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Alignment of Liquid Crystals on the Polymer Films Made by Pulsed Laser Ablation

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We present the results of observation and study of alignment of liquid crystals on glass substrates deposited with polymers by pulsed laser ablation. Polarizing microscopy is used to observe the alignment of 5CB (nematic) and Nobambc (smectic). Depolarising Raman spectroscopy is used to obtain the order parameter $S(=(1/2)\langle 3\cos^2\theta - 1\rangle)$ of the aligned liquid crystal. S for 5CB is obtained 0.90, therefore, the effect of alignment is significant. Atomic force microscopy (AFM) is used to observe the surface morphology of the polymer films, which are found to be quite flat. Pictures of the depositing process and the aligning process show that dipolar interaction and van der Waals force are responsible for the alignment. This provides a new method to study the mechanisms of the interaction between the molecules of liquid crystals with the solid substrates. The technique is also of interest in the applications to Liquid Crystal Displays.

Keywords: Alignment of liquid crystal; polymer; pulsed laser ablation

Most practical applications of liquid crystals require control of molecular alignment on substrates. It has been known for many years that the surface properties of solid substrates play a very important role in the alignment of liquid crystals. Surface effects in liquid crystal have been studied mostly in nematic liquid crystals. The first reason for this is the simplicity of their structures – the local order aligning molecules parallel to each other can

extend to a macroscopic scale. Second, nematic liquid crystals are used in liquid crystal displays, and the surface properties of the display cells play an essential role in their working process. When the nematic phase is placed in contact with another phase (solid substrate), a surface is created which limits the nematic phase. The molecules of the nematic liquid crystal will interact with the substrate and a layer of liquid crystal molecules is formed. Sometimes the interaction induces the parallel alignment of this layer; othertimes the liquid crystal molecules tend to be aligned perpendicular to the substrate. Due to intermolecular interaction a second layer of molecules is formed, and so on. If the aligning force is strong enough, the bulk of liquid crystal will be aligned. Generally, the alignment of liquid crystals on the substrates must consider: 1) the mechanical interaction relating to the surface topology, such as scratches produced by the buffing process and the topography of the evaporated SiO films, that lead to anisotropic elastic interaction [1–3]. It is proposed that the molecules of liquid crystals will be aligned along the topology to minimize the elastic energy [4]; 2) the physichemical interactions of molecules such as dipolar interaction [5], van der Waals force [6, 7], chemical interaction such as hydrogen bond [6] and other interactions. It seems that the latter interactions have played dominant roles in the alignment of liquid crystals and the former interaction has played an auxiliary role. The alignment of liquid crystals are so complex that the mechanisms of the alignment are not well understood. The alignment of liquid crystal molecules is essential for the liquid crystal display. There are many techniques to achieve the alignment of liquid crystals including rubbing the substrates [8–10], coating the substrates with a coupling agent [11], illuminating the bulk of liquid crystal with an ultraviolet laser beam, or illuminating the polymer substrate then using it to align liquid crystal [12, 13], using LB film technique [14, 15], or other methods [3, 16]. Presently, most widely used method in liquid crystal display is to rub the substrates, deposit a thin film of polymer (such as polyimide) on the glass, rub it, then use the rubbed polymer substrates to align the liquid crystals. It is assumed that the rubbing process will cause the orientation of the molecular chains of polymer materials, and the oriented polymer surface can act to align liquid crystal materials. We know the rubbing process will cause organic pollution and electric damages of liquid crystal. Also, because the rubbing conditions may be different in localized area, they will cause defects in the alignment of liquid crystal moleucles, i.e., the reverse twist and reverse tilt. The former is because the different twist directions will cause stripes in static state; the latter is because the pretilt direction will cause stripes with voltage. In this paper we present a new method to achieve

liquid crystal alignment on macroscopic scale. We used pulsed laser ablation to produce nylon, polymide and polytetrafluoroethylene films, and then used them to align liquid crystals. We also studied the mechanisms of the alignment. In large scale liquid crystal display, this method has some advantages in comparison with those usually used, such as buffing polymide films which helps to avoid the organic pollution and static electric damages in the buffing process. At the same time, it can provide much flatter aligning substrates than the rubbing method.

Laser ablation deposition was used to produce polymer films on glass substrates. The operation scheme is illustrated in Figure 1. The light source consisted of an ultraviolet pulsed laser at 248 nm with 30 ns in pulse width and 3 Hz in pulsed frequency. The incident beams were focused by lens and inside on the target at an angle of 45°. The glass substrate was 3.5 cm apart from the polymer target under room temperature. The laser power strength was kept in the range from 0.24 J/cm^2 to 0.32 J/cm^2. The thin film deposition was carried out at high vaccum of 10^{-7} Torr. The angle between the substrate surface and the stage can be changed from 0° to 45° and was kept at 30° in our experiments. The incident pulsed laser beams caused the target material to evaporate and pour out, then condense on the glass substrate, producing the polymer film. We used the polymer film to make a cell with a space of 10 μm. Liquid crystal (5CB) was put into the cell, the cell placed in an oven, and the 5CB heated to the isotropic phase, then cooled to 25°C. The cell was observed under a Leitz polarizing microscope with azimuthal orientation ψ that can be varied from 0° to 360°. When the stage of the microscope is rotated, the cell becomes bright at 45°, 135°, 225° and 315° respectively, and dark at 0°, 90°, 180° 270° (Fig. 2a). This agrees with the transmittance of a uniaxial birefringent liquid crystal which is parallely aligned by the substrate:

$$T(\psi) = (1/2)\sin^2(2\psi)\sin^2(\pi\delta nd/\lambda) \tag{1}$$

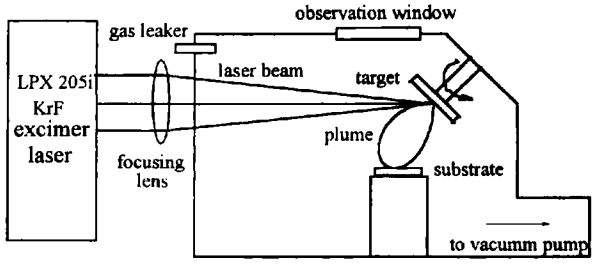
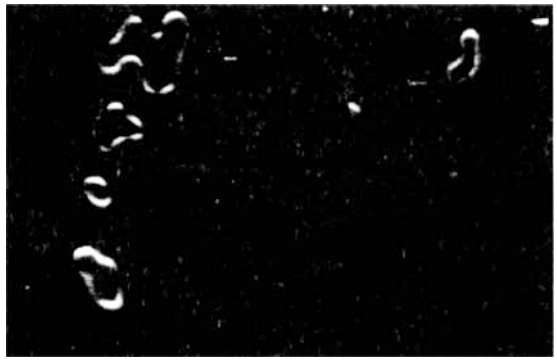
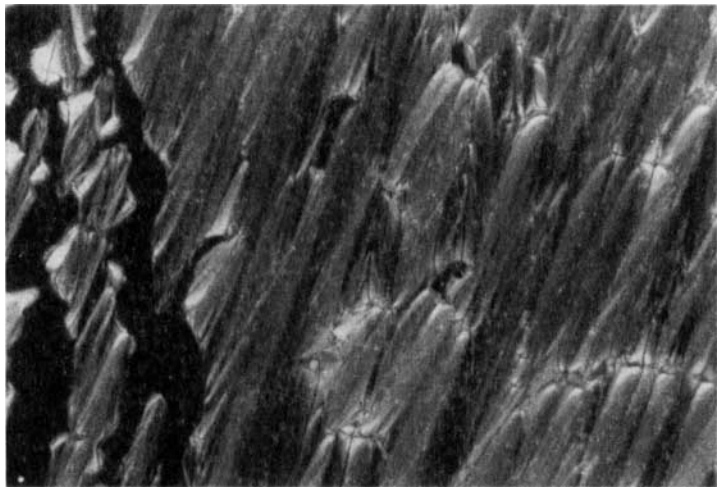


FIGURE 1 The schematic drawing of the pulsed laser ablation system.



(a)



(b)

FIGURE 2 a) A optical micrographic photo of the planar aligned 5 CB on nylon film viewed by polarising Leitz microscope. The pouring direction of the flumes in the depositing process is oriented at 0° with respect to analyzer. The bright points are aligning defects. The magnification is 40. b) A optical micrographic photo of the formation of Nobambc. Nobambc is changing from isotropicphase to smetic phase. (See Color Plate VI).

where δn is the birefringence, λ is the wavelength of the light and d is the cell thickness. The used incident light was bright, so the total transmittance was the average effect of all kinds of wavelengths which shows that the 5CB was in planar alignment.

The aligned effect of liquid crystal can be expressed by the order parameter S: $S = (1/2)\langle 3\cos^2\theta - 1 \rangle$. We have used the depolarising rate of

Raman spectroscopy to obtain S through [17]:

$$\langle \cos^2\theta \rangle = 3\rho_\perp(2\rho_\parallel + 1)/(8\rho_\parallel + 3\rho_\perp + 12\rho_\parallel\rho_\perp) \quad (2)$$

Here $\rho_\parallel$, $\rho_\perp$ is the depolarising rate. In our experiment, a value of 0.90 for S is obtained. The alignment of 5CB is significant.

We also have used nylon film to align smectic liquid crystal Nobambc. Figure 2b is the opitcal micrograph of the aligned Nomabc on the nylon film viewed by the crossed polarizers. The bright area corresponds to the smectic phase and the dark area to the isotropic phase, so the smectic can also be aligned very well.

It has been shown that in the laser ablation the polymer molecules will be decomposited by the laser photons, and even though molecular weight is reduced, the molecules are still very long [18, 19]. In the process of ablation, the polymer material of the target is evaporated under heating of the pulsed laser and the molecules of polymer effuse with high speeds. When they get to the surface of the substrate at high speeds, one end of the molecule will stick to the surface. The friction will reduce its speed but because of the inertia the other end will still move forward quickly. The other point will rotate forward, and finally, the molecule will expand and lay in the surface of the substrates along the O–X direction (Fig. 3). With more and more oriented molecules deposited on the substrate, the oriented nylon film will be produced. Because the polymer deposits on the substrate through a single molecule or mass of several molecules, the film is quite flat. Figure 4 shows the atomic force microscopic (AFM) photo of the morphology of the

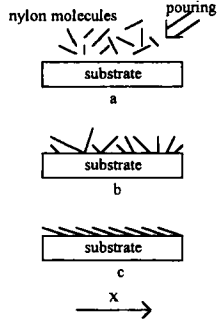


FIGURE 3 The process of the deposition of polymer molecules. The pouring direction is at 45° with respect to analyser. a): the flumes pour out from target. The molecules are disorder; b): molecules begin stick to the glass substrate; c): molecules are oriented on the glass substrate for the effect of inertia.

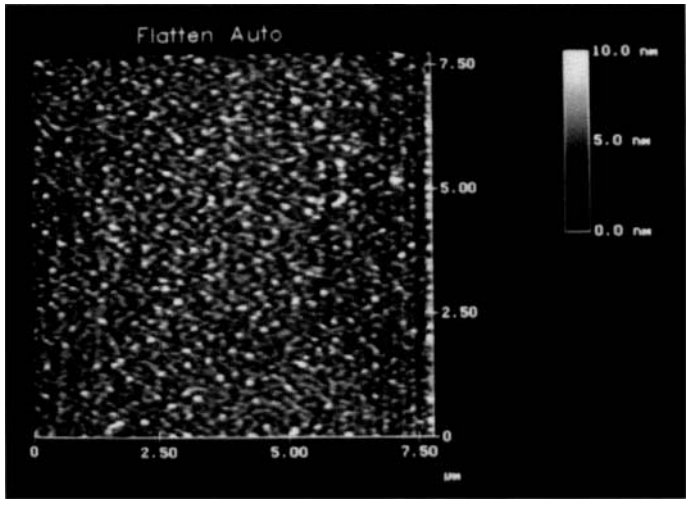


FIGURE 4 A AFM micrographic photo of the surface morphology of the deposited nylon films. (See Color Plate VII).

nylon film produced by pulsed laser ablation. We can see the rough degree is quite small. The quality of film is quite good.

When a cell is made with the deposited polymer film, and some liquid crystal is put into the cell, a surfacial layer will be formed due to interactions between polymer molecules and liquid crystal molecules. The liquid crystal molecules in this layer will be aligned by the dipolar interaction and the Van der Waals force between the molecules of liquid crystal and the polymer molecules. Due to the interactions of liquid crystal molecules, a second aligned layer of molecules will be formed. (Fig. 5). Because the

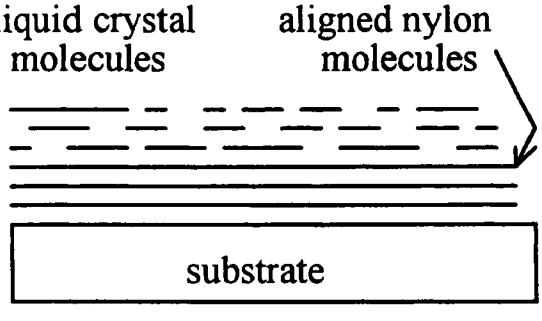


FIGURE 5 The scheme for liquid crystal molecules to be aligned on the oriented molecular chains of polymer films.

aligning force is large, the alignment can expend all the bulk of the liquid crystal, similar to epitaxial growth.

It has been accepted that dipolar interaction and Van der Waals force between the molecules of liquid crystal and the substrate molecules play important roles in the alignment of liquid crystals, such as in the alignment of liquid crystals on L-B films, rubbed polyimide films but few experiments can separate them. In our system, the liquid crystal molecule and the polymer molecule both have dipolar moments; therefore, in the formation of the first layer of liquid crystal, we must consider dipolar interaction and Van der Waals force because they act together. If other materials without dipolar moment are used, such as polyethylene, the dipolar interaction does not occur; only Van der Waals force exists in this case. This provides a method to find whether or not the Van der Waals force has played a dominant role singly in the alignment of liquid crystals. Future study is under way to investigate this property.

In conclusion, we have shown that the ultraviolet laser ablation can be used to deposit polymer films and the film can be used to align liquid crystals. AFM is used to observe the surface morphology of the polymer films. The surface is quite flat. Polarizing microscopy shows that the 5CB and Nobambc are in significant planar alignment on the polymer films which may find important applications in the liquid crystal display. Pictures of the depositing process and the aligning process indicate that the interactions between the substrate molecules and the liquid crystal molecules have played important roles in this respect. This method provides a new way to study the aligning mechanisms of liquid crystals on the substrates.

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