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Laser induced periodic structure on lecithin-doped polyimide film surface and its ability to align liquid crystal molecules

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Abstract

Doping effect of lecithin in polyimide (PI) films on the preparation of laser induced periodic structure (LIPS) was investigated using single-beam polarized pulse UV laser. We found that the regularity of LIPS on lecithin-doped PI film irradiated at 266 nm was better than that at 355 nm and the threshold energy for the preparation of LIPS decreased. The amplitude of LIPS increased with the increase of lecithin content. In addition, lecithin molecules tended to migrate to the film surface after laser irradiation according to FT-IR spectroscopic results. We found that nematic liquid crystal molecules were azimuthally aligned on the irradiated doped PI surface when lecithin content was below 20 wt%, and were vertically aligned when the lecithin content was 30 wt%.

Keywords: Polyimide; Lecithin; Doping effect

1. Introduction

Laser induced periodic structures (LIPS) are a focused interest in recent decades and have been observed on condensed materials, i.e. semiconductors [1], metals [2] and recently polymers such as polystyrene, poly(ethylene terephthalate) and polyethersulfone irradiated by excimer lasers [3–7]. Hiraoka et al initially prepared LIPS in 1994 by using Nd:YAG laser as the light resource at an energy lower than the ablation threshold energy of a polymer [8]. On the mechanism of the LIPS formation, most researchers accepted that the property of a polymer film had important effect on the formation of LIPS, especially the absorption of the film to the incident laser [9–10]. So recent works mostly focused on the preparation of LIPS on different polymer films, i.e. polyimide (PI) and polycarbonate [11–12].

According to the literature on laser ablation of polymers, doping of small molecules, which showed absorbance at incident laser, was helpful to the laser ablation process [13]. From this viewpoint we considered that the doping of small molecules might be helpful to accelerate the LIPS formation at lower energy, because the LIPS formation was a thermal physical process according to Hiraoka's reports [9]. Lecithin, as a typical surfactant, not only shows certain absorbance at the wavelength range of 226–274 nm, but also could decrease the glass transition temperature (T_g) of a doped polymer. In this report, we described the doping effects of lecithin molecules on the LIPS formation on a PI surface. The surface character of the lecithin-doped PI film was investigated by using atomic force microscopy (AFM) and different modes of FT-IR spectroscopic techniques.

Film surface with LIPS could be used in several fields such as optical gratings, data storage and liquid crystal (LC) devices [14–17]. Bryan–Brown's group reported that vertical alignment of LC molecules can be realized by depositing a kind of chromophore on the groove surface and so on voltage-controlled LC device can be fabricated [16]. In a previous study on LIPS [17], we found that LC molecules showed azimuthal alignment behavior on the LIPS surface. If a PI film doped with lecithin, which has the ability to align LC molecules vertically to the film surface [18], can be used to prepare groove surface (LIPS), it is possible to realize the vertical alignment of LC molecules on groove surface. So the alignment behavior of LC molecules on laser irradiated lecithin-doped PI surface was another part of this report.

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2. Experimental

2.1. Materials

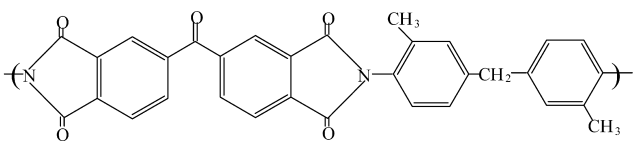
PI was prepared according to the reported method [19]. Its chemical structure is shown in Fig. 1. Lecithin, whose structure was also shown in Fig. 1, was purchased from Yuanju Company, Shanghai. PI dissolved in chloroform (1 wt%) was doped with lecithin at concentrations of 5,10,20 and 30 wt% based on PI, respectively, and then spin-coated onto a clean glass substrate at 1000 rpm. After being dried at 80 °C for 0.5 h and 100 °C for 2 h, films with thickness of about 0.9 μm were obtained according to the results of VASE ellipsometry.

2.2. Generation of LIPS on lecithin-doped PI surface

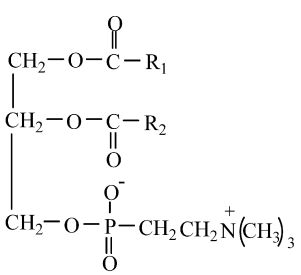
Third ($\lambda = 355$ nm) and fourth ($\lambda = 266$ nm) harmonic frequency of an Nd: YAG laser with Q-factor modulation were used as laser source. The laser pulse length was 6 ns and the frequency was 10 Hz. The laser energy was detected directly by PowerMax 500A. Samples were fixed on an X–Y stage at moving speeds of 0.01 mm/s in *X*-axis direction and 5 mm/s in *Y*-axis direction. The films were exposed in air at an angle of 20° to an unfocused laser beam of about 8 mm in diameter. The incident laser was at S-polarized state. The optical set-up of the preparation of LIPS is shown in Fig. 2. During scanning laser irradiation, the laser shots deposited on the PI film were estimated to be about 10^3 times per square millimeter.

2.3. Characterization of the film surface

Surface topography of laser irradiated PI film was investigated by using AFM (Digital instrument, Nano III) with contact mode. The phase images were detected by using AFM with tapping mode. The contact angle of pure water was recorded on a JC2000A contact angle instrument. All FT-IR measurements were carried out on Equino-55 FT-IR spectrophotometer (Bruker).



(a) PI



(b) Lecithin

Fig. 1. Chemical structures of PI and lecithin.

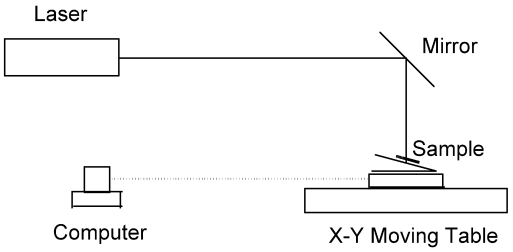


Fig. 2. Optical set-up of LIPS generation.

2.4. Assembly of LC cell

LC cells were assembled by sandwich mode to verify LC alignment behavior. The LC was injected into empty cell by using capillary action under its isotropic temperature. The LC cells were sealed by epoxy resin. Polyethylene film with thickness of 10 μm was used to control the cell space. The alignment behavior of LC molecules was investigated under polarized optical microscopy (POM, LEIKA DMLP).

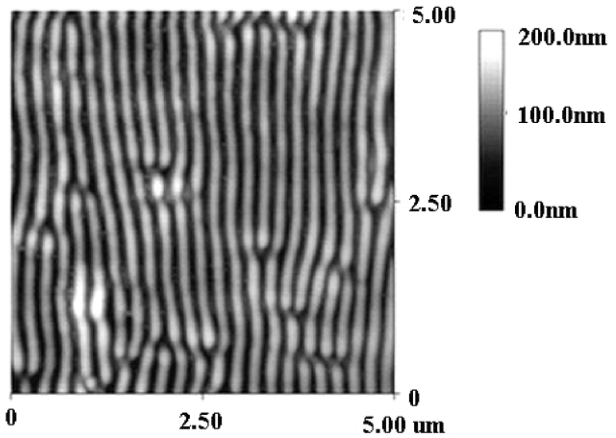
3. Results and discussion

3.1. Doping effect of lecithin on the preparation of LIPS

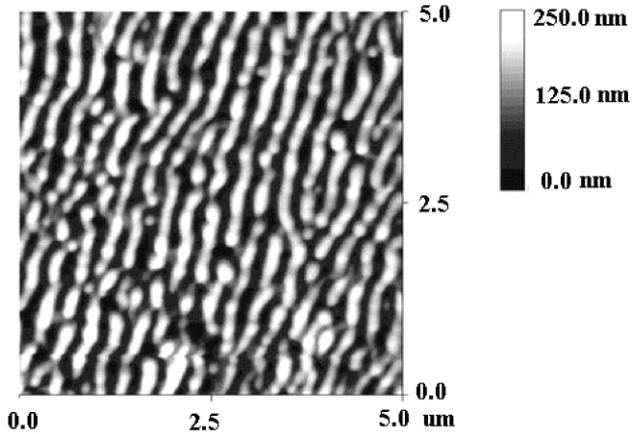
Doping of lecithin into PI film might lead to the phase separation in the film, which leads to the changes of the film surface properties. Phase-mode AFM is a powerful tool to characterize the surface phase separation of a film. Firstly we investigated the surface property of lecithin-doped PI films at the doping level of 5 and 30%, and did not find obvious phase separation between lecithin and PI molecules in the phase AFM images.

3.1.1. Effect of wavelength of incident laser on the preparation of LIPS

A PI film doped with 5 wt% lecithin was used to investigate the effect of the laser wavelength on the LIPS formation. Regular LIPS formed when the film was irradiated at an energy of 1.8 mJ/cm^2 for 266 nm laser (Fig. 3(a)). However, no similar structure was observed for 355 nm laser at such an energy condition. When the laser energy increased to 2.4 mJ/cm^2, irregular LIPS began to appear on the PI film surface (Fig. 3(b)). Generally, the LIPS formation is considered as a thermal physical process induced by laser interference when the energy is below the ablation threshold energy of the material and the absorption of the film to the incident laser is very important for the LIPS formation. The PI and lecithin molecules show strong absorption to the 266 nm laser, which is in favor of LIPS



(a)266nm



(b)355nm

Fig. 3. AFM images of LIPS on lecithin-doped PI surface irradiated by laser with different wavelengths (Lecithin content, 5 wt%). Laser energy: (a) 266 nm, 1.8 mJ/cm^2; (b) 355 nm, 2.4 mJ/cm^2.

formation. However, the absorptive coefficient of PI is rather small and the lecithin molecules show no absorption at 355 nm wavelength, so higher energy is required to prepare LIPS. On the other hand, the irradiation at high laser energy would lead to the decomposition of lecithin molecules. So it is not easy to obtain regular LIPS on the lecithin-doped PI film for 355 nm laser.

In the following discussions, the fourth harmonic frequency of Nd:YAG (266 nm) was used apart from special indication.

3.1.2. Effect of doping level on the generation of LIPS

Fig. 4 is the typical AFM images of LIPS on PI film with different lecithin contents. The PI film showed no LIPS character under laser irradiation at an energy of 1.8 mJ/cm^2 when no lecithin was doped. However, for the doped PI film, regular LIPS was observed on the film at this laser energy and the amplitude of LIPS increased with the increase of the doping level in the range of 0–20 wt%. When the doping level was 30 wt%, the LIPS became irregular and its amplitude decreased (Figs. 4(d) and 5).

The above results led to the conclusion that the doping of lecithin resulted in the decrease in the threshold energy of LIPS formation (It must be pointed out here that the threshold energy in our experiments was obtained under the scanning mode, which was different from that obtained under spot-laser irradiation e.g. literature [20]). The reason for the decrease of threshold energy might lie in the following two aspects: (1) Lecithin molecules might act as the plasticizer to PI molecules, which might lead to the increase in the free volume and the molecular mobility of PI. The increase in PI chain mobility was in favor of the formation of LIPS [21]. (2) Lecithin molecules showed absorption to the incident laser, which promoted the absorption of the film and accelerated the formation of LIPS.

3.1.3. Effect of laser energy on the formation of LIPS

AFM was used to investigate the dependence of the LIPS amplitude on the laser energy. PI film at the doping level of 5 wt% was used as the sample. Fig. 6 is the relationship between the LIPS amplitude and the laser energy. In the range of 1.8–3.8 mJ/cm^2, the amplitude of LIPS increased with the increase of the laser energy. When the laser energy was lower than 1.8 mJ/cm^2 or higher than 4.2 mJ/cm^2, no LIPS character was observed on the lecithin-doped PI surface. Obviously there was threshold energy to generate LIPS structure on the PI surface. When the laser energy was lower than this energy, no LIPS structure was observed on the film surface. However, when the laser energy was higher enough, the irradiation of pulse laser would lead to the ablation of the film. In addition, when the doping level was 30%, the LIPS became inconsistent though similar periodicity still existed on the film surface.

3.1.4. Mechanism of LIPS formation

There were already several models provided to explain the mechanism of LIPS formation such as surface electromagnetic waves [22], surface scattering waves [23] and [24]. But the exact mechanism of the LIPS formation was still not clear so far. For the mechanism of LIPS formation on polymer film, we considered that the phenomenon was related to the interference of the light. When a sample is exposed to a polarized laser beam, the original unevenness of the film will scatter the incident laser. Meanwhile, the surface scattered wave interferes with the incident laser beam, which results in the modulated distribution of the energy on the surface. The region receiving high energy on the surface is heated to a higher temperature greater than T_g of the polymer and the region receiving low energy is much cooler. Then, the molecular

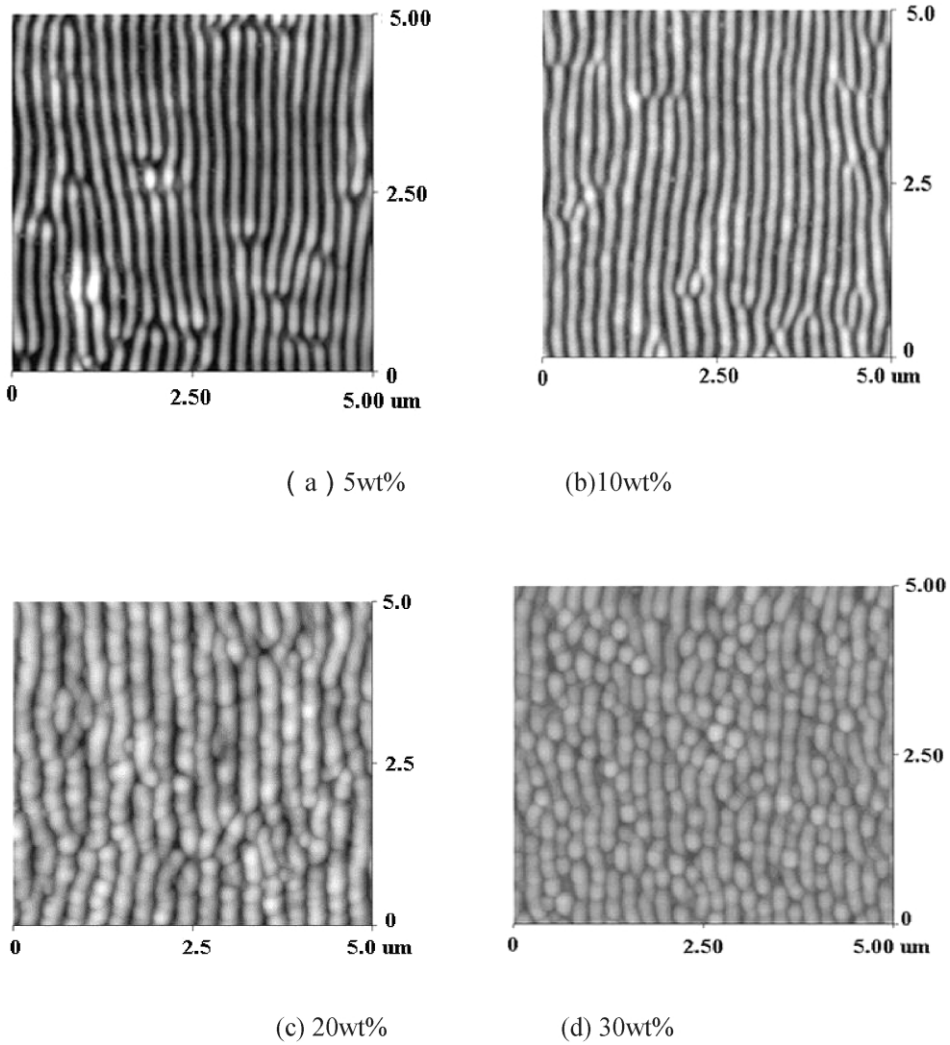


Fig. 4. Typical AFM images of PI surface with different lecithin doping levels (Laser energy, 1.8 mJ/cm^2; wavelength, 266 nm).

chains migrate because of the surface tension during the laser pulse and freeze quickly after the laser pulse. After repeated cycles of heating and cooling, the migration of the molecular chains leads to the formation of LIPS. Simultaneously, during the laser irradiation, we also found that the polymer segments tend to align perpendicular to the surface groove of LIPS under the interaction between the dipole of the polymer molecules and the polarized electric field of the incident laser [25]. In terms of this mechanism, the doping

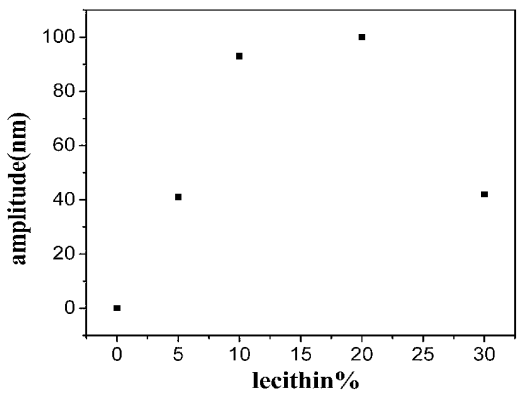


Fig. 5. Relationship between LIPS amplitude and lecithin doping level (Laser energy, 1.8 mJ/cm^2; wavelength, 266 nm).

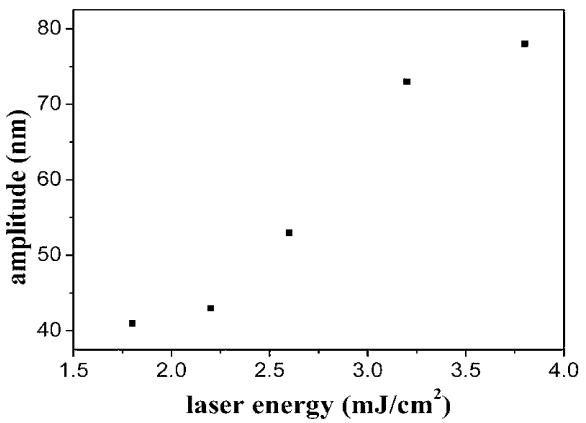


Fig. 6. Relationship between LIPS amplitude and laser energy (Lecithin content, 5 wt%; wavelength, 266 nm).

of lecithin led to not only the increase of the absorption to the incident laser, but also the decrease of T_g of PI film. Both the effects accelerated the LIPS formation on PI film under rather lower energy compared with that on the pure PI film.

3.2. Migration of lecithin molecules in the irradiated PI film

Very high temperature can be achieved on PI film surface during the pulse laser irradiation [26]. Some changes such as decomposition and migration might accompany with the formation of LIPS. FT-IR spectroscopy is an effective tool to characterize chemical structure of organic material, and different modes of FT-IR spectroscopy can be used to characterize the surface and bulk change of a film, respectively. For example, transmission FT-IR can be used to characterize the change in the chemical structure of the bulk film, while the reflective FT-IR can be used to characterize the change of the film surface. The change in the incident angle of IR can lead to the difference in the penetration depth of the IR light, which can be used to characterize the distribution profile of special chemical group along the normal direction of the film. In this work two modes of FT-IR spectroscopy were used to characterize the changes in the lecithin molecules in the laser irradiated PI film: transmission FT-IR, and varied angle reflective FT-IR.

Transmission FT-IR was applied to characterize the change of lecithin molecules in the bulk PI film. When the lecithin-doped film was irradiated at the energy of 1.8 mJ/cm^2, no obvious change was found between the spectra of the lecithin-doped PI film before and after laser irradiation, which indicated that the lecithin molecules did not decompose at this energy condition. However, we found that the film surface became opalescent after the laser irradiation. This might be the result of the migration of lecithin molecules to the surface. For varied angle reflective FT-IR spectroscopy, if we assumed the normal incident angle as 0°, the absorptive spectrum can reflect the information more closely to the film surface with the increase of the reflection angles of the IR light. So varied angle reflective FT-IR was used to characterize the distribution of lecithin along the normal direction of the irradiated film. We investigated the change of the absorptive areas of the O–P–C group at different incident angle of the detective IR light. We used the absorptive band of phenyl group at 1506 cm^{-1} as the inner standard. The absorptive area was estimated according to the following formula:

$$A_{\mathrm{O-P-C},\theta,\mathrm{normalized}} = A_{\mathrm{O-P-C},\theta} \times (A_{\mathrm{phenyl},0^\circ}/A_{\mathrm{phenyl},\theta})$$

Where A_θ is the detective absorptive area of the group band and $A_{\mathrm{normalized}}$ is the normalized absorptive area of the group band. The result is shown in Fig. 7. The absorptive area of O–P–C group increased obviously with the increase of the incident angle of the IR light. The results showed the lecithin molecules tended to rich on the film surface.

The lecithin molecule is highly hydrophilic. By detecting the contact angle of water on the laser irradiated surface, we can further verify the migration of lecithin molecules to the surface. Before laser irradiation, the contact angle of water on the lecithin-doped PI surface was about 65°, after laser irradiation, we found that the contact angle decreased obviously with the increase of laser energy. When the laser energy was about 3.2 mJ/cm^2, the contact angle decreased to about 37°. This result was in good agreement with varied angle reflective FT-IR result.

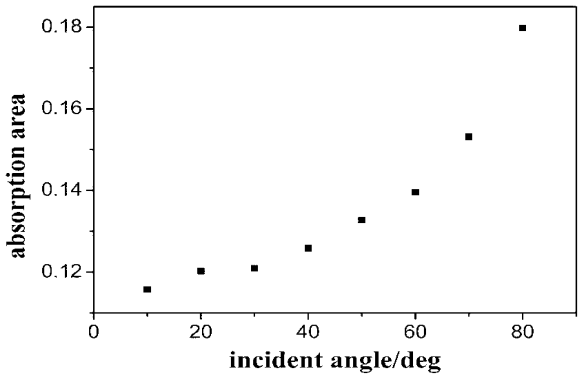
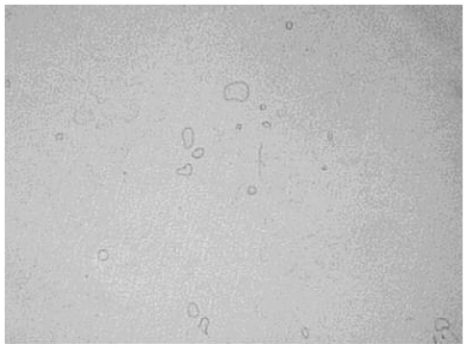


Fig. 7. Relationship between absorbance of O–P–C group and the incident angle in varied angle reflective FT-IR measurement (Laser energy, 1.8 mJ/cm^2; lecithin concentration, 5 wt%; wavelength, 266 nm).

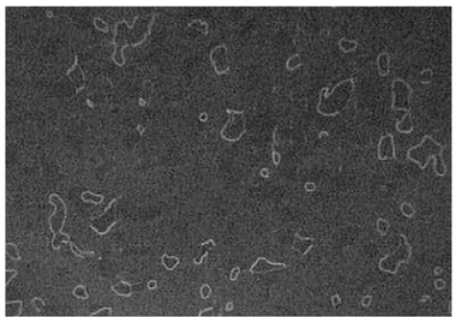
3.3. Alignment of nematic LC molecules on laser irradiated lecithin-doped PI surface

It is well known that LC molecules can show homogenously alignment on groove surface and the directors of LC tend to align along the groove in order to minimize the elastic distortion energy of the LC system. To investigate the alignment behavior of nematic LC molecules on the laser irradiated lecithin-doped PI surface, a series of experiments was carried out by using crossed POM. When the LC molecules align homogeneously on the plane of the film, the light transmittance will be changed alternatively when the LC cell is rotated under crossed POM. However, when the LC molecules align vertically to the surface plane, the light transmittance will be almost blocked by the LC cell.

Fig. 8 is POM images of the LC cell assembled with two irradiated PI films doped with 5 wt% lecithin under crossed POM. The lecithin-doped PI film was irradiated by polarized laser at an energy of 1.8 mJ/cm^2. The LIPS on the two substrates of the LC cell was perpendicular to each other. The light transmittance was changed alternatively when the LC cell was rotated around the normal direction of the LC cell, which indicated that the LC molecules aligned azimuthally on the doped PI film surface. LC cells assembled with irradiated PI films doped with 10 and 20 wt% lecithin were also investigated by using the same method and identical results were obtained. But when the doping level reached 30 wt%, the LC cell showed different alignment behavior. No light transmitted when the LC cell



0° /90°



45°

200μm

Fig. 8. POM images of LC cell with 5 wt%-lecithin-doped PI film (Laser energy, 1.8 mJ/cm^2; wavelength, 266 nm).

was rotated around its normal direction under crossed POM, which indicated that the LC molecules aligned vertically to the substrate surface. According to previous literature [18], the dipole interactions between lecithin molecules and LC molecules drove the LC molecules to align vertically to the surface azimuthal plane.

Electro-optical property of the LC cell assembled with PI at different doping level was detected by using POM. The LC cell was assembled with one mechanically rubbed PI and one laser irradiated lecithin-doped PI film and the rubbing direction was perpendicular to the LIPS direction on lecithin-doped PI surface. It should be pointed out here that different LC molecules for different LC cells were used when the lecithin content was at different doping level. For the cell assembled with PI at a doping level of 5%, electro-positive LC was used (The directors of LC molecules are parallel to the electric field after voltage applied), and for the cell assembled with PI at a doping level of 30%, electro-negative LC was used (The directors of LC molecules are perpendicular to the electric field after voltage applied). All the LC cells were investigated under their normal black condition, which can be realized by changing the relative polarization direction of the polarizers. Fig. 9(a) shows the transmitted intensity versus applied voltage characteristics of the cell with PI film at a doping level of 5%. In this cell

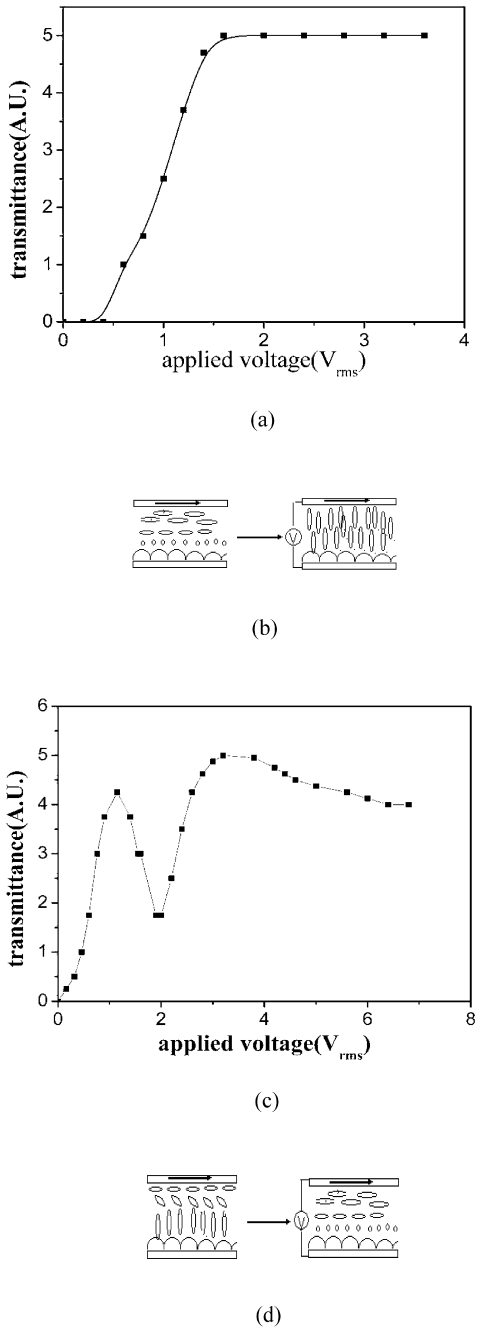


Fig. 9. Electro-optical properties of LC cell with different lecithin contents, (a) and (b) 5%; (c) and (d) 30% (Laser energy, 1.8 mJ/cm^2; wavelength, 266 nm).

the LC directors aligned along the groove on the lecithin-doped PI surface before any voltage was applied, but with the increase of the applied voltage, the directors aligned along the electric field, so the LC cell shows light field under parallel mode POM. The change of the LC arrangement in the cell is shown in Fig. 9(b). The LC cells assembled with PI films at doping levels of 10 and 20 wt% were also investigated by using the same method and identical results were obtained. For the cell with PI at a doping level of 30%, the transmitted intensity versus applied voltage character-

istics was detected under crossed POM and the result is shown in Fig. 9(c). More complex behavior was obtained for this cell. Without any voltage applied, the LC directors on the lecithin-doped LIPS surface aligned vertically to the surface, and almost no light transmitted through the cell under crossed POM. With the increase of applied voltage, the directors of the LC molecules tended to arrange perpendicularly to the electric field and the light transmittance increased with the applied voltage. Simultaneously the light transmittance of the LC cell showed slight vibration at the applied voltage of around 2 V. We repeated this experiment several times and identical results were observed. The vibration of the light transmittance might result from the irregularity of the LIPS or the decrease of the LIPS amplitude on the lecithin-doped PI surface. The exact reason for this vibration would be investigated in the future work. When the applied voltage increased to 4 V the light transmittance increased to a stable value. The arrangement of the LC molecules in the cell after voltage applied is also shown in Fig. 9(d).

4. Conclusions

The effects of doping of lecithin molecules on the preparation of laser induced periodic surface structure were investigated. Lecithin dopant can accelerate the formation of LIPS on PI film surface. Regularity of LIPS was higher when the wavelength of the incident laser was 266 nm compared with that of 355 nm. The amplitude of LIPS increased with the increase of laser energy. After laser irradiation, lecithin molecules tended to migrate to the film surface. The LC molecule aligned azimuthally on the laser irradiated lecithin-doped PI film when the doping level did not exceed 20 wt%. However, the LC molecules tended to align vertically on the laser irradiated lecithin-doped PI film when the doping level was 30 wt%.

Acknowledgements

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