser induced periodic microgroove surface. We obtained surface microgrooves with different depths by changing the laser fluency, and the polarized optical microscopic results clarified the effects of the surface microgroove and surface molecular orientation on the LC alignment.

2. Experimental

The polyimide used in this experiment is based on 4,4'-diamino-3,3'-diphenylmethane and benzophenone-3,3',4,4'-tetracarboxylic dianhydride²¹. Its chemical structure was shown in Fig.1. Polyimide films were made by dissolving the polyimide in N-methyl-2-pyrrolidone (10%wt) and spin coating onto a glass substrate. After being dried at 100 °C for 3 hours, and films with 1 μm thickness were obtained. Liquid crystal molecules, TEB-60 ($n_e=1.677$, $\Delta n=0.161$), was provided by Slichem Liquid Crystal Materials Co., Shijiazhuang, China. It is a mixture of several compounds. It is in its nematic state at room temperature (LC temperature range: -20-60°C).

The surface topographic profiles of laser-irradiated polyimides were detected with a Digital Instruments Nano IIIa scanning probe microscope in air condition using a contact mode. The alignment behavior of LC cells on the polyimide surface was investigated by a crossed polarized optical microscopy (LEICA-DMLP) at room temperature.

Large area periodic structure on polyimide surface was prepared by using optical set-up shown in Fig.2. The laser used in this study was a Nd:YAG laser operated on its third harmonic (355nm). The repetition rate and the pulse duration were 10Hz and 5 ns, respectively. The incident angle of the s-polarized pulse laser beam was 20°. The laser fluency was in the range of 20mJ/cm²-50mJ/cm².

3. Results and Discussion

3.1 Laser irradiated periodic microgroove on polyimide surface

In this study we used two different laser fluencies of 24mJ/cm² and 40mJ/cm², respectively, to irradiate polyimide surface. The AFM results were showed in Fig.1.

The top photos A and B were the AFM images of surface microgrooves generated using laser fluencies of 24 mJ/cm^2 and 40 mJ/cm^2 , respectively. The bottom was the cross section profiles corresponding to the top images. The AFM results showed that the depth of surface periodic structure were about 10 nm and 45 nm , respectively, and the periodicity of the surface grooves was not obviously changed.

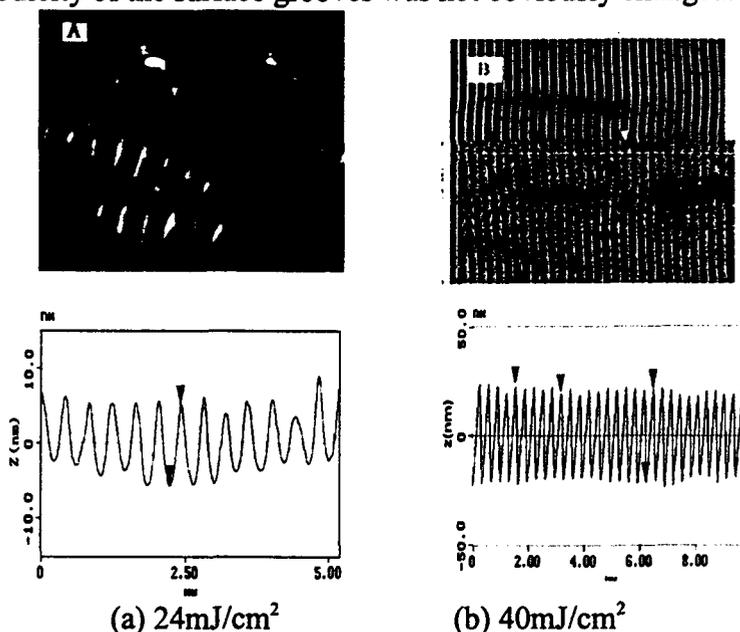


Fig.1 AFM photographs of laser induced microgrooves on polyimide surface

3.2 Alignment behavior of LC molecules on the irradiated surface

To determine the alignment of LC molecules on the laser-irradiated polyimide surface, the two laser-irradiated polyimide films with surface microgrooves of various depths (on glass substrates) were cut to two parts and then assembled with the surface microgroove of the two parts parallel to each other to form two LC cells. The cell prepared from the polyimide film with shallow microgrooves (10 nm) was named Cell 1, while that based on polyimide with deep microgrooves (45 nm) was named Cell 2. The cells were then put into the optical set-up as Fig. 2 with the direction of the microgrooves parallel to the polarizer. The change in the intensity of the transmission light with the rotation angle of the LC cells was described in Fig. 3. It was observed that the intensity exhibited a periodical change for every 90° and the rotation angle was $45, 135, 225, 315^\circ$, while the intensity was minimal when the rotation angle was $0, 90, 180, 270^\circ$ for both cells, indicating the existence of obvious alignment of the LC molecules. In addition, from the relationship between the rotation angle and the transmittance, it can be concluded that the LC molecules aligned in the direction parallel or perpendicular to the polarizer, that is parallel to the microgroove direction or the orientation direction of polymer molecular.

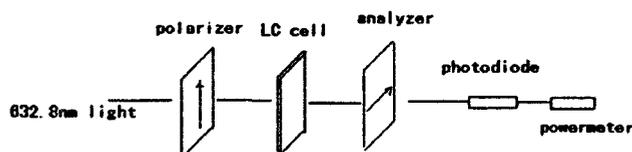


Fig.2 Optical setup for liquid crystal cell birefringence measurements

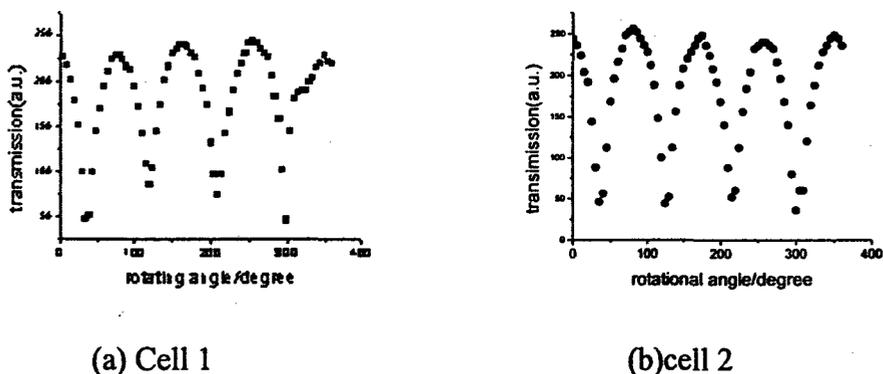


Fig.3 Optical setup for liquid crystal cell birefringence measurements

To further clarify the alignment direction of LC, we assembled LC cells using one mechanically rubbed polyimide and one laser-irradiated polyimide and the rubbing direction and the microgroove direction were perpendicular to each other. The cells using polyimide having shallow (10 nm) microgrooves was named Cell 3, while that with polyimide having deep (45 nm) microgrooves was named Cell 4. A crossed polarized optical microscopy was used to investigate the alignment direction of LC cells. If the rubbing direction was parallel to the polarization direction of the polarizer initially, then rotating Cell 3 by 0° and 90° led to extinction, while rotating by 45° and 135° gave light field. In contrast, rotating Cell 4 by 0° and 90° gave a light field and 45° and 135° led to extinction. The alignment of LC molecules may be controlled by the microgrooves or the surface polyimide molecular orientation. If it is controlled by the microgrooves, (whose direction is perpendicular to the orientation direction of the polyimide molecules in this case), then the LC cell behaves as a twisted (90°) nematic displaying mode: Rotating the LC cell by $0, 90, 180, 270^\circ$ leads to light field, while rotating by $45, 135, 225, 315^\circ$ gives extinction. In contrary, if the alignment of the LC molecules is controlled by the surface molecular orientation, then the LC cell behaves as a parallel non-twisted displaying mode: Rotating the LC cell by $45, 135, 225, 315^\circ$ leads to light field, while rotating by $0, 90, 180, 270^\circ$ gives extinction. This indicates that the alignment of LC molecules in Cell 4 was controlled by the surface microgroove, while that in Cell 3 was controlled by the surface molecular orientation. It can then be concluded that the surface molecular orientation controlled the alignment of LC molecules when the depth of the surface microgrooves is small, while the microgrooves became

decisive in the control of the alignment of LC molecules when the depth was increased to a certain level.

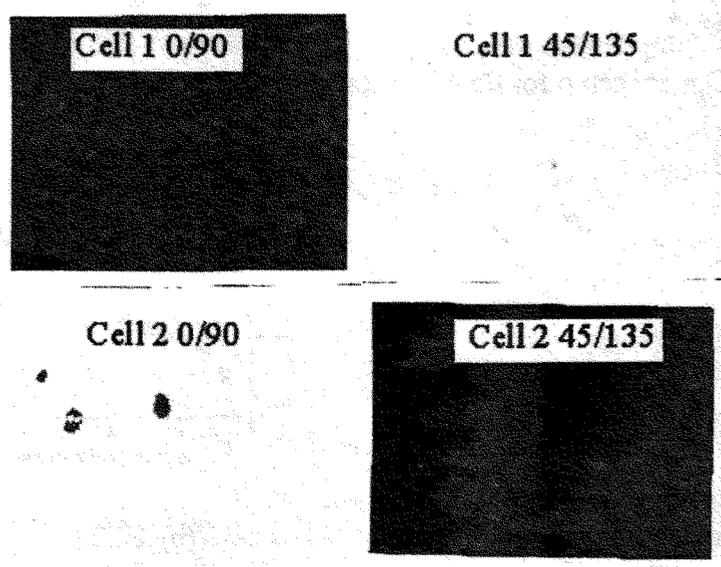


Fig. 4 Images observed to the crossed polarized optical microscopy of LC cells with various rotation angle.

To know the microgroove depth in which the decisive factor of the control of the alignment of LC molecules was changed from surface molecular orientation to microgroove, following study was conducted using a special laser scanning mode. Under this mode, the exposure time of the margin area of the surface was much longer than that of the central area, which meant that deposited energy in the margin area was greater than that in the central area of the scanning region. The depth of the surface microgroove decreased from the margin (55nm) to the center (2.6nm) as shown in Fig.5. When this polyimide film was used to assemble the LC cell in the way identical to Cells 3 and 4, the transitional displaying mode was clearly observed in the polarized microscope: Light field occurred in the margin area while extinction occurred in the central area when the LC cell was at the initial place. This result indicated that the orientation of polymer molecules was the main factor to align the LC molecules in the central part of the scanning area, while in the margin area, the microgroove effect was more important and consequently aligned the LC molecules in the groove direction. This study further confirmed the above conclusion. Using AFM measurement, the depth for the displaying mode transition was found to be 12-14nm.

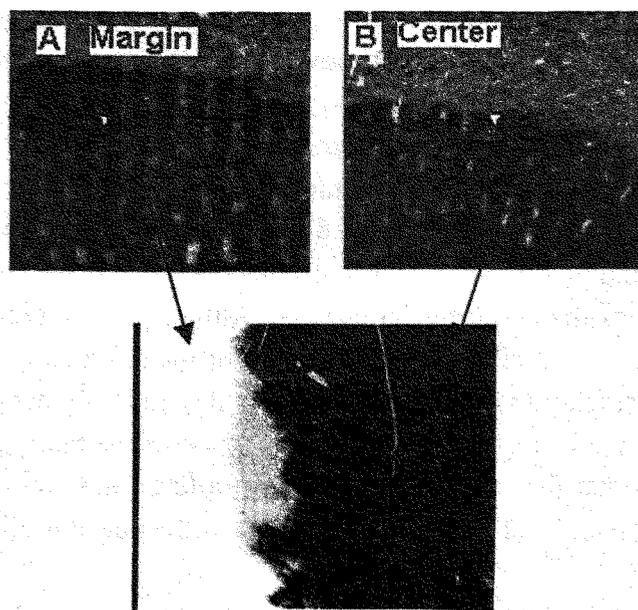


Fig.5 Microgroove structure with different depths at different area and optical anisotropy of LC cells. The inner is the cross-section of the AFM. The arrows represent the corresponding region in the scanned surface.

3.3 Mechanism of LC alignment

Berreman⁽⁷⁾ first suggested that the free energy of the system was strongly related to the alignment direction of the LC molecules and maintained that the alignment of the director, \mathbf{n} , of the LC molecules in the microgroove direction led to the lowest free energy (F_{\parallel}) and the most stable system, while the alignment of the LC molecules in the direction perpendicular to the microgroove direction would lead to an increased bending elastic strain and the highest free energy (F_{\perp}). The difference between F_{\perp} and F_{\parallel} can be described by

$$\Delta F = 2 \pi^3 k a^2 / \lambda^3 \quad (3)$$

where a is the depth of the microgroove, λ is the periodicity of the microgroove and k is the characteristic parameter of the LC⁽⁴⁾. Meanwhile, “molecule-molecule interaction” theory⁽⁷⁻¹²⁾ indicates that the oriented polymer surface molecules has anisotropic interaction with the LC molecules and the system has a minimal free energy when the director of the LC molecules is parallel to the orientation direction of the polymer molecules (and in our experiments, perpendicular to the microgroove direction).

From the above experimental results we can conclude that the “molecule-molecule interaction” and surface “microgroove effect” are the two competitive factors in determining the alignment property of LC molecules. For the laser-induced microgrooves on polyimide surface, the periodicity of the microgrooves is unchanged for fixed laser wavelength and incident angle. The change in the laser energy leads to only the change of the depth of the microgrooves. As the depth is increased, the

decrease in the free energy when the LC molecules align in the microgroove direction is increased. When the depth of the microgrooves is small, the interaction between the surface polyimide molecules or segments and the LC molecules is the main factor in the reduction of the free energy of the system and the LC molecules tend to align in the orientation direction of polyimide molecules. As the depth of the microgrooves is increased, the microgroove effect is enhanced and if the microgroove effect exceeds the effect of the orientation of the polymer molecules, the LC molecules would tend to align in the direction of the surface microgroove. Although the increase in the laser energy might also lead to the increase in the degree of the orientation of the polymer molecules and the interaction between the LC molecules and polymer molecules, this increase does not seem to be as significant as the increase of the microgroove effect. It can therefore be seen that the “surface microgroove effect” and “molecule-molecule interaction” orientation are not exclusive, but both influence the alignment of LC molecules.

Our results also indicate indirectly that the alignment of the LC molecules on a rubbed polymer surface is the coordinated results of the “microgroove effect” and “molecule-molecule interaction”. Since the depth of the grooves generated by mechanical rubbing is generally small (generally $\leq 10\text{nm}$), the effect of polymer molecular orientation is the relatively important factor in determining the alignment of the LC molecules, as most of the studies revealed⁽¹⁻⁶⁾. Meanwhile, the polymer surface with deeper microgrooves could lead to the alignment of LC molecules in the direction of the microgroove^{6,22,23}.

Reference

- 1) D. W. Berreman: Phys. Rev. Lett. **28** (1972) 1683.
- 2) H.V. Kanel, J.D. Litster, J. Melngailis, H. I. Smith: Phys. Rev. A, **24** (1981) 2713
- 3) E.S. Lee, P. Vetter, T. Miyashita, T. Uchida: Jpn. J. Appl. Phys.**32** (1993) L1339.
- 4) G. P. Bryan-Brown, C. V. Brown, I. C. Sage, V.C. Hui: Nature, **392** (1998) 365.
- 5) X. T. Li, N. Nlmeria, P. Rochon: Appl. Phys. Lett. **74** (1999) 3791.
- 6) A. Parfenov, N. Tamaoki, S. Ohnishi: Appl. Phys. Lett.**87** (2000) 2043.
- 7) J.P. Castellano: Mol. Cryst. Liq. Cryst. **294** (1983) 33.
- 8) J. M. Geary, J. W. Goodby, A. R. Kmetz, J. S. Patel: J. Appl. Phys. **62** (1987) 4100.
- 9)N. A. J. M. van Aerle, M. Barmantlo, R. W. Hollering: J. Appl. Phys.,**74** (1993) 3111.
- 10) X. Wei, X. W. Zhuang, S. C. Hong, T. Goto, Y. R. Shen: Phys. Rev. Lett. **82**(1999) 4256
- 11) M.H. Kim, J.D. Kim, T. Fukuda, H. Matsuda: Liq. Cryst. **27** (2000) 1633.
- 12) X. Wei, S. C. Hong, X. W. Zhuang, T. Goto, Y. R. Shen: Phys. Rev. E. **62** (2000) 160.
- 13) H. Niino, Y. Kawabata, A. Yabe: Jpn. J. Appl. Phys.**28** (1989) L2225.
- 14) P. E. Dyer, R.J. Farley, R. Giedl: Appl.Phys.Lett.**64** (1994) 3389.
- 15) H. Aoyama, Y. Yamazaki, N. Matsuura, H. Mada, S. Kobayashi: Mol. Cryst. Liq.

Cryst. 72 (1981) 127

16) D.S. Seo, S. Kobayashi: Mol. Cryst. Liq. Cryst. 339 (2000) 1.

17) Q. H. Lu, Z.G. Wang, J. Yin, Z.K. Zhu, H. Hiraoka: Appl. Phys. Lett. 76 (2000) 1237.

18) H. Niino , A. Yabe, S. Nagano: Appl. Phys. Lett. 54 (1989) 2159.

19) M. Bolle , H. Lazare: Appl. Phys. Lett. 73 (1993) 3516.

20) H. Hiraoka , H. Sendova : Appl. Phys. Lett. 64 (1994) 563.

21) Q. H Lu, J.Yin, H.J. Xu, J.M. Zhang, L.M. Sun, Z.K. Zhu, Z.G. Wang: J. Appl. Polym. Sci. 72 (1999) 1299.

22) H.V. Kanel, J.D. Lister, J.Melngis , H.I. Smith:Phys.Rev. A24 (1983) 2713.

23) E.L. Wood, G.W. Bradbery, P.S. Cann , J.R. Samble:J. Appl.Phys.82 (1997)2483.