Unusual Alignment of Liquid Crystals on Rubbed Films of Polyimides with Fluorenyl Side Groups

Suk Gyu Hahm,[†,‡,§,⊥,||] **Taek Joon Lee,**[†,‡,§,⊥,||] **Taihyun Chang,**[†,‡,§,⊥,||] **Jin Chul Jung,**[†,#]
Wang-Cheol Zin,[†,#] **and Moonhor Ree***[,†,‡,§,⊥,||]

Polymer Research Institute, Department of Chemistry, National Research Lab for Polymer Synthesis & Physics, Center for Integrated Molecular Systems, BK School of Molecular Science, and Department of Materials Science & Engineering, Pohang University of Science & Technology (Postech), Pohang 790-784, Republic of Korea

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ABSTRACT: We synthesized two polyimides (PIs), poly(4,4′-(9,9-fluorenyl)diphenylene cyclobutanyltetracarboximide) (CBDA-FDA) and poly(4,4′-(9,9-fluorenyl)diphenylene pyromellitimide) (PMDA-FDA), and investigated in detail the surface morphology, molecular orientation, and nematic liquid crystal (LC) alignments of rubbed CBDA-FDA and PMDA-FDA films. The rubbed CBDA-FDA film surface was found to contain microgrooves that run parallel to the rubbing direction, but was found to induce LC alignment perpendicular to the rubbing direction. In contrast, the rubbed PMDA-FDA film surface was found to contain unusual meandering microgrooves that run perpendicular to the rubbing direction; this is the first report of such structures on a rubbed PI film. The PMDA-FDA film surface was found to induce LC alignment parallel to the rubbing direction. Even though these two PI films have quite different groove structures and LC alignment behaviors, the polymer main chains in their surfaces lie in the film plane and are preferentially oriented along the rubbing direction, and the fluorenyl side groups lie in the out-of-plane and are preferentially oriented perpendicular to the rubbing direction. These LC alignment, anchoring energy, surface morphology, and polymer segmental orientation results indicate that LC alignments on the surfaces of rubbed PI films are determined by the interplay between the directionally anisotropic interactions of the LC molecules with the oriented polymer main chain segments, the oriented fluorenyl side groups, and the microgrooves. The directionally anisotropic interactions of the LC molecules with the oriented polymer chain segments were found to be much stronger than those with the directionally developed microgrooves. We conclude that CBDA-FDA and PMDA-FDA PIs are promising alignment layer materials for the fabrication of advanced LC display devices.

Introduction

Polyimides (PIs) have been widely used in the microelectronics industry as dielectric materials because of their advantageous properties, including their excellent optical transparency, adhesion, heat resistance, dimensional stability, mechanical and dielectric properties, and adhesion.[1,2] One of the most recently developed applications of PIs is their use as liquid crystal (LC) alignment layers for flat-panel LC display (LCD) devices.[3−8] Such PI film surfaces need to be treated if they are to produce uniform alignments of LC molecules.[3−8] A rubbing process using a velvet fabric is currently the only technique adopted in the LCD industry for treating PI film surfaces in the mass-production of flat-panel LCD devices. This process has become the method of choice because of its simplicity and the control with this method of both the LC anchoring energy and the pretilt angle.[3−8] The rubbing of all PI films reported so far has been found to create microgrooves along the rubbing direction and to orient polymer main chains along the rubbing direction.[3−8] For most rubbed PI films, the unidirectional microgrooves and oriented polymer main chains cooperatively align LC molecules along the rubbing direction because of their anisotropic interactions with the LC molecules.[3−6] However, in two cases, the rubbed films of PIs have been found to align LCs perpendicular to the rubbing direction.[7,8] The first case is a series of poly(*p*-phenylene 3,6-bis(4-(*n*-alkyloxy)phenyloxy)pyromellitimide)s (Cn-PMDA-PDA PIs) in which the *n*-alkyloxy group has ≤7 carbons; the mechanism of their perpendicular LC alignment was recently investigated in detail.[7] The second case is poly(4,4′-(9,9-fluorenyl)diphenylene cyclobutanyltetracarboximide) (CBDA-FDA).[8] Despite the interesting perpendicular LC alignment behavior of rubbed films of this PI, the LC alignment mechanism has not yet been determined. If the exact mechanism of such an unusual LC alignment is to be found, the rubbing-induced orientations of all CBDA-FDA chain segments and the rubbed film surface morphology must be quantitatively and comprehensively investigated.

In the present study, we synthesized CBDA-FDA and its analogue, poly(4,4′-(9,9-fluorenyl)diphenylene pyromellitimide) (PMDA-FDA) (Figure 1), and then investigated quantitatively the orientational distributions of the polymer chain segments in the surfaces of their films by using linearly polarized Fourier transform infrared (FTIR) spectroscopy and optical retardation analysis. We also examined the films' surface topographies using high spatial resolution atomic force microscopy (AFM). Further, rubbed films were used to assemble antiparallel and 90°-twisted nematic (TN) LC cells, and the alignment behaviors, pretilt

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* To whom all correspondence should be addressed. Telephone: +82−54−279−2120. Fax: +82−54−279−3399. E-mail: ree@postech.edu.

[†] Polymer Research Institute, Pohang University of Science & Technology (Postech).

[‡] Department of Chemistry, Pohang University of Science & Technology (Postech).

[§] National Research Lab for Polymer Synthesis & Physics, Pohang University of Science & Technology (Postech).

[⊥] Center for Integrated Molecular Systems, Pohang University of Science & Technology (Postech).

[||] BK School of Molecular Science, Pohang University of Science & Technology (Postech).

[#] Department of Materials Science & Engineering, Pohang University of Science & Technology (Postech).

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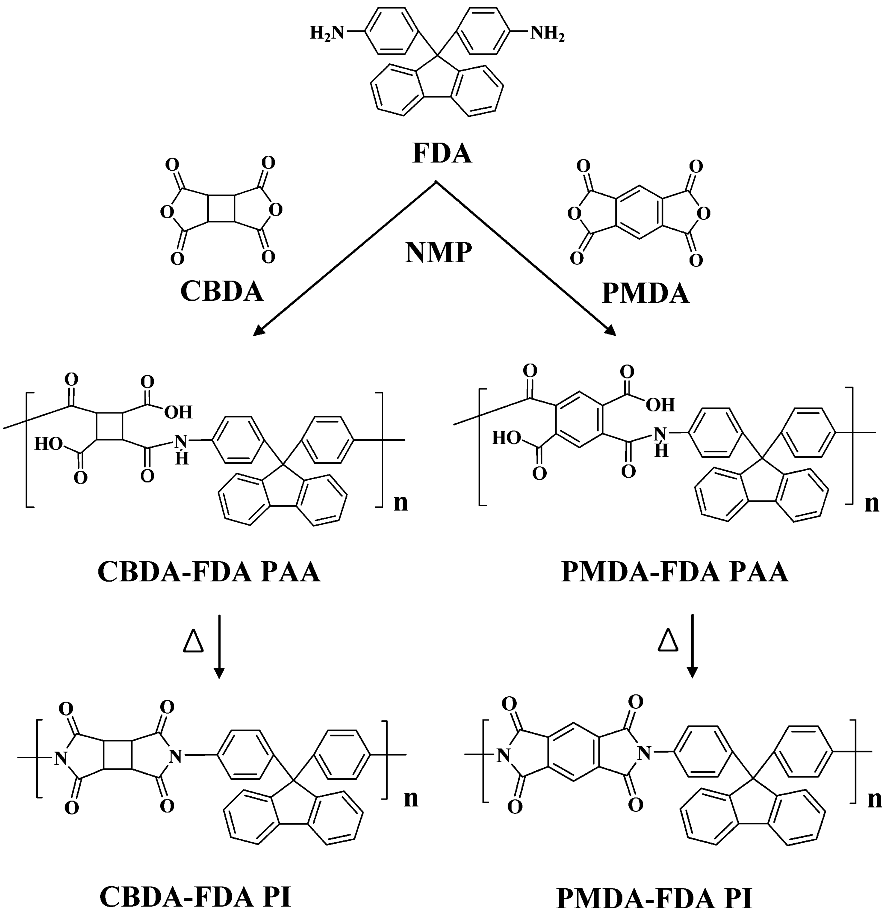

Figure 1. Synthetic scheme and chemical structures of polyimides (PIs) with fluorenyl side groups: CBDA-FDA PI and PMDA-FDA PI.

angles, and anchoring energies of the LC molecules in the cells were determined. The films were found to have very interesting surface morphologies and LC alignment behaviors, which have not previously been reported. The observed LC alignments, pretilt angles and anchoring energies are discussed by taking into account the interactions of the LC molecules with the oriented polymer chain segments and the surface morphologies.

Experimental Section

Materials and Polymer Synthesis. Pyromellitic dianhydride (PMDA), which was purchased from Chriskev Company, was purified by recrystallization from acetic anhydride and subsequent drying under reduced pressure. In the same manner, cyclobutanyltetracarboxylic anhydride (CBDA), which was purchased from Aldrich Company, was purified. 9,9′-Bis(4-aminophenyl)fluorene (FDA), obtained from Aldrich Company, was purified by sublimation under reduced pressure. *N*-Methyl-2-pyrrolidinone (NMP) was purchased from Aldrich and purified by distillation over calcium hydride under reduced pressure.

Poly(4,4′-(9,9-fluorenyl)diphenylene cyclobutanyltetracarboxamic acid) (CBDA-FDA PAA), a poly(amic acid) (PAA) was prepared in a round-bottom flask filled with dry nitrogen gas by slowly adding the equivalent mol of CBDA into the FDA dissolved in dry NMP by stirring vigorously (Figure 1). Once the CBDA addition was complete, the reaction flask was sealed tightly and stirring was continued for 2 days to make the polymerization mixture completely homogeneous. In the same manner, poly(4,4′-(9,9-fluorenyl)diphenylene pyromellitamic acid) (PMDA-FDA PAA) was prepared in NMP from PMDA and FDA monomer (Figure 1). Solid contents of the synthesized PAA solutions were 10% (w/v). Each PAA solution was filtered with PTFE membranes of 1.0 μm pore size. For the synthesized PAA precursors, inherent viscosity measurements were performed at a concentration of 0.1 g/dL in NMP at 25.0 °C: 0.98 for CBDA-FDA PAA and 0.96 for PMDA-FDA PAA.

PI Films and LC Cell Preparation. Each PAA solution was diluted to 2% (w/v) with dried NMP and then the diluted PAA solution was spin-coated onto NaCl windows for transmittance FTIR spectra, gold-coated silicon substrates for external reflection FTIR spectra, silicone substrates for AFM images, and indium tin oxide (ITO) glass substrates for optical retardations and LC cell assemblies, followed by drying on a hot plate at 80 °C for 1 h. The dried PAA films were thermally imidized in an oven with a dry nitrogen gas flow by a three-step imidization protocol: 150 °C/60 min, 200 °C/60 min, and 250 °C/120 min with a ramping rate of 2.0 °C/min. After the thermal imidization, the samples were cooled to room temperature with a rate of 10 °C/min. The resulting PI films were measured to have a thickness of around 100 nm, using a spectroscopic ellipsometer (model M2000, J. A. Woollam) and an α-stepper (model Tektak3, Veeco). The PI films coated onto the substrates were rubbed at various rubbing strength parameters using a laboratory rubbing machine (Wande) with a roller covered with a rayon velvet fabric (model YA-20-R, Yoshikawa, Japan). The rubbing strength parameter L was varied by changing the cumulative rubbing time for a constant rubbing depth, 0.25 mm: $L = Nl[(2\pi nr/60v) - 1]$ where L is the total length of the rubbing cloth which contacts a certain point of the polymer film, l is the contact length of circumference of rubbing roller which varies with the rubbing depth, N is the cumulative number of rubbings, n and r are the speed (rpm) of and the radius of rubbing roller, respectively, and v is the velocity (cm/s) of the substrate stage.

Some of the rubbed PI films on glass substrates were cut into 2.5 cm × 2.5 cm pieces and then used for assembling two different LC cells as follows. First, paired pieces cut from each glass substrate were assembled together antiparallel with respect to the rubbing direction by using 50 μm thick spacers, injected with a nematic LC, 4-*n*-pentyl-4′-cyanobiphenyl (5CB) [n_e(extraordinary refractive index) = 1.717 and n_o(ordinary refractive index) = 1.53] containing 1.0 wt % Disperse Blue 1 as a dichroic dye, and then sealed with an epoxy glue, giving antiparallel nematic LC cells. Second, paired pieces from each glass substrate were assembled together orthogonal to the rubbing direction by using silica balls of 4.0 μm diameter as spacers, injected with the LC and then sealed with an epoxy glue, giving 90°-twisted nematic LC cells (TN LC cells). All the prepared LC cells were found to be uniform and homogeneous throughout by optical microscopy.

Measurements. The surface morphology of the PI films was measured before and after rubbing, using an atomic force microscope (Digital Instruments, model Multimode AFM Nanoscope IIIa) in contact mode. The film surface was scanned using an ultralever cantilever (with a 26 N/m spring constant and 268 kHz resonance frequency). Image processing and data analysis were performed using a software program provided by Digital Instruments. Optical phase retardations were measured using an optical set up equipped with either a photoelastic modulator (model PEM90, Hinds Instruments) with a fused silica head or a quarter plate (Oriel). The optical phase retardation measurements were calibrated with a $\lambda/30$ plate standard [Wave plate zero order $\lambda/30$ ($\lambda = 632.8$ nm), Altechna]; λ is the wavelength of a laser light source. Samples were installed perpendicular to the incident beam direction. Optical phase retardations were measured as a function of the angle of rotation of the samples. Transmitted FTIR spectroscopic measurements were carried out on a Bomem DA8 FTIR spectrometer equipped with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector and a single diamond polarizer (Harrick Scientific). Samples were installed perpendicular to the incident beam direction. While rotating the polarizer, IR spectra were recorded at a resolution of 4 cm^{-1} under vacuum as a function of the angle of rotation, and 256 interferograms were accumulated. In addition, external reflection FTIR spectra were measured with p-polarized radiation at an angle of the incidence of 82°, using a single diamond polarizer and a Seagull attachment (Harrick Scientific); the spectral resolution was 4 cm^{-1}. To ensure a high signal-to-noise ratio, 1024 scans were accumulated. Sample and source compartments were evacuated to 0.5 Torr.

The LC alignment of antiparallel LC cells was examined using an optical setup that was equipped with a He−Ne laser (632.8 nm wavelength), a polarizer, a photodiode detector, and a goniometer. In the measurement, the laser beam was incident perpendicular to the surface of the LC cell mounted on the goniometer, and these components were placed between the polarizer and the detector. Light absorption of the dichroic dye aligned together with the LC molecules in the cell was then monitored as a function of the angle of rotation of the cell. The pretilt angle α of the LC molecules was measured using a crystal rotation apparatus.[5] For the TN LC cells, azimuthal anchoring energy was measured by using an ultraviolet−visible (UV−vis) spectrophotometer (model S-300, Scinco, Korea) equipped with two Glan-Laser prisms (model PGL5015, Casix, China); the analyzer was mounted on a motorized goniometer (model SKIDS−PH, Sigma Koki, Japan). Each TN cell was placed between the polarizer and the analyzer. UV−vis spectra were recorded at 0.8 cm^{-1} resolution as a function of the angle of rotation of the analyzer in the range 0−180° with an interval of 1.0°. In these measurements, the rotation angles giving a minimum transmittance in the UV−vis spectra were determined. Of the rotation angles for which measurements were carried out, one angle was chosen by considering the nature of the birefringence dispersion of the LC and used for determining the twist angle at which the easy axes of the upper and lower substrates of the cell occur.[9] The azimuthal anchoring energies of the LCs on the rubbed PI film surfaces were estimated from the twist angle using the optical parameters of the LC.[9]

Results and Discussion

Surface Morphology. Using the AFM technique, we examined the surfaces of the PI films in detail before and after they had been rubbed with various rubbing strength parameters. Parts a and b of Figure 2 show AFM images of unrubbed CBDA-FDA and PMDA-FDA films, respectively. The CBDA-FDA film was found to have a root-mean-square (rms) roughness of 0.310 nm over an area of 1.0 × 1.0 μm^2. The rms roughness of the PMDA-FDA film was found to be 0.260 nm over an area of 1.0 × 1.0 μm^2. These unrubbed films are overall very smooth.

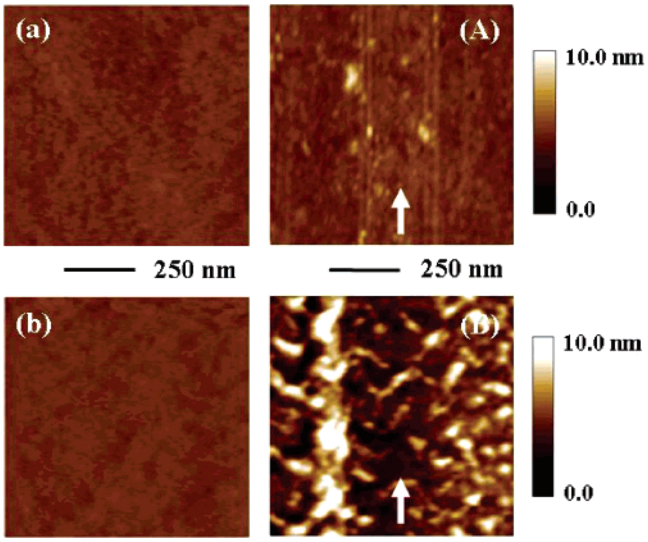

Figure 2. Surface AFM images of PI films before and after rubbing at a rubbing strength parameter of 129.6 cm: (a) unrubbed CBDA-FDA PI; (A) rubbed CBDA-FDA PI; (b) unrubbed PMDA-FDA PI; (B) rubbed PMDA-FDA PI. The arrow in the AFM image denotes the rubbing direction.

Parts A and B of Figures 2 show representative AFM images of the PI films after rubbing at a rubbing strength parameter of 129.6 cm. As can be seen in Figure 2A, the rubbed CBDA-FDA film has weakly developed microgrooves that run parallel to the rubbing direction, which resemble those reported for rubbed films of conventional PIs used in the LCD industry.[3,4] The developed microgrooves are around 40 nm or larger in size. The rms surface roughness of this rubbed PI film is 0.511 nm over an area of 1.0 × 1.0 μm^2, which is higher than that of the unrubbed film. In contrast, a new type of meandering microgroove structure that runs in a direction perpendicular to the rubbing direction can be seen in the rubbed PMDA-FDA film (Figure 2B). This is the first report of such structures in a rubbed PI film. Thus, the observed surface morphology is a significant departure from the surface morphologies reported so far for all other PI alignment layers.[3−7] However, similar meandering microgrooves have recently been reported in rubbed films of polystyrene (PS).[9] The developed meandering microgrooves have a dimension of around 100 nm. The rubbed PMDA-FDA film has an rms surface roughness of 1.861 nm over an area of 1.0 × 1.0 μm^2. This film surface is much rougher than that of the rubbed CBDA-FDA film. The observed surface morphology might be due to the characteristic deformation response of PMDA-FDA to the shear force caused by contact of fibers with the surface during the rubbing process.

Rubbing-Induced Molecular Orientation. Dichroic IR spectral analyses were conducted for the CBDA-FDA and PMDA-FDA films before and after rubbing by using polarized transmission FTIR spectroscopy, which can only detect vibrational modes with in-plane components. In these measurements the unrubbed CBDA-FDA and PMDA-FDA films were found to exhibit isotropic spectra (data not shown), indicating that the unrubbed films are both isotropic in the film plane.

In contrast, the rubbed PI films were found to exhibit anisotropy in the dichroic IR spectra: one measured with IR

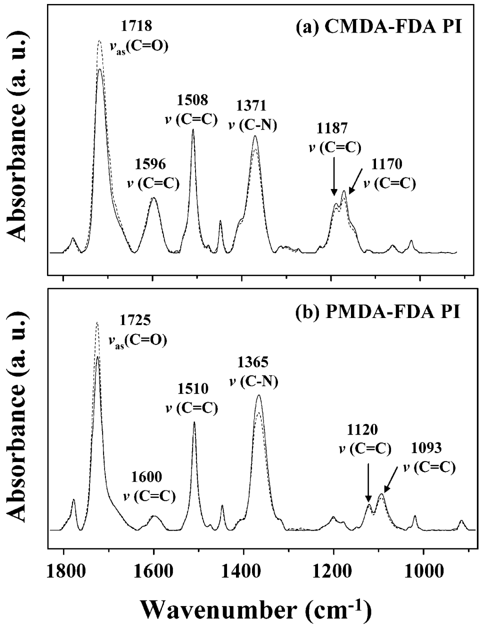

Figure 3. FTIR dichroic spectra of PI films rubbed with a rubbing strength parameter of 129.6 cm. The solid and dashed lines are the FTIR spectra with the IR light polarized parallel to the rubbing direction and with the IR light polarized parallel perpendicular to the rubbing direction, respectively.

light polarized parallel to the rubbing direction and the other with IR light polarized perpendicular to the rubbing direction. Figure 3a shows representative dichroic IR spectra of a CBDA-FDA film rubbed at a rubbing strength parameter of 129.6 cm. The spectrum of the CBDA-FDA film contains bands due to C═O stretching vibrations at 1780 and 1718 cm^{-1}, C═C vibrations of the para-substituted benzene ring at 1596 and 1508 cm^{-1}, C═C vibrations of the ortho-substituted benzene ring at 1187 and 1170 cm^{-1}, and the C−N imide group at 1371 cm^{-1}. As can be seen in Figure 3b, the spectrum of a PMDA-FDA film rubbed at a rubbing strength parameter of 129.6 cm contains bands due to C═O stretching vibrations at 1780 and 1725 cm^{-1}, vibrations of the para-substituted benzene ring at 1600 and 1510 cm^{-1}, vibrations of the ortho-substituted benzene ring at 1120 and 1093 cm^{-1}, and the C−N imide group at 1365 cm^{-1}. All IR bands were assigned with the aid of results reported previously for other PIs.[10]

In these dichroic IR spectra, the imide C−N band for the rubbed CBDA-FDA and PMDA-FDA films is more intense when the polarization of the incident IR beam is parallel to the rubbing direction. The imide C−N bond is a part of the polymer backbone that lies along the main polymer chain axis. Thus, as a result of rubbing the main axes of the polymer chains are preferentially oriented parallel to the rubbing direction. Moreover, the bands corresponding to the C═O asymmetric vibration of the imide ring (at 1718 cm^{-1} for CBDA-FDA and 1725 cm^{-1} for PMDA-FDA) are more intense when the polarization of the incident beam is perpendicular to the rubbing direction. This indicates that the bond axis of the imide ring C═O is more favorably oriented perpendicular to the rubbing direction than in other directions. As can be seen in Figure 1, the bond axis of the imide ring C═O lies along a direction at an angle of around 70° with respect to the long axis of the CBDA and PMDA units. The asymmetric C═O vibration results indicate that the long axes of the CBDA and PMDA units are both preferentially oriented parallel to the rubbing direction, which coincides with the orientation direction of the C−N imide bond.

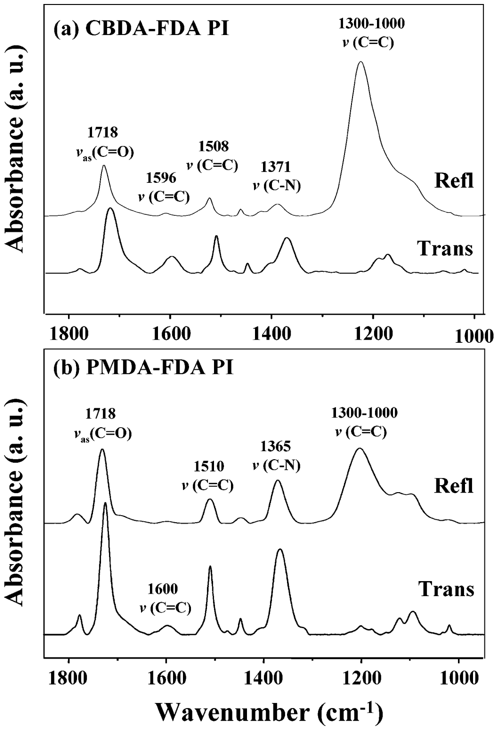

Figure 4. FTIR spectra of PI films rubbed with a rubbing strength parameter of 129.6 cm: Key: Refl, external reflection mode; Trans, transmission mode.

On the other hand, the bands in the dichroic IR spectra of the rubbed CBDA-FDA and PMDA-FDA films corresponding to the vibrations of the para-substituted benzene rings in the FDA units have almost the same intensities (Figure 3). This suggests that the para-directors of the two para-substituted benzene rings in the FDA units are most likely to lie in a direction at an angle of around 45° with respect to the rubbing direction in both films. In contrast, the intensities of the bands corresponding to the vibrations of the ortho-substituted benzene ring in the fluorenyl moiety of the FDA unit depend on the direction of the linearly polarized IR beam used in the dichroic IR spectrum measurements (Figure 3). These vibrational bands are slightly more intense when the polarization of the incident beam is parallel to the rubbing direction, suggesting that the ortho-director of the two ortho-substituted benzene rings in the fluorenyl moiety is most likely to lie in a direction that is slightly more parallel than perpendicular to the rubbing direction. These IR results suggest that the direction of the fluorenyl moiety is perpendicular to the rubbing direction, whereas the para-directors of the para-substituted benzene rings that link the fluorenyl moieties to the backbone lie between the parallel and perpendicular directions.

In addition, the rubbed PI films were investigated with external reflection IR spectroscopy by using linearly polarized beams. Representative reflection IR spectra are displayed in Figure 4 alongside those measured in the transmission mode. In these measurements, the IR light was linearly polarized parallel to the rubbing direction and propagated toward the rubbing direction. As can be seen in Figure 4a, the C−N imide band, the band due to the C═O asymmetric stretching vibration of the imide ring, and that due to the C═C vibrations of the para-substituted benzene ring are more intense in the transmission IR spectrum of the rubbed CBDA-FDA film than in the external reflection IR spectrum. In contrast, the band due to the C═C vibrations of the ortho-substituted benzene ring in the fluorenyl moiety of the FDA unit is significantly more intense

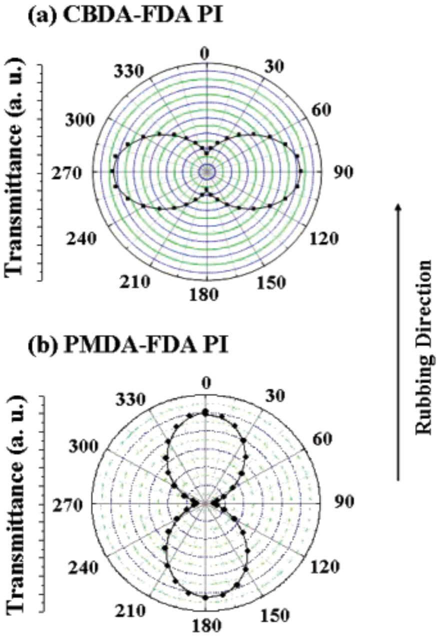

Figure 5. Polar diagrams of the variation of the retardation with the angle of rotation of the film in optical phase retardation measurements of PI films rubbed at a rubbing strength parameter of 129.6 cm.

in the external reflection IR spectrum than in the transmission IR spectrum. Similar results were obtained for the rubbed PMDA-FDA film (Figure 4b). These results indicate that for both the rubbed CBDA-FDA and PMDA-FDA films all the main chain segments preferentially lie in the film plane, and the fluorenyl side groups favorably lie in the out-of-plane of the films.

In summary, the IR results indicate that in CBDA-FDA and PMDA-FDA rubbed films the main chain segments lie in the film plane and are oriented preferentially along the rubbing direction, and the fluorenyl side groups lie in the out-of-plane of the films and are preferentially oriented perpendicular to the rubbing direction.

To obtain information about the optical properties of the polymer chains in the rubbed PI films, an optical phase retardation technique was used. Figure 5 displays polar diagrams of the variations of the transmitted light intensity [=(in-plane birefringence) × (phase)] with the angle of rotation of PI films rubbed at a rubbing strength parameter of 129.6 cm. As can be seen in Figure 5a, for the rubbed CBDA-FDA film the maximum transmitted light intensity arises for the direction 270° ↔ 90°, which is perpendicular to the rubbing direction, and the minimum light intensity arises for the direction 0° ↔ 180°, which is parallel to the rubbing direction. As discussed above, the polymer main chains in the rubbed films are oriented parallel to the rubbing direction and the fluorenyl side groups are oriented orthogonally to the polymer main chain. Thus, Figure 5a indicates that the refractive index in the direction along the polymer main chains is lower than that orthogonal to the polymer main chains; i.e., CBDA-FDA is a negative birefringent polymer.

In contrast, the maximum intensity of transmitted light for the rubbed PMDA-FDA film arises for the direction 0° ↔ 180°, and the minimum light intensity arises for the direction 270° ↔ 90° (Figure 5b). Thus, the anisotropic polar diagram indicates that the refractive index in the direction along the polymer main chains is higher than that orthogonal to the polymer main chains, i.e., PMDA-FDA is a positive birefringent polymer.

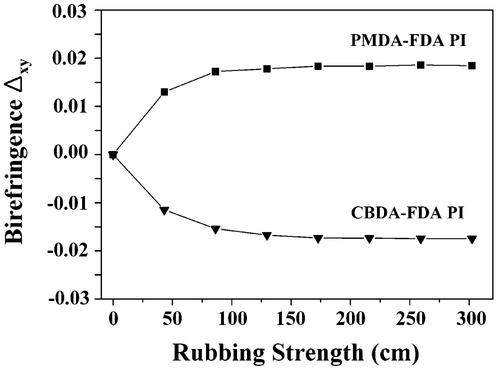

Figure 6. Variations of the in-plane birefringence Δ_{xy} with rubbing strength parameter of rubbed PI films.

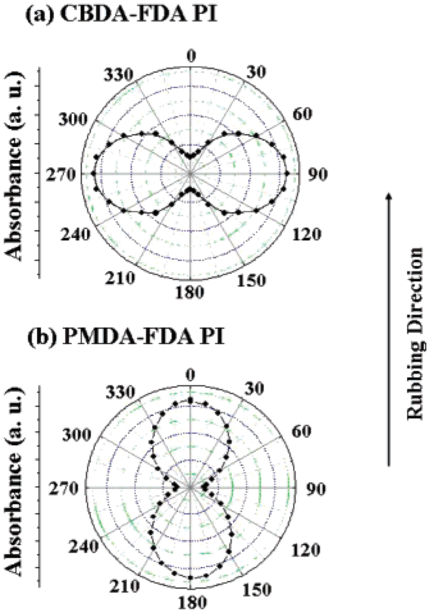

Figure 7. Polar diagrams of the light absorbance of the dichroic dye aligned together with the LC molecules in antiparallel LC cells, measured as a function of the angle of rotation of the cell. 5CB was used as a nematic LC. The used PI films were rubbed at a rubbing strength parameter of 129.6 cm.

This difference in the optical properties of the PIs is attributed to the difference in their chemical structures (Figure 1). The optical retardation results indicate that the polarization of the aliphatic CBDA unit along its long axis is lower than that of the aromatic PMDA unit along its long axis.

Figure 6 shows the variations of the in-plane birefringence Δ_{xy} with rubbing strength parameter for the PI films. For the CBDA-FDA film, the magnitude of Δ_{xy} rapidly increases with rubbing strength parameter up to 129.6 cm, and then levels off with further increases in the rubbing strength parameter. For the PMDA-FDA film, Δ_{xy} rapidly increases with rubbing strength parameter up to 86.4 cm, and then levels off with further increases in the rubbing strength parameter. Overall, the absolute value of Δ_{xy} is slightly larger for the PMDA-FDA film than for the CBDA-FDA film when the films are rubbed at the same rubbing strength parameter. These results confirm that the polymer chains in the surfaces of the PI films are oriented along the rubbing direction by the rubbing process and that the preferential orientation can be achieved by rubbing at rubbing strength parameters greater than 86.4 cm for PMDA-FDA and 129.6 cm for CBDA-FDA.

LC Alignment and Anchoring Energy. Figure 7 shows polar diagrams of the absorbances of LC cells fabricated with

PI films rubbed at a rubbing strength parameter of 129.6 cm. As is clear from Figure 7a, the LC cell of the rubbed CBDA-FDA film exhibits maximum absorbance along the direction 270° ↔ 90°, which is perpendicular to the rubbing direction. The anisotropy of this polar diagram indicates that the LC molecules in contact with the rubbed CBDA-FDA film surface are induced homogeneously to align perpendicular to the rubbing direction. This LC alignment is quite different from those observed for conventional PI alignment layer materials.[3−6]

To understand this LC alignment, we need to consider all the factors possibly involved in the interactions of the LC molecules with the rubbed PI film surface as follows.

First, we examine dimensions of the CBDA-FDA PI chain and the surface morphology, and then consider the possible interactions of the LC molecules with the PI chains and the microgrooves at the film surface. The 5CB LC molecule used in the present study is ca. 1.8 nm in length and ca. 0.25 nm in diameter; this dimension is comparable to those of the chemical repeat unit of the main chain backbone and of the fluorenyl side group (Figure 1). In contrast, the microgrooves developed along the rubbing direction are around 40 nm or larger in size and their rms roughness is around 0.511 nm, as discussed earlier. The dimensions of these surface structures seem to be large to effectively interact with and align LC molecules. These facts and the observed LC alignment suggest that the LC molecules are more likely to be aligned by interactions with the polymer chain segments, rather than by the microgrooves.

Second, in general an LC molecule consists of an aromatic mesogen and an aliphatic tail, and the aromatic mesogen component may favorably interact with the aromatic components of an alignment layer film via $\pi-\pi$ interactions, whereas the aliphatic tail may undergo van der Waals type interactions with the film's aliphatic components. Taking these facts into account, two aromatic phenyl rings and one aliphatic cyclobutanyl ring per chemical repeat unit in the PI chains oriented along the rubbing direction favorably interact with the aromatic biphenyl mesogen unit and the *n*-pentyl tail of the 5CB LC molecule respectively, contributing to the tendency to align the LC molecule along the rubbing direction. In contrast, two aromatic phenyl rings in the fluorenyl side group oriented perpendicular to the rubbing direction also interact with the aromatic biphenyl mesogen unit of the LC and then tend to align the LC molecule perpendicular to the rubbing direction. Here, the contribution of two imide rings per chemical repeat unit is additionally considered. For each imide ring, the imide C−N bond is a part of the main chain backbone but the two carbonyl C═O bonds are more favorably oriented parallel to the side group rather than to the main chain. The imide carbonyl groups have more polar character than the imide C−N bond, so that the four carbonyl groups per chemical repeat unit may more favorably interact with the polar cyano group of the LC molecule than do the two imide C−N bonds. Thus, the oriented imide carbonyl groups also tend to align the LC molecule perpendicular to the rubbing direction. Considering these possible interactions, the observed LC alignment suggests that the LC molecules are more likely to be aligned by anisotropic interactions with the aromatic rings in the fluorenyl side groups and the imide carbonyl groups oriented perpendicular to the rubbing direction, which override anisotropic interactions with the aromatic rings, the aliphatic rings, and the imide bonds in the polymer main chains oriented along the rubbing direction and with the microgrooves developed along the rubbing direction.

Figure 7b shows a representative polar diagram of the absorbances of LC cells fabricated with the rubbed PMDA-FDA PI films. As can be seen in the figure, the LC cell of the rubbed PMDA-FDA film exhibits maximum absorbance along the direction 0° ↔ 180°, which is parallel to the rubbing direction. The director of this polar diagram is in contrast to those observed in the LC cell fabricated with the ribbed CBDA-FDA PI films. The anisotropy of this polar diagram indicates that the LC molecules in contact with the rubbed PMDA-FDA film surface are induced homogeneously to align parallel to the rubbing direction. The LC alignment is quite different from that observed at the rubbed CBDA-FDA PI films.

This LC alignment can also be understood with considering all the factors possibly involved in the interactions of the LC molecules with the rubbed PMDA-FDA PI film surface in the same manner as discussed for the LC alignment at the rubbed CBDA-FDA PI film above. First, the meandering microgrooves developed perpendicular to the rubbing direction are around 100 nm in size and their rms roughness is around 1.861 nm, as discussed earlier, which are much larger than that of the LC molecule. Furthermore, the LC alignment is quite different from those observed for PS alignment layer films that have a surface morphology composed of meandering microgrooves developed perpendicular to the rubbing direction.[9] These facts and the observed LC alignment suggest that the dimensions of the meandering microgrooves perpendicularly developed at the film surface are too large to effectively interact with and align LC molecules, and thus the LC molecules are more likely to be aligned by interactions with the polymer chain segments, rather than by the meandering microgrooves. Second, PMDA-FDA PI has chemical structure similar to that of CBDA-FDA PI (Figure 1). The preferential orientations of the polymer chain segments determined at the rubbed PMDA-FDA PI film are comparable with those observed at the rubbed CBDA-FDA PI film, as discussed earlier. In addition, it is noted that the phenyl ring of the PMDA unit, which is inserted into the backbone instead of cyclobutanyl ring in the CBDA-FDA PI, was determined to be preferentially oriented along the rubbing direction. Taking these facts into account, the observed LC alignment suggests that the LC molecules are favorably aligned by anisotropic interactions with the aromatic rings and the imide bonds in the polymer main chains oriented along the rubbing direction, which overrides the anisotropic interactions with the aromatic rings of the fluorenyl side groups and the imide carbonyl groups oriented perpendicular to the rubbing direction and with the meandering microgrooves developed perpendicular to the rubbing direction.

Taken together, the above LC alignment, surface morphology, and polymer segmental orientation results indicate that LC alignment on the rubbed PI film surfaces is determined by a play-off between the directionally anisotropic interactions of the LC molecules with the oriented segments of the polymer main chains, the oriented segments of the side groups, and the microgrooves. The results further indicate that the interactions of the rubbed PI film surface components with LC molecules are in the increasing order microgroove < cyclobutanyl group ≤ imide bond < imide carbonyl group < phenyl ring. In conclusion, the unusual tendency of LC molecules to align perpendicular to the microgrooves developed at the rubbed PI film surfaces is primarily driven by directionally anisotropic interactions of the LC molecules with the preferentially oriented phenyl rings whose number is higher than that of the phenyl rings oriented to the other direction. When the number of the phenyl rings oriented to one direction is same with that of the phenyl rings oriented to the other direction, the LC alignment is governed by cooperatively anisotropic interactions of the LC

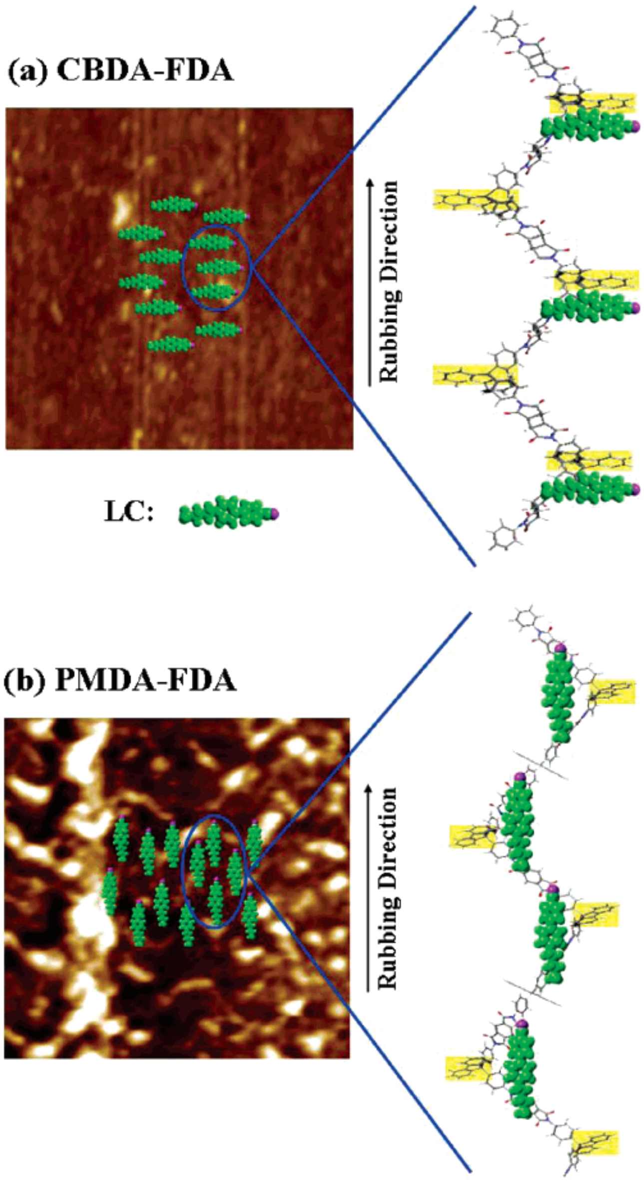

Figure 8. Schematic configuration model of a representative chain of PI molecules oriented at the rubbed PI film surface, and the LC alignment induced by the polymer molecules.

molecules with the other film surface components, in particular other polymer segments (for example, imide carbonyl group) oriented to the coincident direction.

From these results, we suggest a configuration model for the PI chains oriented by the rubbing process and for their alignment of LC molecules. Figure 8 displays a symbolic, schematic configuration model including a representative chain of the oriented PI molecules and LC molecules aligned by the oriented polymer chain.

Taking into account the observed LC alignment behaviors, the pretilt angle of the LCs in the LC cell was measured along the director of the LC alignment by using the crystal-rotation method. For both the LC cells fabricated with the rubbed films of the two PIs, the measured LC pretilt angles were found to be in the range 0−1.0°, depending on the rubbing strength parameters employed in the rubbing process. Overall, both PI films induce LC molecules to align with low pretilt angles on the rubbed film surfaces.

It was previously reported that the pretilt angle of LC molecules in contact with a rubbed film surface is predominantly governed by the nature and length of the side groups that are oriented by the rubbing process, and in part by the inclination of the polymer main chains oriented along the rubbing direction.[4−7,9] Taking these facts into account, the length of the fluorenyl side group of the PIs considered here is too small to induce LC molecules to anchor with a high pretilt angle at the rubbed film surface. Furthermore, the biphenyl mesogen of the 5CB LC molecule may directionally and anisotropically interact with the parallel oriented polymer main chains laid in the film plane and with the perpendicularly oriented fluorenyl side groups, of which the para-direction is positioned in the out-of-plane of the film, via a $\pi-\pi$ interaction, and the *n*-pentyl tail of the LC molecule may favorably interact with the parallel oriented polymer main chains laid in the film plane via van der Waals forces, cooperatively causing the LC molecule to align with a low or zero pretilt angle.

TN cells were then prepared and found to be very stable and homogeneous throughout. These TN LC cells were used in measurements with a UV−visible spectroscopic technique of the twist angles of the LC molecules. The twist angles were found to be 90° for all the LC cells, regardless of the rubbing strength parameter and the type of PI polymer. From this measured twist angle, the anchoring energies of the LC molecules on the rubbed films of both the PIs were estimated to be much greater than 1×10^{-3} J/m^2. This anchoring energy is very high and is comparable to those of LC cells fabricated with rubbed films of conventional PIs currently used in the LCD industry. These results therefore indicate that both the perpendicular LC alignment on the rubbed CBDA-FDA film and the parallel LC alignment on the rubbed PMDA-FDA film are very stable.

Conclusions

The surface morphologies and molecular orientations of rubbed CBDA-FDA and PMDA-FDA films were investigated in detail using AFM microscopy, linearly polarized IR spectroscopy, and optical retardation analysis. The LC alignment behaviors and the anchoring energies of LC molecules on the rubbed films were also determined.

The rubbed CBDA-FDA film surfaces contain microgrooves that run in the rubbing direction. However, the rubbed PMDA-FDA film surfaces have unusual meandering microgrooves that run perpendicular to the rubbing direction; this is the first report of such meandering microgroove structures in a rubbed PI film. For films rubbed under the same rubbing conditions, the CBDA-FDA films were found to be smoother than the PMDA-FDA films.

Despite the different surface morphologies of the rubbed films, for both the CBDA-FDA and PMDA-FDA film surfaces the polymer main chains lie in the film plane and preferentially orient along the rubbing direction, whereas the fluorenyl side groups lie in the out-of-plane direction and preferentially orient perpendicular to the rubbing direction.

The rubbed CBDA-FDA film surface induces LC alignment perpendicular to the microgrooves developed along the rubbing direction. The anchoring energy of this perpendicular LC alignment was found to be very large and comparable to those observed for conventional PI alignment layers, which induce LC alignment parallel to the rubbing direction. The unusual tendency of LC molecules to align perpendicular to the rubbing direction with large anchoring energies is driven by their favorable anisotropic interactions with the perpendicularly oriented fluorenyl side groups, which override their interactions with the parallel oriented polymer main chains consisting of two phenyl rings and one cyclobutanyl ring per chemical repeat unit and the microgrooves in the film surface. However, the rubbed PMDA-FDA film surface induces LC alignment parallel to the rubbing direction with a very high anchoring energy, even though this film surface contains perpendicularly developed meandering microgrooves and fluorenyl side groups that are perpendicularly oriented. The tendency of LC molecules to align parallel to the rubbing direction with large anchoring energies is driven by their favorable anisotropic interactions with the parallel oriented polymer main chains containing three phenyl rings per chemical repeat unit, which override their interactions with the perpendicularly oriented fluorenyl side groups and with the unusual meandering microgrooves in the film surface.

In conclusion, the LC alignment, anchoring energy, surface morphology, and polymer segmental orientation results indicate that LC alignment on the surfaces of rubbed PI films is determined by the interplay between the directionally anisotropic interactions of the LC molecules with the oriented segments of the polymer main chains, the oriented fluorenyl side groups, and the microgrooves. However, for the rubbed PI films examined in our study, the directionally anisotropic interactions of the LC molecules with the oriented polymer segments, namely the polymer main chain and side group components, were always much stronger than those of the LC molecules with the directionally developed microgrooves. The CBDA-FDA and PMDA-FDA PIs of this study are promising alignment layer materials for the fabrication of advanced LC display devices.

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