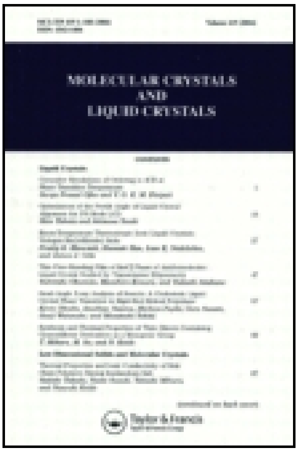

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Comparison of Liquid Crystal Alignments on Rubbed and Linearly Polarized UV-Irradiated Polyimide Surfaces

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Comparison of Liquid Crystal Alignments on Rubbed and Linearly Polarized UV-Irradiated Polyimide Surfaces

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Liquid crystals' surface morphologies, molecular reorientation, alignment, and nematic pretilt angles on polyimide surfaces were studied. The polyimide molecules contained cinnamoyl side groups; they were treated by irradiation with linearly polarized ultraviolet light or rubbing. Root-mean-square surface roughnesses over 1.0 $\mu m \times 1.0$ μm areas were 0.282, 0.260, and 2.073 nm for untreated, irradiated (1.0 J/cm^2), and rubbed (strength, 65 cm) films, respectively. The optical axis of the irradiated film was perpendicular to the light's direction of polarization; in the rubbed film it was parallel to the rubbing direction. Rubbing resulted in higher retardation than irradiation. The orientations of liquid crystal molecules on the films coincided with their polymer chain orientations. Fabricating LC cells with rubbed film resulted in higher pretilt angles than using irradiated film.

Keywords Linearly polarized ultra-violet light; nematic liquid-crystal; polyimide; pretilt angle; rubbing process; surface energy

Introduction

Polyimides (PIs) are used as liquid crystal (LC) alignment layers in liquid crystal displays (LCDs), because of their excellent optical transparency, good chemical stability, adhesion, heat resistance, dimensional stability, and insulation [1–5]. Mechanical rubbing can easily align PI molecules suitable for large-scale production of LCDs [5–8]. Rubbed polyimide films have been studied greatly to elucidate the mechanism of LC molecules' alignment on their surfaces. Rubbing has been shown to generate microgrooves in PI films in the direction of rubbing, LC molecules then preferentially align along the grooves [9–11]. However, near edge X-ray absorption fine structure (NEXAFS) spectroscopy [12,13], surface second-harmonic generation (SHG) [14,15], grazing incidence X-ray scattering (GIXS) [16], and linearly polarized infrared (IR) spectroscopy studies [6,17,18] have further shown that rubbing also aligns the polyimide chain segments in the rubbing direction, which is responsible for the LC alignment.

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LC alignment has been attempted using irradiation to prepare aligned LC layers for LCD devices without rubbing [19–25]. Photo-induced LC alignment using linearly polarized ultraviolet light (LPUVL) can be classified into three types according to the photochemical reaction responsible for the photoalignment [26,27]: first, azobenzene dye containing materials [19,20] that reversibly isomerize between their *trans* and *cis* forms upon irradiation; second, photodegradation by LPUVL [21,22]; and third, materials containing [2+2] photodimerizable moieties, such as cinnamate, styrylpyridine, chalcone, and coumarin [2–4,23–25].

The mechanisms of irradiation- and rubbing-induced alignment of the main chains and the side groups of polymers with photodimerizable moieties and the alignment behavior of LCs on these films are not fully understood and require further study, the subject of this work. The LC alignment is believed to depend on the competition of various physical and chemical interactions between the LC molecules and the LC alignment layer surface, it is very important to determine the role of surface anisotropy and morphology in LC alignment [33]. In this work, the polymer chain reorientation and morphology of the PI films with LPUVL treatment and rubbing treatment were investigated by photoelastic modulator (PEM) and atomic force microscope (AFM), respectively. In addition, the alignments of LC molecules on the films were also studied. How the treatments affected the films' surface morphologies and pretilt angles of LCs in LC cells fabricated using the films are discussed.

Experimental

Film Preparation

1.0 wt.% 6F-C3-CI PI (Fig. 1) in tetrahydrofuran was filtered (0.45 μm pore size, PEFE membrane syringe filter) and spin-coated onto substrates at 2500 rpm, giving films 120 nm thick. The spin-coated films were then dried in a vacuum chamber at 60°C for 1 h and at 120°C for 10 h. Silicon wafer and indium tin oxide (ITO) glass substrates were used for AFM measurements and for film retardation measurements and LC cell assembly, respectively. Films' thicknesses were measured by ellipsometery (model VASE, Woollam, USA). Irradiation with linearly polarized ultra-violet light (LPUVL, 3.0 mW/cm^2) was conducted using a linear dichroic polarizer (Oriel) in a high-pressure Hg lamp system (2.0 kW, model UVE-2001S, SAN-EI electroric, Japan) equipped with an optical filter (Milles Griot), which transmitted a band beam of wavelengths 260–380 nm. Irradiation was

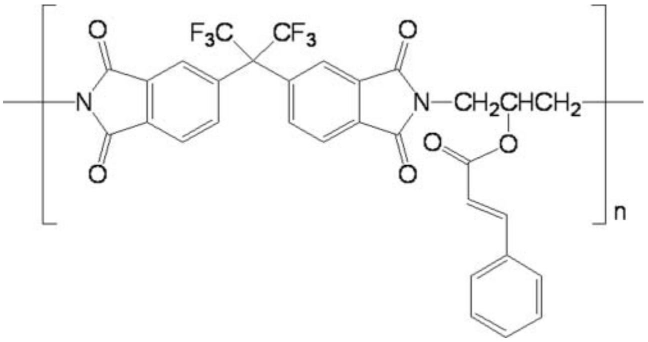

Figure 1. 6F-C3-CI polyimide.

conducted under vacuum. The films used in LC cells were irradiated at a tilt angle, i.e. the angle between the plane of the film and the propagation plane of the light, of 45°. Exposure was measured using an photometer (model IL-1350, International Light, USA) fitted with a sensor (model SED-240, International Light). Films were rubbed using a laboratory rubbing machine (Wande Company) with a rayon velvet-coated roller (Yoshikawa Company, YA-20-R). The rubbing strength (L) was varied by changing the cumulative rubbing time to achieve a constant rubbing depth of 0.15 mm: $L = Nl[(2\pi rn/60v)\text{-}1]$, where L is the total length of the rubbing cloth contacting a certain point of the polymer film (mm), l is the contact length of the circumference of the rubbing roller (mm), N is the cumulative number of rubbings, n and r are the speed (rpm) and the radius (cm) of the rubbing roller, respectively, and v is the velocity (cm/s) of the substrate stage.

LC Cell Fabrication

6F-C3-CI PI solution was spin-cast onto ITO glass substrates for optical retardation measurements and LC cell assembly. LC cells were prepared by adhering two pieces of polymer film to ITO glass slides. These were then rubbed or irradiated and assembled together anti-parallel to each other along the longer axis of the ITO glass slide. For polar anchoring energy measurements, 50 μm separation was maintained between the LC cells. The assembled LC cells were filled with 4-pentyl-4-biphenylcarbonitrile (5CB, Aldrich, USA). The cells were determined to be homogeneous throughout by optical microscopy. Linearly polarized light absorption was used to measure LC director orientation. A nematic LC (5CB), containing 1.0 wt% Disperse Blue 1 (Aldrich) dichroic dye, was injected into the cell and the injection hole was sealed with an epoxy glue, giving antiparallel nematic LC cells.

Measurements

Surface images were obtained using a tapping mode atomic force microscope (Digital Instruments, mode Multimode AFM Nanoscope IIIa). An ultralever cantilever (26 N/m spring constant and 268 kHz resonance frequency) was used for scanning. Films' optical phase retardation was measured using an optical setup described elsewhere [28]. The linearly polarized He–Ne laser beam (632.8 nm) was incident normal to the surface of the film, and the transmitted light intensity was monitored with respect to the angle of rotation of the film from the surface normal. LC alignment was characterized from the absorption of the laser beam, allowing polar diagrams to be constructed. The LC cell was perpendicular to the incident laser beam during measurement. The LC molecules' pretilt angles were measured using crystal rotation apparatus. Their alignments were also measured by ellipsometry, which determined the direction of the LC directors in the anti-parallel cells in transmission mode. The anisotropic ellipsometry data were fitted with respect to the in-plane Euler angle [29].

Results and Discussion

Atomic force microscopy (AFM) showed that the untreated 6F-C3-CI PI film had a 0.282 nm root-mean-square (rms) surface roughness over a 1.0 μm × 1.0 μm area (Fig. 2(a)). Exposure to 1.0 J/cm^2 LPUVL decreased this to 0.260 nm (Fig. 2(b)). Rubbing polymer film generally results in scratches and grooves on a scale of tens to hundreds of nanometer in the rubbing direction [6]. However, the representative 65 cm-rubbed 6F-C3-CI PI film did not show grooves and its rms surface roughness was 2.073 nm (Fig. 2(c)). The variation of the

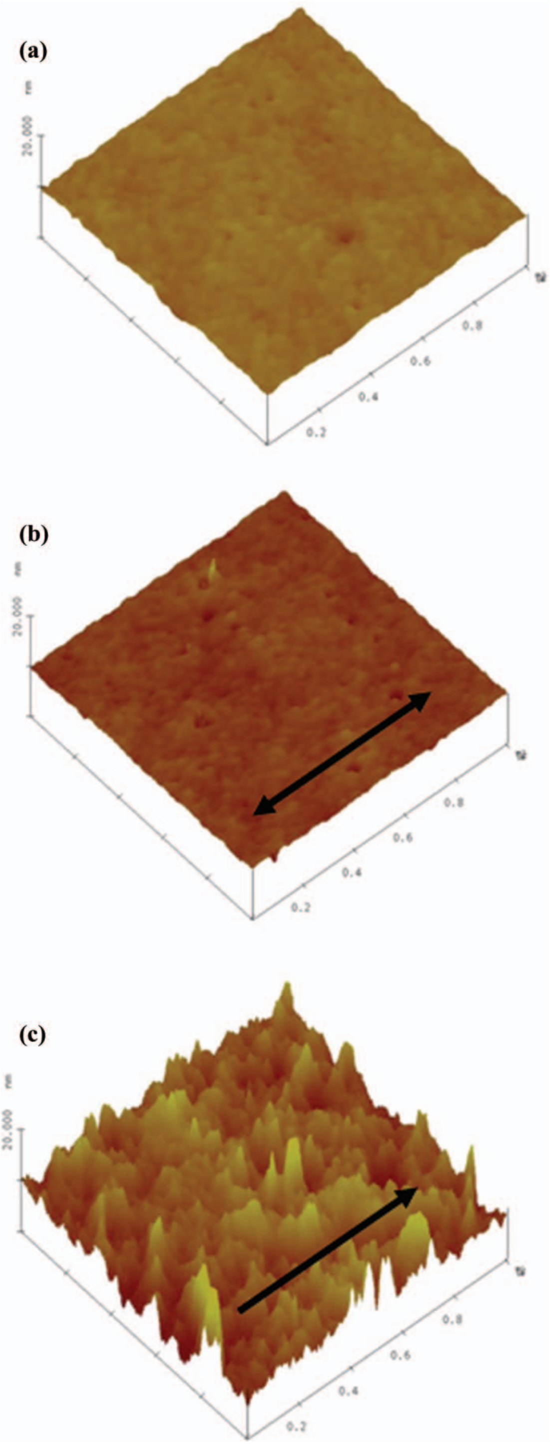

Figure 2. AFM images of 6F-C3-CI PI films: (a) untreated, (b) LPUVL-irradiated at 1.0 J/cm^2, and (c) rubbed with a rubbing strength parameter of 65 cm. The arrow indicates the directions of LPUVL polarization and rubbing.

rubbed films' surface morphologies likely arose from their different deformation responses to the shear forces produced by contact with the fibers of the velvet fabric during rubbing.

Films' optical phase retardation was measured at 632.8 nm with respect to the angle of rotation of their surfaces by PEM. The polymer chain alignment direction and optical retardation value in the film plane of rubbed PI film and LPUVL exposed PI film can be determined from PEM experiment. The unrubbed PI film reveals no optical phase retardation dependence with respect to the angle of rotation, indicating that the unrubbed PI film is isotropic in the film plane. In contrast, the 65 cm-rubbed film's polar diagram of transmittance [= (birefringence)×(phase)] with respect to its angle of rotation shows that it exhibited maximum transmittance in the direction 0°↔180°, i.e. parallel to the rubbing, and minimum transmittance in the direction 90°↔270°, i.e. perpendicular to the rubbing (Fig. 3(a)). The polar diagrams confirm that rubbing aligned the main directors of the 6F-C3-CI PI chains in the direction of the rubbing regardless of rubbing strength [6]. Optical retardation along the main director of the polar transmittance diagram was determined for the variously rubbed samples. Retardation rapidly increased with rubbing strength up to *ca.* 20 cm and leveled off with stronger rubbing (Fig. 3(b)).

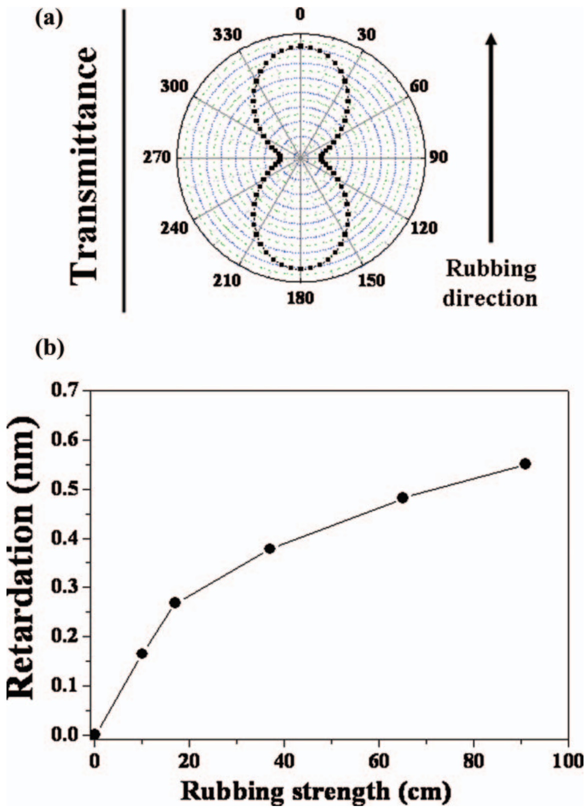

Figure 3. (a) Polar diagram of transmitted light intensity (=(in-plane birefringence) × (phase)) as a function of the angle of film rotation. Data are from optical phase-retardation measurements of 65 cm-rubbed 6F-C3-CI PI film. (b) Optical retardation (=(in-plane birefringence) × (thickness)) of variously rubbed films.

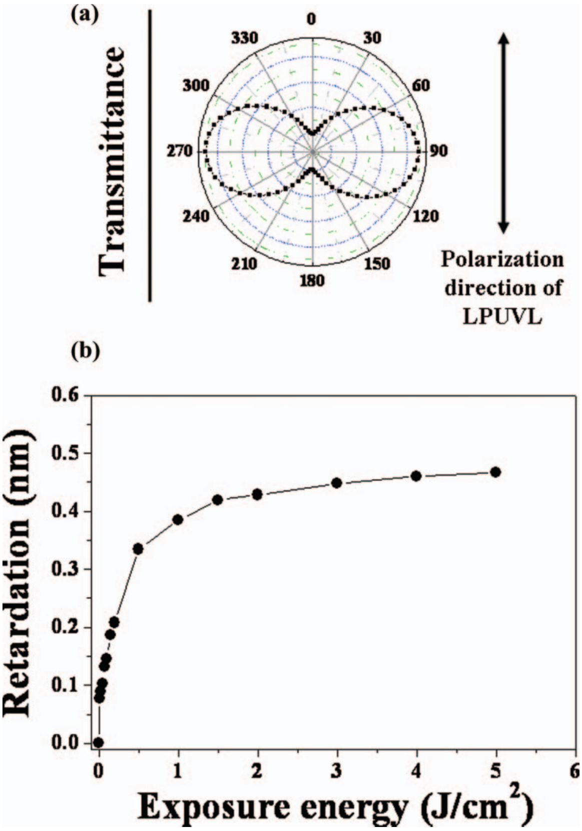

Figure 4. (a) Polar diagram of transmitted light intensity (=(in-plane birefringence) × (phase)) as a function of the angle of film rotation. Data are from optical phase-retardation measurements of 1.0 J/cm2-irradiated film. (b) Optical retardation (=(in-plane birefringence) × (thickness)) of variously irradiated films.

In addition, optical phase retardation of LPUVL treated PI films was measured. The untreated PI film shows no optical phase retardation dependence as a function of rotation angle, indicating that the untreated PI film is isotropic in the film plane. However, the polar diagram of transmittance with respect to the angle of rotation of the film irradiated with 1.0 J/cm^2 LPUVL shows that the film's optical axis was in the 90°↔270° direction, i.e. perpendicular to the light's polarization (0°↔180°) (Fig. 4(a)). Here, the optical axis represents the orientation of high electron density, meaning that the direction of high-electron density segments of the polymers, i.e. main and side chains, was along the optical axis of the film's plane. This perpendicular polar diagram may be due to unreacted side groups and reoriented polymer main chains in the film [2–4]. Generally, the main reaction of polymers with cinnamoyl derivative side groups upon UV irradiation is [2+2] photodimerization in the solid film state. The directional photo-reaction of the cinnamoyl moieties led to unreacted cinnamoyl moieties in the films remaining perpendicular to the light's polarization. Main chains also partially reoriented to be perpendicular to the light's polarization [2–4,28]. Retardation rapidly increased with increasing exposure energy up to *ca.* 0.2 J/cm^2, decreased slowly upon subsequent increases to 3.0 J/cm^2, and then leveled off with further

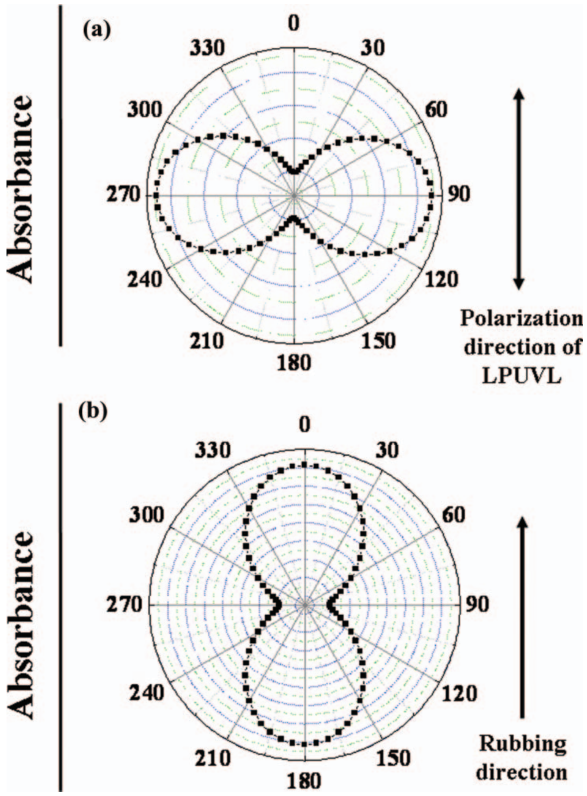

Figure 5. Polar diagrams of absorption measured from anti-parallel LC cells incorporating various 6F-C3-CI PI films with respect to the cells' angle of rotation. Films were (a) 1.0 J/m^2-irradiated and (b) 65 cm-rubbed.

increases (Fig. 4(b)). This indicates that the preferential orientation of the polymer chains was induced by LPUVL only at 0.2 J/cm^2.

In order to investigate the LC alignment on the PI alignment layer, LC cells were prepared from untreated, rubbed and LPUVL exposed PI films. The LC cell assembled from untreated PI film did not show homogeneous LC alignment. However, the LC cells incorporating rubbed or irradiated films were stable and homogeneous throughout. All the anti-parallel LC cells fabricated with irradiated films showed polar diagrams of optical phase retardation with respect to their angle of rotation similar to that of the cell incorporating film irradiated at 1.0 J/cm^2 (Fig. 5(a)). This cell showed maximum absorption perpendicular to the irradiation polarization, coincident with the film's radiation-induced in-plane optical axis (Fig. 4(a)). This indicates that the irradiation-aligned polymer chains induced homogeneous LC alignment in the direction of their orientation, regardless of the chromophore moieties. The representative LC cell incorporating 65 cm-rubbed film exhibited maximum absorption in the direction 0°↔180°, i.e. parallel to the rubbing (Fig. 4(b)). The anisotropy of the polar diagram indicates that the LC molecules in contact with the rubbed surface were homogeneously aligned in the direction of rubbing. The rubbed film showed only small sub-micron scale grooves in AFM image, rather than the commonly observed sub-micrometer-sized grooves, however its LC alignment was homogenous and

Table 1. Dispersion force ratio (surface energy) of 6F-C3-CI PI films' surfaces and LCs' pretilt angles in LC cells

Untreated γ_s^D/γ_s (%)[a]	Rubbing γ_s^D/γ_s (%)	LPUV γ_s^D/γ_s (%)	Rubbing θ_P[b]	LPUV θ_P
93.1	95.1	90.9	3.6°	0.6°

stable. This implies that anisotropic chemical interactions between the aligned surface and the liquid crystal molecules were dominant in these samples, i.e. LC molecules were more likely to be aligned through interactions with the polymer chain segments than by the microgrooves.

The LC molecules' pretilt angles in the LC cells were assessed through crystal rotation and magnetic field measurements (Table 1). LC pretilt angles (θ_p) of 3.6° and 0.6° were respectively observed in the cells incorporating 65 cm-rubbed and 1.0 J/cm^2-irradiated films. Pretilt angle depended on side chain structure.

The relationship between surface energy and pretilt angle was investigated through measuring static water and diiodomethane contact angles on the various films' surfaces. Total surface energy (γ_s) was calculated by summing the dispersion (γ_s^D) and the polar (γ_s^P) force components by the sessil-drop method. The dispersion force ratio of the rubbed film was higher than that of the irradiated film. These results are related to the films' surface roughnesses. Previous work has reported that hydrophobic surfaces show higher pretilt angles than hydrophilic surfaces [30–32]. Therefore, the dispersion force ratio (γ_s^D/γ_s) of the polymer film surfaces was related to the LCs' pretilt angles.

Conclusions

Untreated and irradiated 6F-C3-CI PI films showed relatively smooth and clean surfaces with respective rms roughnesses over 1.0 μm × 1.0 μm areas of 0.282 and 0.260 nm. Rubbing increased surface roughness. The optical axis of the irradiated film was perpendicular to the polarization of the irradiation (90°); that of the rubbed film was parallel to the rubbing. The rubbed films showed higher retardation than the irradiated films. Anti-parallel LC cells fabricated with irradiated film had the main directors of the LCs oriented perpendicular to the irradiation's polarization. Cells incorporating rubbed film had LCs' main directors aligned in the rubbing direction. The LCs' orientations were coincident with those of the films' polymer chains. Cells with rubbed films showed higher pretilt angles than than those with irradiated films. These results indicate that pretilt angle is related to the surface energy of the film, which in turn depends upon the surface treatment.

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