Role of the *n*-Alkyl End of Bristles in Governing Liquid Crystal Alignment at Rubbed Films of Brush Polymer Rods

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ABSTRACT: A series of poly(*p*-phenylene 3,6-bis(4-(*n*-alkyloxy)phenyloxy)pyromellitimide)s (C*n*-PMDA-PDA PIs) with various lengths of the *n*-alkyl bristle end group, which are well-defined polymer rods with two bristles per repeat unit of the polymer rod backbone, were studied as thin films using atomic force microscopy, optical retardation, and linearly polarized infrared spectroscopy before and after rubbing with a velvet fabric, and their nematic liquid crystal (LC) aligning abilities were investigated. The LC molecules on the rubbed film surfaces of C*n*-PMDA-PDA PIs with *n*-butyl, *n*-hexyl, and *n*-heptyl bristle end groups were found to be aligned perpendicular to the rubbing direction; this is a significant departure from the parallel LC alignment observed for all conventional PI materials. In contrast, rubbing of the film surfaces of C*n*-PMDA-PDA PI with *n*-octyl bristle end groups induced LC alignment parallel to the rubbing direction. Both the perpendicular and parallel LC alignments were determined to have very large anchoring energies ($>1 \times 10^{-3}$ J/cm^2). The rubbing process was found to create microgrooves in the PI films along the rubbing direction and to orient the polymer main chains and the *n*-alkyl bristle end groups along the rubbing direction but to orient the phenyloxy bristle units perpendicular to the rubbing direction. These results collectively indicate that the *n*-alkyl bristle end groups play an important role in LC alignment and that this role depends on the length of the *n*-alkyl chain; specifically, the parallel oriented *n*-alkyl bristle end groups hinder perpendicular LC alignment because of their van der Waals interactions with the aliphatic tails of the LC molecules. The critical length of the *n*-alkyl bristle end group for the transition from perpendicular to parallel LC alignment at the rubbed PI films is eight carbons (i.e., the *n*-octyl end group). In conclusion, LC alignment on the surfaces of rubbed PI films is determined by a play-off between the directionally anisotropic interactions of the LC molecules with (1) the oriented segments of the polymer main chains, (2) the oriented segments of the bristles, and (3) the microgrooves.

Introduction

Films of aromatic polyimides (PIs) are widely used as liquid crystal (LC) alignment layers in the mass-production of flat-panel LC display devices because of their advantageous properties such as excellent optical transparency, adhesion, heat resistance, dimensional stability and insulation.[1] PI film surfaces need to be rubbed with a velvet fabric to produce a uniform alignment of LC molecules with a defined range of pretilt angles.[1,2] As a consequence, much effort has been devoted to developing high performance PI materials[2,3] and to determining their LC alignment mechanism on rubbed PI film surfaces.[2−8] For most PI films reported to date, the rubbing process was found to create microgrooves along the rubbing direction and also to orient polymer main chains along the rubbing direction.[2−4,7,8] Such unidirectionally developed microgrooves and oriented polymer main chains were found to cooperatively work together to align LC molecules along the rubbing direction through their anisotropic interactions with LC molecules.[2−4,7,8]

However, Chae et al.[5] recently reported that rubbed films of poly(*p*-phenylene 3,6-bis(4-(*n*-butyloxy)phenyloxy)pyromellitimide) (C4-PMDA-PDA PI) align LC molecules perpendicular to the rubbing direction, which is a significant departure from the LC alignment behavior typically observed for rubbed PI films. At the rubbed surface, the phenyloxy units of the bristles were found to be oriented perpendicular to the rubbing direction whereas the polymer main chains and the *n*-butyl end groups of the bristles were determined to be oriented parallel to the rubbing direction; in addition, microgrooves were found to be developed along the rubbing direction.[5,6] Moreover, the rubbing-induced orientations of the polymer segments were found to follow the sequence: PDA (phenyl ring), imide ring, phenyloxy unit, imide C−N bond, and *n*-butyl group.[6] Taking the polymer segmental orientations and microgroove structure into account, the unusual LC alignment is attributed to the strength of the anisotropic intermolecular interactions of the LC molecules with the phenyloxy bristle units oriented perpendicularly to the rubbing direction, which overrides the interactions with the polymer main chains and the *n*-butyl end groups of the

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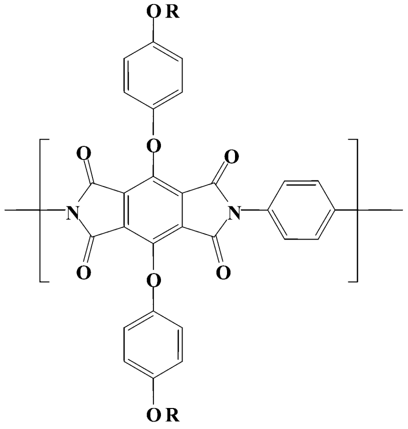

R = $(CH_2)_3CH_3$: **C4-PMDA-PDA PI**
$(CH_2)_5CH_3$: **C6-PMDA-PDA PI**
$(CH_2)_6CH_3$: **C7-PMDA-PDA PI**
$(CH_2)_7CH_3$: **C8-PMDA-PDA PI**

Figure 1. Chemical structures of fully rodlike poly(*p*-phenylene pyromellitimide)s with 4-(*n*-alkyloxy)phenyloxy bristles (C*n*-PMDA-PDA PIs).

bristles oriented parallel to the rubbing direction and with the microgrooves that are created along the rubbing direction.[5,6] Moreover, the LC alignment result confirms that in the rubbed C4-PMDA-PDA PI film, the anisotropic intermolecular interactions of the oriented polymer segments with LCs are much stronger than the anisotropic interactions of the microgrooves with LCs.

In light of the above findings, it is suggested that in the rubbed C4-PMDA-PDA film surface, the strength of anisotropic interaction with LCs increases in the order *microgrooves* $<$ or $\approx$ *n*-butyl end group $<$ *PMDA-PDA backbone unit* $<$ *oxyphenyloxy−PMDA−oxyphenyloxy unit*. Among these preferentially oriented polymer segments as well as the developed microgrooves, the *n*-butyl end group in the bristle seems to be too short in length to make its contribution discernible to the alignment of LCs. Thus, a question rises for the effect of the length of the *n*-alkyl end group in the bristle on the anisotropic interaction with LCs and resulting LC alignment. Further, considering the chemical structure of the polymer, it seems most simple to modify the *n*-butyl end group than the other segments of the polymer in the aspect of polymer synthesis.

Therefore, we in this study synthesized a series of poly(*p*-phenylene 3,6-bis(4-(*n*-alkyloxy)phenyloxy)pyromellitimide)s (C*n*-PMDA-PDA PIs; $n = 4$, 6, 7, and 8) (Figure 1). The surface topographies of nanoscale films of these PIs were examined using atomic force microscopy (AFM), and the orientational distributions of the polymer main chains and the bristles of the PI films were characterized by optical phase retardation analysis and linearly polarized Fourier transform infrared (FTIR) spectroscopy. The alignment of LC molecules in contact with rubbed PI films was investigated and, furthermore, the anchoring energies of the LCs on the films were determined. The measured alignment and anchoring energy characteristics were analyzed to elucidate the anisotropic interactions between the oriented polymer chain segments and the LC molecules. In addition, the contribution of the film surface topography to the alignment and anchoring energy was considered.

Experimental Section

Polyimide Materials and Sample Preparation. Poly(amic acid) (PAA) precursors of C*n*-PMDA-PDA PIs (Figure 1) were prepared in *N*-methyl-2-pyrrolidone (NMP) from the respective dianhydride and *p*-phenylenediamine (PDA), respectively, according to the method described previously:[3,5,6] poly(*p*-phenylene 3,6-bis(4-(*n*-hexyloxy)phenyloxy)pyromellitimide) (C6-PMDA-PDA PI), poly(*p*-phenylene 3,6-bis(4-(*n*-heptyloxy)phenyloxy)pyromellitimide) (C7-PMDA-PDA PI), C4-PMDA-PDA PI, and C8-PMDA-PDA PI. For the synthesized PAA precursors, inherent viscosity measurements were performed at a concentration of 0.1 g/dL in NMP at 25.0 °C: 1.85 for C6-PMDA-PDA PAA, 0.98 for C7-PMDA-PDA PAA, 0.81 for C4-PMDA-PDA PAA, and 0.95 for C8-PMDA-PDA PAA. PI films were prepared by spin casting the PAA solutions onto calcium fluoride windows for the FTIR spectra, onto gold-coated silicon wafers for the AFM images, and onto indium tin oxide (ITO) glass substrates for the optical retardation and LC cell assemblies, followed by drying on a hot plate at 80 °C for 1 h. The dried PAA precursor films were thermally imidized in an oven under dry nitrogen gas flow at 250 °C for 2 h. The resulting PI films were found to have a thickness of around 200 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 densities using a laboratory rubbing machine (Wande) with a roller covered with a rayon velvet fabric (model YA-20-R, Yoshikawa, Japan).[2,5] The rubbing density was varied by changing the cumulative rubbing time for a constant rubbing depth, 0.37 mm.[2,5]

Some of the rubbed PI films on glass substrates were cut into 2.5 cm × 2.5 cm pieces, which were then used in the assembly of 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 Merck nematic LC [n_e (extraordinary refractive index) = 1.5697 and n_o (ordinary refractive index) = 1.4769; Merck] 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 cells). All the prepared LC cells were found to be uniform and homogeneous throughout by optical microscopy. In addition, a solution of the LC in ethyl ether (10 wt % LC) was directly spin-coated onto some of the rubbed PI films, and dried at room temperature for 5 h; the thicknesses of the coated LC layers were found using the spectroscopic ellipsometer to be around 400 nm.

Measurements. Surface images were obtained with a tapping mode atomic force microscope (model Multimode AFM Nanoscope IIIa, Digital Instruments). A silicon cantilever (26 N/m spring constant and 268 kHz resonance frequency) was used for scanning. 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), as described elsewhere.[5,9] The optical phase retardation measurements were calibrated with a $\lambda/30$ plate standard (Wave plate Zero Order $\lambda/30$ (λ = 632.8 nm), Altechna); λ is the wavelength of a laser light source. Samples (rubbed PI films with and without an LC coating) were installed perpendicular to the incident beam direction. Optical phase retardations were measured as a function of the angle of rotation of the samples. FTIR spectroscopic measurements were carried out on a FTIR spectrometer (model DA8, Bomem, Canada) equipped with a single diamond polarizer (Harrick Scientific). Samples were installed perpendicular to the incident beam direction. IR spectra were recorded at 4 cm^{-1} resolution with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector under vacuum as a function of the angle of rotation of the polarizer, and interferograms were accumulated 256 times. The LC pretilt angles were measured in the antiparallel LC cells using a crystal rotation apparatus made in our laboratory.[2,5] For the TN LC cells, the 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 TN cell occur.[10] 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.[10] In addition, the cell gap was determined from the UV−vis spectra.

Results and Discussion

Surface Morphology. Using AFM, we examined the surfaces of the PI films before and after rubbing at a rubbing density of 120. All unrubbed PI films had smooth surfaces with a root-mean-square (rms) roughness of 0.5−0.7 nm over an area of 5 × 5 μm^2 (AFM images not shown). In contrast, all rubbed PI films exhibited microgrooves along the rubbing direction (Figure 2). The surface roughness values along the rubbing direction of the area marked in Figure 2 for the rubbed C4-, C6-, C7-, and C8-PMDA-PDA films were 2.2, 1.6, 4.0, and 3.4 nm respectively, whereas the surface roughness values across the rubbing direction for the same region of the film surfaces were 3.4, 4.2, 7.2, and 3.7 nm. Overall, the microgrooves developed along the rubbing direction are much larger in size than the LC molecules, which have dimensions of ca. 2 nm (length) and 0.3 nm (diameter). The characteristics of the microgrooves on the rubbed film surfaces (i.e., microgroove shape, size, and size distribution, and periodicity of microgroove lines), vary depending on the length of the *n*-alkyl bristle end group in the PI.

Poly(*p*-phenylene pyromellitimide) (PMDA-PDA PI), which corresponds to the backbone of all the PIs tested in this study, is very hard and brittle.[11] In contrast, all of the PIs prepared in this study were relatively ductile, and the ductility increased with increasing length of the *n*-alkyl end group in the bristle. On the basis of these properties, the surface morphologies described above might correlate with the deformation response characteristics of the PI films to the shear force caused by contact with the fibers during the rubbing process, which depend on the length of the *n*-alkyl end group of the bristle.

Molecular Orientation. To obtain information about the orientation of polymer chains produced by the rubbing process, PI films were rubbed and their optical phase retardation measured. Figure 3 displays polar diagrams of the optical phase retardation with respect to the angle of rotation of PI films rubbed with a rubbing density of 120. As seen in Figure 3, all rubbed PI films exhibit a maximum retardation along the direction 180 ↔ 0°, which is parallel to the rubbing direction, but a minimum retardation along the direction 90 ↔ 270°, which is perpendicular to the rubbing direction. All PI chains were determined to be positively birefringent along the rubbing direction by spectroscopic ellipsometry. Taking this fact into account, the polar diagram results confirm that for all rubbed films, the main director of the PI chains after orientation by rubbing is parallel to the rubbing direction. In contrast, the polar diagram of the optical phase retardation of an unrubbed PI film (data not shown) is isotropic with respect to the angle of rotation of the film, confirming that the polymer chains of unrubbed films lie randomly in the film plane.

Figure 4 shows the variation of the in-plane birefringence Δ_{xy} with rubbing density for the PI films, which is produced by the rubbing process. For all PI films, the Δ_{xy} rapidly increases with rubbing density up to a rubbing density of 50 (for C4-PMDA-PDA, C6-PMDA-PDA, C7-PMDA-PDA PI) or 100 (for C8-PMDA-PDA PI) and then more slowly increases with further increases in the rubbing density, finally leveling off above a rubbing density of 300. 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 preferential orientation can be achieved by rubbing at a rubbing density greater than 50 (for C4-PMDA-PDA, C6-PMDA-PDA, C7-PMDA-PDA PI) or 100 (for C8-PMDA-PDA PI).

Figure 5 presents two representative IR spectra of a C6-PMDA-PDA PI film rubbed at a rubbing density of 120, one measured with the IR light polarized parallel to the rubbing direction, the other measured with the IR light polarized perpendicular to the rubbing direction. In both these FTIR spectroscopic measurements, only modes with in-plane components are detected because only normal incidence spectra were measured. The vibrational modes were assigned with the aid of results previously reported for other PIs.[5,12] The bands at 1780, 1733, 1515, and 1364 cm^{-1} are due to the symmetric and asymmetric C═O stretching vibrations of the imide ring, the C═C stretching vibration of the PDA unit, and the C−N stretching vibration of the imide bond respectively, all of which are associated with the polymer main chain structure. The band at 1505 cm^{-1} is due to the C═C stretching vibration of the phenyloxy unit in the side chain. Further, the asymmetric and symmetric CH_2 stretching vibrational modes are detected at 2923 and 2852 cm^{-1} respectively. The IR spectra of the rubbed film differ depending on whether the IR light is polarized parallel or perpendicular to the rubbing direction, indicating that the rubbed PI film is anisotropic in the film plane. Similar dichroic IR spectra were observed for the rubbed films of the other PIs (spectra not shown). In contrast, the unrubbed PI film reveals no IR dichroism dependence (spectra not shown).

IR spectroscopic measurements using a linearly polarized IR light source were further carried out on the rubbed PI film as a function of the angle of rotation of the film. The variations of the peak intensities of selected IR bands with the angle of rotation of the film are plotted in Figure 6 as polar diagrams. As shown in Figure 6, parts a and b, the imide C−N band at 1364 cm^{-1} and the C═C band of the PDA unit at 1515 cm^{-1} are more intense when the incident beam is polarized parallel to the rubbing direction. Both the imide C−N bond and the PDA unit are parts of the polymer backbone, and lie along the polymer main chain axis. The anisotropic polar diagrams of the IR bands corresponding to these moieties indicate that rubbing causes these moieties, and therefore the main axes of the

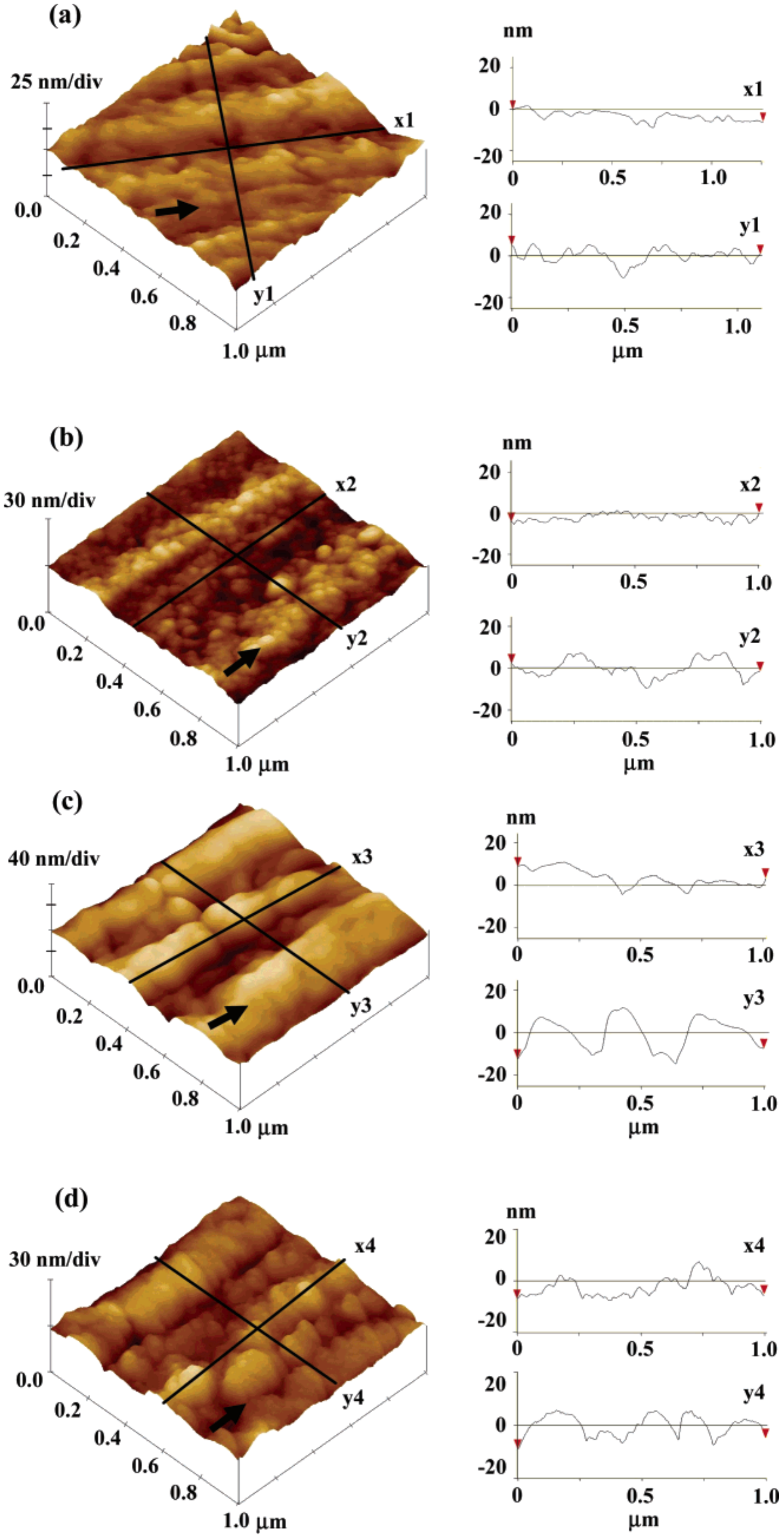

Figure 2. AFM images and surface profiles of C*n*-PMDA-PDA PI films rubbed with a rubbing density of 120: (a) C4-PMDA-PDA PI; (b) C6-PMDA-PDA PI; (c) C7-PMDA-PDA PI; (d) C8-PMDA-PDA PI. The arrow in each AFM image denotes the rubbing direction.

polymer chains, to be oriented along the rubbing direction.

In contrast, as shown in Figure 6c the intensity of the asymmetric C═O vibration of the imide ring at 1733 cm^{-1} is enhanced when the polarization of the IR beam lies along the direction 250° ↔ 70°, which is at an angle of 70° with respect to the rubbing direction, indicating that the imide C═O bond is oriented by rubbing in this

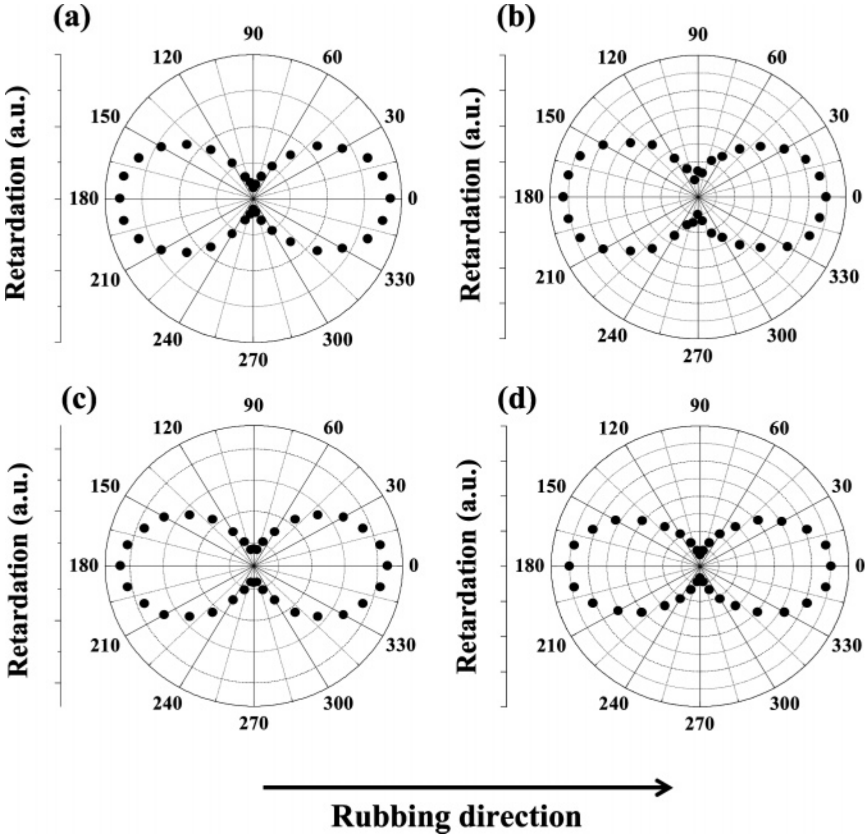

Figure 3. Polar diagrams of the variation of the retardation with the angle of rotation of the film in optical phase retardation measurements of C*n*-PMDA-PDA PI films rubbed with a rubbing density of 120: (a) C4-PMDA-PDA PI; (b) C6-PMDA-PDA PI; (c) C7-PMDA-PDA PI; (d) C8-PMDA-PDA PI.

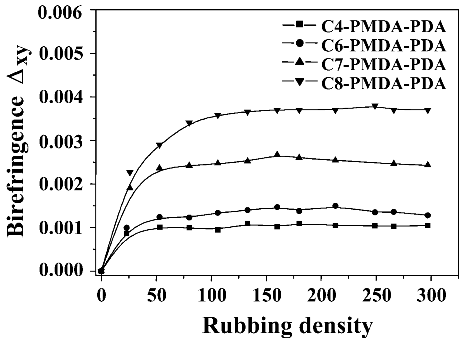

Figure 4. Variations of the in-plane birefringence with rubbing density of rubbed C*n*-PMDA-PDA PI films:

direction. This conclusion is consistent with the chemical structure shown in Figure 1 and with the orientation of the imide C−N bond noted above. The polar diagram for the aromatic C=C vibration of the phenyloxy unit at 1505 cm^{-1} shows that the intensity of this mode is enhanced when the beam polarization is perpendicular to the rubbing direction (see Figure 6d). This suggests that the long axis of the phenyloxy unit in the bristle becomes aligned by the rubbing process in a direction perpendicular to the polymer main chain axis.

Parts e and f of Figure 6 show the polar diagrams for the CH$_2$ asymmetric and symmetric stretching vibrations, which produce peaks at 2923 and 2852 cm^{-1} respectively. The intensities of both these modes are enhanced when the beam polarization is perpendicular to the rubbing direction. Given that the CH$_2$ asymmetric and symmetric stretching vibrations possess dipole moment vectors perpendicular to the alkyl chain axis, we conclude that the *n*-hexyl end group of the bristle is oriented parallel to the rubbing direction by the rubbing process.

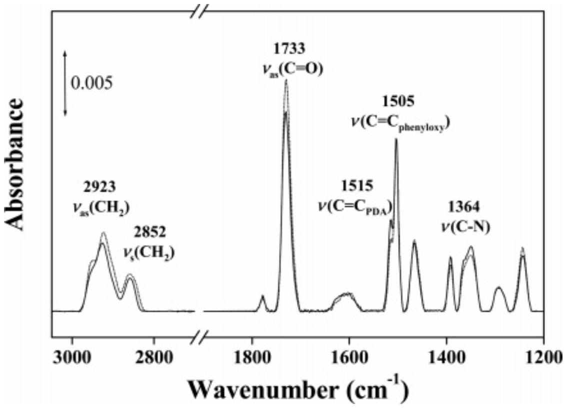

Figure 5. FTIR dichroic spectrum of a C6-PMDA-PDA PI film rubbed with a rubbing density of 120. The solid and dashed lines are the FTIR spectra with the IR light polarized parallel to the rubbing direction and with the IR light polarized parallel perpendicular to the rubbing direction, respectively.

IR spectroscopic measurements using linearly polarized IR light as a function of the angle of rotation of the film were also carried out for rubbed films of the other PIs, yielding results similar to those described above for the rubbed C6-PMDA-PDA film.

The IR results collectively indicate that, for all of the PI films studied, rubbing the film surface causes orientation of the polymers into an arrangement in which the polymer main chains and the *n*-alkyl bristle end groups are oriented parallel to the rubbing direction and the phenyloxy bristle units are oriented perpendicular to the rubbing direction.

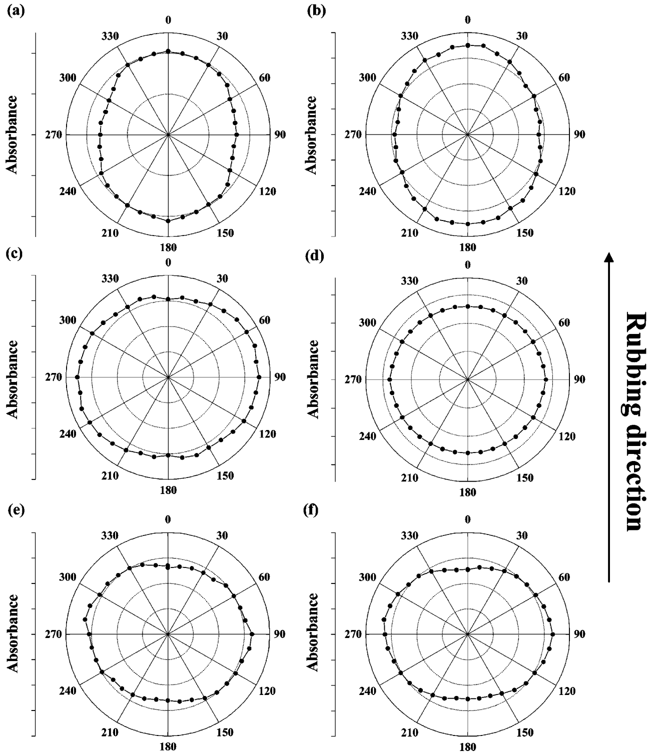

Figure 6. Polar diagrams of the intensities of some specific vibrational peaks of a C6-PMDA-PDA PI film rubbed with a rubbing density of 120, measured with linearly polarized IR spectroscopy as a function of the angle of rotation of the film: (a) v (N−C) at 1364 cm^{-1}; (b) v(C=C$_{\mathrm{PDA}}$) at 1515 cm^{-1}; (c) v_{as}(C=O) at 1733 cm^{-1}; (d) v(C=C$_{\mathrm{Phenyloxy}}$) at 1505 cm^{-1}; (e) v_{as}(CH$_2$) at 2923 cm^{-1}; (f) v_{s}(CH$_2$) at 2852 cm^{-1}.

In light of the above findings on the polymer segmental orientations, it is worth devoting further attention to the Δ_{xy} variations of the PI films with rubbing density shown in Figure 4. As seen in the figure, the Δ_{xy} value at a given rubbing density over the rubbing density range of 0−300 always increases in the order C4-PMDA-PDA PI < C6-PMDA-PDA PI < C7-PMDA-PDA PI < C8-PMDA-PDA PI. Several factors could potentially contribute to this trend. First, consider the contribution to the Δ_{xy} value of the polymer segmental orientations in the rubbed PI films. All the PIs have the same basic chemical structure (a PMDA-PDA backbone, a phenyloxy bristle unit, and an n-alkyl bristle end group), but with different lengths of the n-alkyl bristle end group (see Figure 1). Moreover, as described above, the main director of each polymer segment oriented by the rubbing process is the same for all the PIs. These facts suggest that the contribution of the parallel oriented polymer backbone and of the perpendicular oriented phenyloxy bristle unit to the Δ_{xy} value should be the same for all PI films rubbed at a given rubbing density. However, the contribution of the parallel oriented n-alkyl end group in the bristle to the Δ_{xy} value will depend on its length, with longer n-alkyl end groups contributing more positively to the Δ_{xy} value. Second, consider the degree of overall polymer chain orientation in the PI films rubbed at a given rubbing density. As mentioned in "Surface Morphology" section, the deformation response characteristics of PI films to the shear force caused by contact with the fibers during the rubbing process are related to the film ductility, which is in turn associated with the length of the n-alkyl end group of the bristle. As a result, the degree of overall polymer orientation in PI films rubbed at the same rubbing densities will vary across the series of PIs tested in the present study. Therefore, the different Δ_{xy} values in the PI films rubbed at a given rubbing density are attributed to differences in the contributions of the n-alkyl end group orientations as well as to differences in the degree of overall polymer chain orientation in the rubbed films.

LC Alignment. Figure 7 shows polar diagrams of the variation of the optical phase retardation with the angle of rotation of PI films rubbed at a rubbing density of 120 and coated with LC. As is clear from Figure 7, parts a−c, the LC coated films of C4-PMDA-PDA, C6-PMDA-PDA, and C7-PMDA-PDA PIs exhibit a maximum retardation along the direction 90 ↔ 270°, which lies perpendicular to the rubbing direction. These results indicate that the LC molecules in contact with the rubbed film surfaces are induced homogeneously to align perpendicular to the rubbing direction, consistent with previous findings for a C4-PMDA-PDA PI film rubbed with a rubbing density of 180.[5] These LC alignments are quite different from those for conventional PI alignment layer materials.[1−4]

In combination with the surface morphology results described above, these data show that the LC molecules are induced to align perpendicular to the grooves created along the rubbing direction, indicating that the alignment of LCs is not directly induced by the grooves but by other effects. This LC alignment is also perpendicular to the alignments of both the polymer main chains and the n-alkyl bristle end groups (i.e., n-butyl, n-hexyl, and n-heptyl), which are oriented preferentially along the rubbing direction, but is parallel to the alignment of the phenyloxy bristle units, which are oriented perpendicular to the rubbing direction. The observed perpendicular alignments of the LC molecules therefore imply that the LC molecules are anchored to the rubbed film surface by their strong anisotropic molecular interactions with the oriented phenyloxy bristle units, which override the interactions with the polymer main chains and the n-alkyl bristle end groups (i.e., n-butyl, n-hexyl, and n-heptyl) as well as with the microgrooves that are created along the rubbing direction, and align the LC molecules along the oriented phenyloxy bristle units.

As seen in Figure 7d, the LC coated film of C8-PMDA-PDA PI, on contrary, exhibits a maximum retardation along the direction 180 ↔ 0°, which lies parallel to the rubbing direction. This result indicates that the LC molecules in contact with the rubbed film surfaces are induced homogeneously to align parallel to the rubbing direction.

The C8-PMDA-PDA PI has the same backbone and phenyloxy bristle units as the other Cn-PMDA-PDA PIs (i.e., C4-PMDA-PDA, C6-PMDA-PDA, and C7-PMDA-PDA PIs), but has one to four more carbons in its n-alkyl bristle end groups. Thus, the length of the n-alkyl bristle end group seems to play an important role in the alignment of LC molecules in contact with the rubbed surface; apparently the roles played by the polymer main chain and the phenyloxy bristle unit in LC alignment are redundant for these PIs. These results indicate that the critical length of the n-alkyl bristle end group that governs a transition from perpendicular to parallel LC alignment on rubbed PI films is eight carbons (i.e., as in the n-octyl end group).

In general, an LC molecule is composed of an aromatic mesogen and an aliphatic tail. The aromatic mesogens

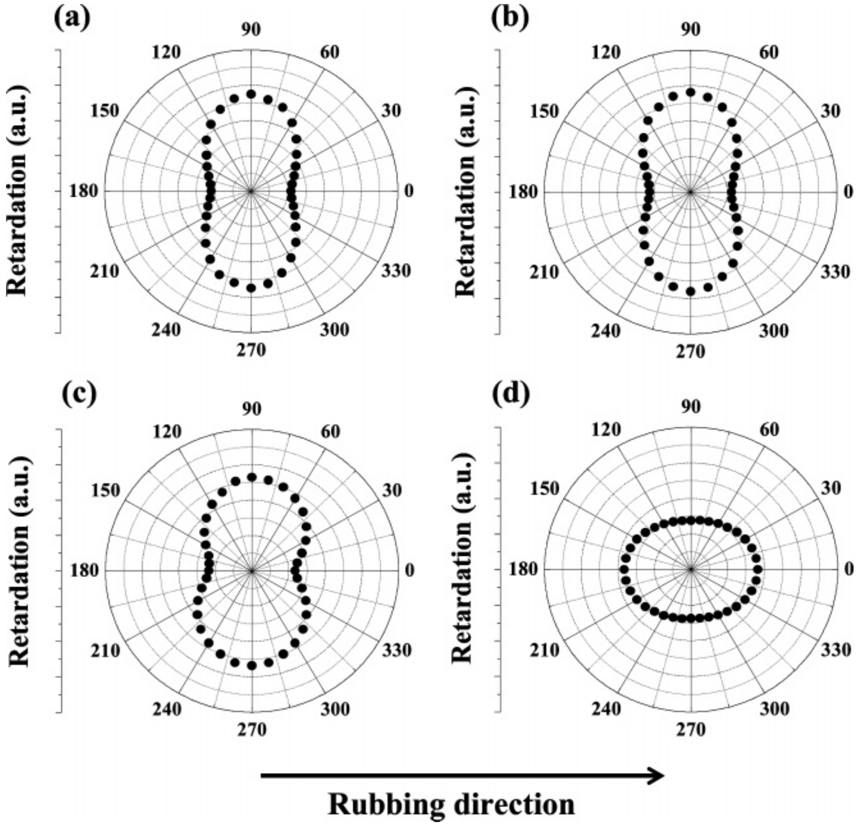

Figure 7. Polar diagrams of the variation of retardation with the angle of rotation of the LC coated film in optical phase retardation measurements of rubbed C6-PMDA-PDA PI films coated with LC: (a) C4-PMDA-PDA PI; (b) C6-PMDA-PDA PI; (c) C7-PMDA-PDA PI; (d) C8-PMDA-PDA PI. The films were rubbed with a rubbing density of 120.

might favorably interact with the phenyl ring components of the PIs via $\pi-\pi$ interactions, while the aliphatic tails might undergo van der Waals type interactions with the *n*-alkyl bristle end groups of the PIs. This van der Waals interaction might become more favorable as the *n*-alkyl bristle end group becomes longer. Thus, the van der Waals interactions with the *n*-alkyl bristle end groups oriented parallel to the rubbing direction might hinder the perpendicular LC alignment that is driven by the perpendicularly oriented phenyloxy bristle units; these interactions are also in competition with the contributions of the parallel oriented polymer main chains and the grooves created along the rubbing direction to the anisotropic molecular interactions with LC molecules. The negative contributions of the oriented *n*-alkyl bristle end groups in ≤ 7 carbons are not large enough to alter the observed perpendicular LC alignments to a parallel LC alignment. However, the presence of oriented *n*-octyl bristle end groups does result in parallel LC alignment.

Taking the observed LC alignment into account, we used the crystal-rotation technique to determine the pretilt angle of the LCs along the direction perpendicular to the rubbing direction. The LCs in the cells fabricated with rubbed films of C6-PMDA-PDA and C7-PMDA-PDA PIs did not exhibit any pretilt angle outside the range 25−55°, as observed in LC cells fabricated with rubbed films of C4-PMDA-PDA PI.[5] Outside this range, the LC pretilt angle could not be measured because of the limits of the measurement technique. We suspect that the pretilt angles of LCs in contact with the rubbed films of these PIs along a direction perpendicular to the rubbing direction lie in the range 25−55°, depending upon the rubbing density. For comparison, the LC in the cells fabricated with rubbed films of C8-PMDA-PDA PI exhibits a pretilt angle of 75°; namely, the rubbed C8-PMDA-PDA PI film induces a homeotropic LC alignment with a pretilt angle of 75° in which the main director projected to the film plane is parallel to the rubbing direction.

LC Anchoring Energy. With the observed LC alignment in mind, TN cells were prepared and used in measurements of the twist angle of the LC molecules with a UV−vis spectroscopic technique. All the TN cells exhibited a twist angle of 90°, regardless of rubbing density. From this measured twist angle, the anchoring energies of the LC molecules on the rubbed films of all the PIs are estimated to be much greater than 1×10^{-3} J/cm^2. This anchoring energy is comparable to those found for the rubbing type PIs currently used in the LC display industry. These therefore indicate that both the perpendicular alignments of LC molecules on the rubbed films of C4-PMDA-PDA, C6-PMDA-PDA, and C7-PMDA-PDA PIs and the parallel alignment of LC molecules on the rubbed C8-PMDA-PDA PI film are very stable.

Conclusions

Rubbed films of C4-, C6-, C7-, and C8-PMDA-PDA PI, which are well-defined brush PIs composed of two aromatic−aliphatic bristles per repeat unit of a fully rodlike backbone, were investigated in detail using AFM microscopy, optical retardation analysis and linearly polarized IR spectroscopy in order to elucidate their surface morphology and molecular orientation. The LC alignment behavior and the anchoring energy of LC molecules on the rubbed films were also determined.

The rubbed surfaces of all the PI films exhibited microgrooves along the rubbing direction; however the microgroove features (i.e., microgroove shape, size, and size distribution, and periodicity of microgroove lines) depended on the lengths of the *n*-alkyl bristle end group in the PI. At the surfaces of all of the rubbed PI films, the polymer main chains and the *n*-alkyl bristle end groups were oriented along the rubbing direction, whereas the phenyloxy bristle units were oriented perpendicular to the rubbing direction.

The rubbed film surfaces of C4-, C6-, and C7-PMDA-PDA PI induced LC alignment perpendicular to the rubbing direction. The anchoring energies of these perpendicular LC alignments were very large, with values comparable to those observed for conventional PI alignment layers, which induce LC alignment parallel to the rubbing direction. The unusual tendency of LC molecules with large anchoring energies to align perpendicular to the rubbing direction is driven by the favorable anisotropic interactions of LC molecules with the perpendicularly oriented phenyloxy bristle units, which override the interactions of the LC molecules with the polymer main chains, the *n*-alkyl bristle end groups, and the grooves in the film surface. However, rubbed surfaces of the C8-PMDA-PDA PI film induced LC alignment parallel to the rubbing direction, even though this PI has only one to four more carbons in the *n*-alkyl bristle end group in comparison to the other PIs.

Taken together, the LC alignment, surface morphology, and polymer segmental orientation results indicate that the *n*-alkyl bristle end groups play an important role in LC alignment on rubbed C*n*-PMDA-PDA PI films, and that this role is dependent on the length of the *n*-alkyl chain; specifically, the *n*-alkyl bristle end groups oriented parallel to the rubbing direction hinder perpendicular LC alignment because of their van der Waals interactions with the aliphatic tails of the LC molecules. The critical length of the *n*-alkyl bristle end group at which the LC alignment at the rubbed PI films changes from perpendicular to parallel is eight carbons (i.e., the *n*-octyl end group).

In conclusion, LC alignment on the surfaces of rubbed PI films is determined by a play-off of the directionally anisotropic interactions between the LC molecules with (1) the oriented segments of the polymer main chains, (2) the oriented segments of the bristles, and (3) the microgrooves.

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References and Notes

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