RELATION BETWEEN THE ORIENATIONS OF POLYMER ALIGNMENT LAYER AND LIQUID CRYSTAL MOLECULES

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Effects of surface topology and polymer molecule orientation on the liquid crystal (LC) orientation have been examined using photolithography and Langmuir-Blodgett techniques. It has been clarified that the polymer orientation in the alignment layer affects more effectively than surface topology. UV/Visible spectroscopy has shown that the elevation angle of the polymer main chain in the alignment layer from the substrate plane does not correspond to the LC pretilt angle, which suggests that long alkyl side chains produce high pretilt angle for some polyimides.

1. Introduction

Liquid crystal (LC) materials are successfully used in display devices. Controlling the liquid crystal molecules orientation is quite important for producing good quality LC devices (LCD). A rubbing technique is commonly used to achieve an LC alignment. The substrate surface is rubbed with a cloth or other polishing material prior to introducing the LC material and the director of the liquid crystals aligns along this rubbing direction. The pretilt angle, which is defined as the angle between the LC director and the substrate surface plane, is also an important factor for LCD production. The mechanism how liquid crystal molecules are aligned on the rubbed surface has not been fully understood yet. Both surface topology [1,2] and molecular orientation [3,4,5,6] are discussed to affect the alignment of LCs. In these studies, Langmuir-Blodgett (LB) technique is effectively used to examine the relation between the orientations of the alignment polymer layer and LC molecules [4,5,6]. Factors affecting the pretilt angle are also studied extensively [7,8,9]. Long alkyl chains seem to influence the pretilt angle. Another study shows the asymmetric triangles in polymer backbone generated through the rubbing process plays an important role for giving a pretilt angle [10].

In this paper, I report how LC molecules align 1) on PTFE rubbed surfaces [11], 2) on fine stripe patterns, 3) on highly anisotropic polymer LB films, 4) on the surfaces where fine patterns are fabricated in highly anisotropic polymer LB films such that the groove/ridge direction is oblique to the polymer's main chain direction, 5) on surfaces where highly anisotropic polymer LB films are obliquely deposited with regard to the direction of the fine patterns [12]. I also
report the relation between the LC pretilt angle and the elevation angle of polymer main chain from the substrate surface, where the elevation angle is measured using UV/Vis spectroscopy.

2. Experimental

Chemicals

Chemicals which were used in the experiment are shown in Fig. 1. Nematic liquid crystal material, 4-pentyl-cyclohexyl-4'-cyanobenzene (PCH5), was supplied by E. Merck. Oil red O (1,2,5-dimethyl-4-(2,5-dimethylphenylazo)-phenylazo)-2-naphtol) was purchased from Fluka Chemicals. Polyphthalocyanine and polyglutamate were synthesized and were characterized as published [13,14,15]. High molecular weight polymethylmethacrylate (PMMA) (molecular weight: $9.5 \times 10^5$) was purchased from KTI Chemicals.

A polyimide material which gives a high pretilt angle and has an absorption maximum in the UV region was used for the pretilt angle measurement.

Substrate modification

A glass microscope slide (10mmx25mmx1mm) was used as the substrate. For PTFE rubbing, a substrate was placed on a heater equipped with a sample holder. A PTFE square rod (8mmx8mmx27mm) was contacted to the substrate and rubbed at 1mm/s under 1kg/cm$^2$ pressure while the temperature was maintained at 130°C during the rubbing process. For stripe pattern fabrication, PMMA, which works as a positive deep UV photoresist, was spin-coated onto a substrate from chlorobenzene solution and then baked at 120°C for 30 min. The film thickness was varied by controlling the spinning speed and the solution concentration. UV light (253.7nm) from a low pressure Hg-lamp was used to irradiate the sample through a photomask which had a pattern of 1 μm lines and spacings. An irradiation time of 20 min was sufficient to obtain the desired pattern. The film was developed in a methylisobutylketone and isopropanol 1:2 mixed solution for 1 min and rinsed in isopropanol for 1 min. It was postbaked at 80°C for 30 min. The film thickness was measured using an Alpha-step (Tencor Instruments). Polyglutamate or polyphthalocyanine was deposited using the
LB technique with a Lauda Film Balance. Pure Milli-Q water was used as the subphase. The substrates were treated with a 1:1 hexamethyldisilazane and chloroform mixed solution for a few hours to promote a good film deposition. For polyglutamate deposition, the surface pressure and subphase temperature were maintained at 19 mN/m and at 20°C, respectively. For polyphthalocyanine deposition, they were 25 mN/m and 6°C. Deposition speed was 3.5 mm/min. A Y-type deposition occurred in both cases and the transfer ratio was unity. The anisotropy of the molecular orientation was checked by measuring the dichroic ratio of particular bands in polarized UV/Vis or IR spectra.

The photosensitive polyglutamate used in this work acts as a negative photoresist. Patterns of 1 μm lines and spacings were fabricated in polyglutamate LB films with a photomask in the same way as described for PMMA. The LB film was irradiated with the light of a high pressure Hg-lamp filtered through a UG11 filter (transparency region 250-400nm) for 30 min. The film was developed in a 1:1 chloroform and ethanol mixed solution for 1 min and rinsed in isopropanol for 1 min.

Quartz substrates were used for UV/Vis spectra measurement to check the elevation angle of the polyimide polymer main chain against the substrate surface. Polyimide was spin-coated on the quartz substrate and baked at 200°C for 1 hr.

Liquid crystal cell

An LC cell was fabricated by putting two substrates together in such a way that the two modified surfaces face each other and the rubbing, dipping or stripe directions were parallel for the two substrates. Two thin bands of 7.5 μm-thick Kapton film were used as a spacer. The two substrates were fixed together by an adhesive. The LC was introduced into the cell by capillary action above the clearing point of the LC.

An LC cell for the pretilt angle measurement was fabricated using the quartz substrates coated with polyimide alignment layer whose UV/Vis spectra, and hence, the elevation angle of the polymer main chain had been measured. Normal rubbing technique was applied to the substrates for pretilt angle measurement. The rubbing direction was antiparallel for a pair of the substrates. Polymer sphere spacers with 50 μm diameter were used and the nematic LC material without chirality was introduced to the cell.

Measurement

A Mettler FP82 hot stage, controlled by a Mettler FP80 processor, was used to control the temperature. The temperature was lowered from 2°C above the clearing point to room temperature at a rate of 0.1°C/min. Though PCH5 crystallizes at 30°C, it can be supercooled to room temperature and the experiment was carried out in this supercooled nematic state. The LC texture was observed using a polarizing microscope. The light intensity propagating through the sample cell between two crossed polarizers was measured by a photodiode situated in the image plane of the microscope. Absorption spectra in the UV-Vis region were measured by a Perkin-Elmer Lambda 9 Spectrophotometer or Shimadzu UV 365 Spectrophotometer. Pretilt angles were measured using a crystal rotation method.
3. Results and Discussion

The LC cell prepared with PTFE rubbed substrates showed a homogeneous texture. The light intensity which has passed through a birefringent film between two crossed polarizers is given by Equation 1,

\[ A'^2 = A^2 \sin^2 2\theta \sin^2 \left[ \frac{d(n_1 - n_2)}{\lambda} \right] \]  

where \( A' \) and \( A \) are the amplitudes of the transmitted and incident light, respectively, \( \theta \) is the angle between the polarization vectors of the incident light and the optical axis of the sample film, \( d \) is the film thickness, \( n_1 \) and \( n_2 \) are the ordinary and extraordinary refractive indices of the sample, respectively, and \( \lambda \) is the incident wavelength. If the director of the LC aligns along the rubbing direction, the LC will behave as a uniaxial medium and the transmitted light intensity will follow Equation 1. The transmitted light intensity through the cell is plotted against the angle \( \theta \) between the rubbing direction and the polarization vector of the incident light in Fig.2. Minima occur at \( \theta = 0^\circ, 90^\circ \) and the maxima at \( \theta = 45^\circ, 135^\circ \). This means that the LC molecules align either parallel or perpendicular to the rubbing direction. In order to check the molecular orientation further, the axially extended azo dye, oil red O, was incorporated into PCH5 (1x10^-7 mol%) and the absorption spectra of the cell were measured for polarized light with changing \( \lambda \). The elongated guest dye molecules, whose transition moment is parallel to the long molecule axis, are known to be incorporated parallel to the director of the host LC. Each absorption spectrum shows a maximum at 520 nm. The magnitude of this absorbance at 520 nm is plotted against \( \lambda \) in Fig.2 as well. It is clearly shown in Fig.2 that the LC molecules align along the rubbing direction.

The effect of surface topology on the LC molecule orientation was examined using PMMA stripe patterns. The stripe patterns with 650 Å and 2,000 Å thick films were used. The orientation was checked in the same manner as in the previous case. It has been shown that the LC molecules align along the stripe direction.

For polyphthalocyanine and polyglutamate LB films, their main chains align along the dipping direction [13, 14, 15], which fact was...
checked using polarized UV/Vis and IR spectra. The LC molecules alignment was checked on these LB films and it has been clarified the LC molecules align along the polymer main chain direction even for a monomolecular layer.

It has been found that both stripe patterns and anisotropic LB films induce an orientation of the LC molecules. In order to elucidate which factor is more effective, stripe patterns were fabricated in highly anisotropic polyglutamate LB films in such a way that the polymer main chain direction was tilted by 25° to the stripe direction. A fairly thin (630 Å) polyglutamate LB film were used.

Fig. 3 shows the angular dependence of the polarized light absorption and the transmitted light intensity between crossed polarizers. The absorption maximum occurs at 25° and so does the transmitted light minimum. This result clearly shows that the LC long axis coincides with the polyglutamate helical main chain axis instead of the stripe direction. This suggests that the polymer main chain orientation has a stronger...
effect on the LC alignment than the surface topology. In order to further check the influence of the two factors, a PTFE rubbed surface and a PMMA stripe pattern were covered with a highly oriented polyphthalocyanine LB film whose orientation can be easily checked using UV/Vis spectroscopy. Polyphthalocyanine LB films were deposited on PTFE rubbed glass or on a 2350 Å-thick PMMA stripe pattern of 1 µm lines and spacings. The dipping direction was tilted 25° away from rubbing or stripe direction. The angular dependence of the polarized light absorption of the polyphthalocyanine on the PTFE rubbed surface and on the PMMA stripe pattern is shown in Fig.4 and Fig.5, respectively. Polyphthalocyanine has a transition moment perpendicular to the polymer main chain direction. It is obvious from Fig.4 and Fig.5 that the polyphthalocyanine main chain axis lies at an angle of 25° to the rubbing or stripe direction. The angular dependence of the transmitted light intensity for the PTFE rubbed and polyphthalocyanine LB film modified cell is shown in Fig.4. The angular dependences of the transmitted light intensity and dye absorption for the cell whose surfaces were modified with the PMMA stripe pattern and polyphthalocyanine LB film are shown in Fig.5 as well. Both figures clearly show that the LC molecules align along the dipping direction instead of the rubbing or stripe direction. These results show that the orientation of the polymer molecules in the alignment layer has a greater effect on the LC orientation than a surface topology.

Polyimide which gives high pretilt angle was checked using UV/Vis spectroscopy. This polyimide shows an absorption peak at 245 nm. The intensity of this absorption band for polarized light was examined for various angles. The angular dependence of the absorption in the plane of the substrate shows random orientation of the polymer main chain before rubbing and uniaxial orientation along the rubbing direction after a rubbing process. The strongest absorption was measured for the polarization direction that coincides with the rubbing direction, which means the transition moment of this polyimide lies along the polymer main chain axis. Assuming the polymer main chain, and hence the transition moment, is tilted from the substrate plane at the angle of γ and the film is thin enough to neglect the unaffected homogeneous layers, the
Absorbance (Abs) will be a function of the incident light angle as:

\[ \text{Abs} = k t \cos^2(\theta_\text{inc} - \phi)/\cos \theta \]  

(2)

where \( k \) is a proportionality constant, \( t \) is the film thickness, \( \theta \) is the incident angle and \( \phi \) is the angle of refraction. Thus, \( \text{(Abs)} \times \cos \theta \) has maximum at \( \theta = \phi \). Thus \( \phi \) will be obtained through the refractive index of the film. Such relations are plotted before and after the rubbing treatment in Fig. 6 (a) and (b), respectively. From these figures it is clearly shown that polyimide main chains lie flat on the substrate before rubbing but they incline upward to the rubbing direction with a certain elevation angle. The refractive index of the polyimide for 245 nm was measured to be 1.97 using ellipsometry. The elevation angle, which can be easily deduced from this refractive index, and the LC pretilt angle are listed in Table I. Though the pretilt angle is very large, the elevation angle is not so large. And the pretilt angle becomes very small when the polyimide is immersed in an organic solvent, while the elevation angle does not change so much. From these results, it is concluded that the high pretilt angle of this polyimide alignment layer does not originate from the fact that the polymer main chain is tilted from the substrate plane. The high pretilt angle is possibly due to long alkyl side chains of the polyimide.

![Fig. 6 Angular dependence of polyimide film absorption: (a) before rubbing, (b) after rubbing.](image)

Table I. Relation between elevation angle of the polymer main chain and the liquid crystal pretilt angle.

<table>
<thead>
<tr>
<th>Elevation Angle(°)</th>
<th>Pretilt Angle(°)</th>
<th>Film Thickness(Å)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>11.8</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>2.1</td>
<td>300</td>
<td>Treated with organic solvent</td>
</tr>
</tbody>
</table>
4. Conclusions

The factors affecting the LC molecules orientation have been investigated using photolithography technique and LB technique, together with UV/Vis spectroscopy. It has been clarified that the polymer orientation in the alignment layer affects on the LC alignment more effectively than surface topology. It has also been elucidated that the elevation angle of the polymer main chain in the alignment layer from the substrate plane does not necessarily correlate to the LC pretilt angle and long alkyl side chains can produce high pretilt angle.

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6. References