

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/228507100>

Rubbing-Induced Surface Morphology and Polymer Segmental Reorientations of a Model Brush Polyimide and Interactions with Liquid Crystals at the Surface

ARTICLE in CHEMISTRY OF MATERIALS · JULY 2003

Impact Factor: 8.35 · DOI: 10.1021/cm034055m

CITATIONS

46

READS

21

10 AUTHORS, INCLUDING:



Seung Woo Lee

Yeungnam University

208 PUBLICATIONS 3,992 CITATIONS

SEE PROFILE



Byeongdu Lee

Argonne National Laboratory

205 PUBLICATIONS 6,467 CITATIONS

SEE PROFILE

Rubbing-Induced Surface Morphology and Polymer Segmental Reorientations of a Model Brush Polyimide and Interactions with Liquid Crystals at the Surface

Seung Woo Lee,[†] Boknam Chae,[†] Byeongdu Lee,[†] Wooyoung Choi,[†]
Seung Bin Kim,^{*,†} Sang Il Kim,^{†,§} Su-Moon Park,[†] Jin Chul Jung,^{*,‡}
Kyung Hoon Lee,^{‡,§} and Moonhor Ree^{*,†}

Department of Chemistry, Center for Integrated Molecular Systems, BK21 Program, Division of Molecular and Life Sciences, Polymer Research Institute, Department of Materials Science & Engineering, and Center for Advanced Functional Polymers, Pohang University of Science & Technology, San 31, Hyoja-dong, Pohang 790-784, Republic of Korea

Received February 12, 2003. Revised Manuscript Received May 30, 2003

Poly{*p*-phenylene-3,6-bis[[4-(*n*-octyloxy)phenyl]oxy]pyromellitimide} (C8-PMDA-PDA PI), a model brush polymer with a fully rodlike backbone, was determined to be positively birefringent by prism coupling analysis. Films of the PI were examined in detail by optical retardation and polarized infrared spectroscopy before and after mechanical rubbing with a velvet fabric. In addition, the alignment behavior of liquid crystal (LC) molecules in contact with rubbed films of the model polymer was investigated. Atomic force microscopic imaging revealed that rubbing caused microgrooves, as well as fine grooves (around 100 nm in size) with a surface morphology that resembled ground-beef, to develop parallel to the rubbing direction. The morphologies of these grooves are attributed to the structure of the fabric fibers and the shear deformation characteristics of the polymer. At the rubbed surface, the polymer main chains and the *n*-octyl end groups of the bristles were determined to be oriented parallel to the rubbing direction whereas the phenyloxy units of the bristles were found to be oriented perpendicular to the rubbing direction. When LC molecules were placed in contact with the rubbed PI films, the LC molecules formed a uniformly aligned structure with a pretilt angle ranging from 25 to 87° along the rubbing direction, depending on the rubbing density. The tendency to form this structure was attributed to the favorable anisotropic interactions of the LC molecules with the parallel reoriented polymer main chains and *n*-octyl end groups of the bristles in the rubbed surface, as well as with the microgrooves and fine grooves aligned parallel to the rubbing direction. The large pretilt angles were favored despite the relatively short alkyl side end group of the PI, which contains only half of the 16 carbons generally required to achieve large pretilt angles of LCs. This result suggests that the *n*-octyl end groups of the bristles play a critical role in the generation of large pretilt angles, most likely through favorable interactions between these groups and the aliphatic tails of the LC molecules.

Introduction

Recently we reported a series of novel dianhydride monomers, 3,6-bis[[4-(*n*-alkyloxy)phenyl]oxy]pyromellitic dianhydrides (C*m*-PMDAs, where *m* is the number of carbons in the *n*-alkyloxy group) and their polyimides (PIs) prepared from various aromatic diamines including *p*-phenylenediamine (PDA).¹ Among these polymers, C*m*-PMDA-PDA PIs prepared from C*m*-PMDAs and PDA are of particular interest because of their well-defined brush polymer structure composed of two aro-

matic–aliphatic bristles per chemical repeat unit of the fully rodlike polymer backbone. Such brush polymer rods are expected to have segmental polymer reorientation and liquid crystal (LC) alignment characteristics different from those of conventional PI alignment layer materials. In the present study we examined poly{*p*-phenylene-3,6-bis[[4-(*n*-octyloxy)phenyl]oxy]pyromellitimide} (C8-PMDA-PDA PI) as a model brush polymer composed of a fully rodlike backbone (see Figure 1). Optical phase retardation analysis and linearly polarized Fourier transform infrared (FTIR) spectroscopy were used to elucidate the orientational distributions of both the polymer main chains and the bristles (i.e.

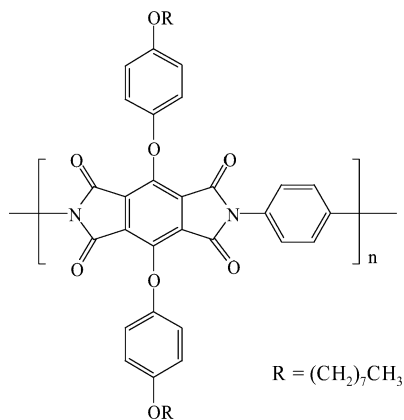
* To whom all correspondence should be addressed. Tel: +82-54-279-2120 (M.R.), +82-54-279-2106 (S.B.K.). Fax: +82-54-279-399. E-mail: ree@postech.edu (M.R.), sbkim@postech.edu (S.B.K.).

[†] Department of Chemistry, Center for Integrated Molecular Systems, BK21 Program, Division of Molecular and Life Sciences, and Polymer Research Institute.

[‡] Polymer Research Institute, Department of Materials Science & Engineering, and Center for Advanced Functional Polymers.

[§] Present address: Samsung Electronics Co., Giheung, Gyeonggi-do, Republic of Korea.

(1) (a) Lee, K. H.; Jung, J. C. *Polym. Bull.* **1998**, *40*, 407. (b) Lee, S. W.; Kim, S. I.; Park, Y. H.; Ree, M.; Lee, K. H.; Jung, J. C. *Mol. Cryst. Liq. Cryst.* **2000**, *349*, 271. (c) Lee, S. W.; Kim, S. I.; Park, Y. H.; Ree, M.; Lee, K. H.; Jung, J. C. *Mol. Cryst. Liq. Cryst.* **2000**, *349*, 279. (d) Jung, J. C.; Lee, K. H.; Sohn, B. S.; Lee, S. W.; Ree, M. *Macromol. Symp.* **2001**, *164*, 227.



C8-PMDA-PDA PI

Figure 1. Chemical structure of C8-PMDA-PDA PI, a well-defined brush polymer composed of a fully rodlike aromatic backbone and aromatic-aliphatic bristles.

side groups) of the PI film before and after rubbing. In addition, the surface topography was examined using atomic force microscopy (AFM). To investigate the alignment behavior of LC molecules in contact with rubbed films of C8-PMDA-PDA PI, we prepared LC cells by assembling two rubbed films in an antiparallel orientation with respect to the rubbing direction using a spacer and injected a nematic LC, 4-*n*-pentyl-4'-cyanobiphenyl (5CB), into the cells. The alignment behavior of LC molecules in contact with the rubbed films was then analyzed with reference to the anisotropic interactions between the reoriented polymer chain segments and the LC molecules. In addition, the contribution of the film surface topography to the LC alignment was considered.

Experimental Section

Materials and Film Preparation. Poly(amic acid) (PAA), a soluble precursor of C8-PMDA-PDA PI (shown in Figure 1), was prepared in *N*-methylpyrrolidone (NMP) from C8-PMDA and PDA following the method developed previously by our group.¹ The C8-PMDA-PDA PAA precursor had an inherent viscosity of 0.95 at a concentration of 0.1 g/dL in NMP at 25.0 °C. The PI films were prepared by spin-casting a solution of 2 wt % C8-PMDA-PDA PAA in NMP onto calcium fluoride (CaF₂) windows (25 mm diameter × 2 mm thickness) for FTIR spectroscopic analysis, gold-coated silicon wafers (15 mm × 10 mm) for AFM imaging, and indium–tin oxide glasses for optical retardation and LC cell assembly, 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 had thicknesses of around 200 nm, as determined using a spectroscopic ellipsometer (J. A. Woollam Co., model M-44) and an α -stepper (Veeco Co., model Tektak3). The PI films coated onto the substrates were rubbed at various rubbing densities using a laboratory rubbing machine (Wande Co.) with a roller covered with a rayon velvet fabric (Yoshikawa Co., YA-20-R).^{2,3} The velvet fabric had a density of 24 000 fibers/cm², and each fiber had dimensions of 1.85 mm (height) × 15 μ m (diameter). The rubbing density (L/l) was varied by changing the cumulative

rubbing time for a constant rubbing depth (0.35 mm): $L/l = N[(2\pi rn/60v) - 1]$, where L is the total length of the rubbing cloth which contacts 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 radius (cm) of the rubbing roller (rpm), respectively, and v is the velocity (cm/s) of the substrate stage.^{2,3} In addition, relatively thick PI films (thickness $\sim 5 \mu$ m) were prepared on cover slide glasses for refractive index measurements.

LC Cell Preparation. To prepare the cells for testing LC alignment behavior, rubbed PI films on glass substrates were cut into pieces of dimensions 2.5 × 2.5 cm and paired pieces from the same glass substrate were assembled in an antiparallel configuration with respect to the rubbing direction by using polyester film spacers of thickness 50 μ m. A nematic LC, 5CB (Aldrich Chemical Co.), containing 1.0 wt % Disperse Blue 1 (Aldrich Chemical Co.) as a dichroic dye, was injected into the cell gaps, and then the injection hole was sealed with an epoxy glue. The dichroic dye molecule used in these experiments absorbs at 632.8 nm, the wavelength of a He–Ne laser light, and aligns with 5CB LC molecules.^{2,3} After sealing, the LC cells were heat-treated for 5 min at 40 °C, a temperature slightly higher than the nematic-to-isotropic transition temperature of 5CB, to remove any flow-induced memory arising from the LC injection process.

Measurements. The surface morphology of the PI films was measured before and after rubbing, using an atomic force microscope (ThermoMicroscopes Co., model AutoProbe CP Research) in noncontact mode. The film surface was scanned using an ultralever cantilever (17 N/m spring constant and 320 kHz resonance frequency) with a tip-to-sample distance of 10–40 nm. Image processing and data analysis were performed using the IP 2.0 software program provided by ThermoMicroscopes Co. Optical phase retardation was measured using a phase retardation analyzer built in our laboratory. In these measurements, the laser beam was incident normal to the film surface and the transmitted light intensity (=in-plane birefringence × phase) was monitored as a function of the angle of rotation of the film sample with respect to the surface normal. FTIR spectroscopic measurements were carried out on a Bomem DA8 FTIR spectrometer equipped with a polarizer (single diamond polarizer, Harrick Scientific). Samples were installed perpendicular to the incident beam direction. While rotating the polarizer, IR spectra were recorded at 4 cm^{−1} resolution with a liquid-nitrogen-cooled mercury cadmium telluride detector under vacuum, as a function of the angle of rotation, and 256 interferograms were accumulated. The LC alignment in a LC cell containing Disperse Blue 1 dichroic dye was examined using an optical setup^{2,3} that was equipped with a He–Ne laser (632.8 nm wavelength), a polarizer, a photodiode detector, and a goniometer. In these measurements, the laser beam was incident normal 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 LCs 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.^{2,3} In addition, refractive index measurements were performed on PI films of thickness approximately 5.0 μ m using a prism coupler⁴ equipped with a He–Ne laser source (632.8 nm wavelength). The refractive index in the film plane (n_{xy}) was measured in the transverse electric mode, and the refractive index out of the plane (n_z) was obtained in the transverse magnetic mode. All of these measurements were performed using a cubic zirconia prism of $n = 2.1677$ at a wavelength of 632.8 nm.

(2) (a) Lee, K.-W.; Paek, S.-H.; Lien, A.; During, C.; Fukuro, H. *Macromolecules* **1996**, *29*, 8894. (b) van Aerle, N. A. J.; Tol, J. W. *Macromolecules* **1994**, *27*, 6520. (c) Kim, S. I.; Ree, M.; Shin, T. J.; Jung, J. C. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2909.

(3) Kim, S. I.; Pyo, S. M.; Ree, M.; Park, M.; Kim, Y. *Mol. Cryst. Liq. Cryst.* **1998**, *316*, 209.

(4) (a) Goh, W. H.; Kim, K.; Ree, M. *Korea Polym. J.* **1998**, *6*, 241. (b) Ree, M.; Kim, K.; Chang, H. *J. Appl. Phys.* **1997**, *81*, 698. (c) Ree, M.; Chu, C. W.; Goldberg, M. J. *J. Appl. Phys.* **1994**, *75*, 1410. (d) Ree, M.; Shin, T. J.; Lee, S. W. *Korea Polym. J.* **2001**, *9*, 1.

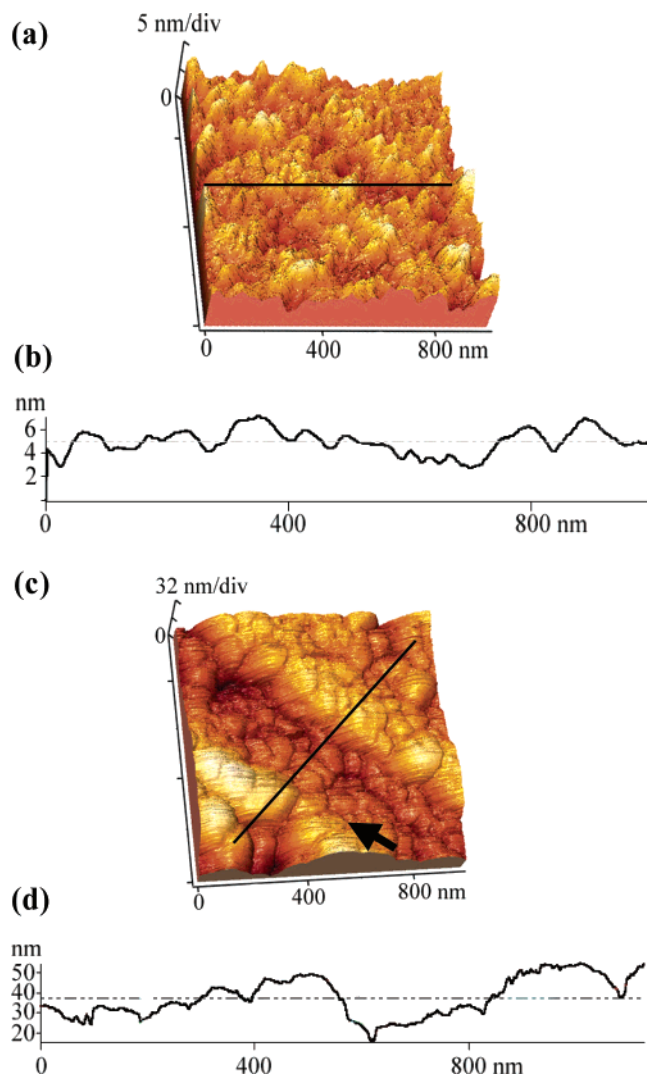


Figure 2. AFM images and surface profiles of a C8-PMDA-PDA PI film before and after rubbing with a rubbing density of 180: (a) image scanned over an area ($1 \times 1 \mu\text{m}^2$) of the unrubbed film; (b) surface profile taken from the arrow line in the image in part a; (c) image scanned over an area ($1 \times 1 \mu\text{m}^2$) of the rubbed film; (d) surface profile taken from the arrow line in the image in part c.

Results and Discussion

Surface Topography. Figure 2a shows an AFM image of the surface of the C8-PMDA-PDA PI film prior to rubbing treatment. The PI film has a spikelike surface morphology with a periodicity of around 70 nm and a root-mean-square (rms) roughness of 0.7 nm (Figure 2b). The morphology and roughness of the surface might arise from the aggregation and molecular ordering characteristics of the polymer chains during the drying and thermal imidization process after spin-casting. Another possibility is that the surface morphology and roughness, at least in part, reflect the surface roughness of the gold-coated substrate on which the film was spin-cast.

For the PI film rubbed with a rubbing density of 180, large-scale AFM imaging clearly shows microgrooves with widths of around $3.1 \mu\text{m}$ aligned parallel to the rubbing direction (data not shown); the height difference between the peaks and troughs in these microgroove lines is in the range of 80–100 nm, and the rms surface

roughness across the microgroove lines is 30 nm. An AFM image of the flat area of the peak of one such microgroove line is shown in Figure 2c. This flat area has an rms roughness of 16.1 nm (see Figure 2d). As is clearly seen in Figure 2c, the microgroove line is composed of submicrogroove lines with widths of around 500 nm aligned parallel to the rubbing direction. Each submicrogroove is made up of fine grooves (around 100 nm in size) like pebbles. The fine grooves are developed along the submicrogrooves, giving rise to a morphology that resembles the surface of ground beef. This surface morphology is somewhat different from the morphologies of rubbed films prepared from commercial PI alignment layer materials with flexible polymer backbones.⁵ Taking into consideration the structure of the rubbing fibers,⁶ we conjecture that the microgroove lines are created by the contact of the fibers whereas the submicrogroove lines are generated by the contact of subfibrous filaments at the fiber ends.

The surface morphology described above might result from the deformation response characteristic of PI films to the shear force caused by contact with the fibers during the rubbing process. For example, hardness or ductility may directly correlate to the shear-induced deformation process of a polymer. In general, ductile polymers more easily deform under shear to give a well-developed structure. Taking into account the correlation of hardness and ductility to shear deformation, the surface morphology results suggest that the C8-PMDA-PDA PI film is relatively ductile despite its fully rodlike backbone, PMDA-PDA PI. In fact, the rodlike PMDA-PDA PI is known to be very brittle, hard.⁴ Thus, the ductile nature of the C8-PMDA-PDA PI film originates from the [4-(*n*-octyloxy)phenyl]oxy side groups incorporated as bristles.

Optical Analysis. For an unrubbed C8-PMDA-PDA PI film of thickness $5.0 \mu\text{m}$, in-plane and out-of-plane refractive indices (n_{xy} and n_z) were measured at a wavelength of 632.8 nm. The PI film exhibits refractive indices of $n_{xy} = 1.620$ and $n_z = 1.608$, indicating that the refractive indices of the PI film are anisotropic with a positive out-of-plane birefringence, i.e., $\Delta_{xy-z} (= n_{xy} - n_z) = 0.012$. In thin films, long-chain polymer molecules tend to lie in the film plane, resulting in an out-of-plane birefringence in the film: in general, this tendency of polymer in-plane orientation increases strongly as the film becomes thinner and as the polymer chain becomes more rigid.⁴ Taking this fact into account, the positive value of the measured Δ_{xy-z} , therefore, indicates that the C8-PMDA-PDA PI is a positive birefringent polymer chain whose polarizability is larger along the polymer chain axis than along the direction normal to the polymer chain axis, and the PI polymer chains lie preferentially in the plane of the thin film rather than randomly in the thin film. Here it is additionally noted that the preferentially in-plane-oriented PI chains are randomly located in the film plane.

(5) (a) Kim, Y. B.; Olin, H.; Park, S. Y.; Choi, J. W.; Komitov, L.; Matuszczyk, M.; Lagerwall, S. T. *Appl. Phys. Lett.* **1995**, *66*, 2218. (b) Kim, Y. B.; Ban, B. S. *Liq. Cryst.* **1999**, *26*, 1579. (c) Zhu, Y.-M.; Wang, L.; Lu, Z.-H.; Wei, Y.; Chen, X. X.; Tang, J. H. *Appl. Phys. Lett.* **1994**, *65*, 49.

(6) Ree, M.; et al. Unpublished optical and scanning electron microscopic results.

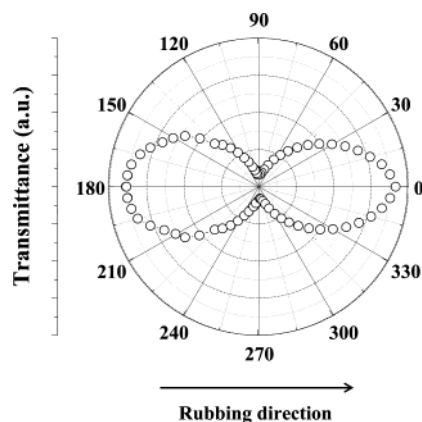


Figure 3. Polar diagram of the transmitted light intensity taken from optical phase retardation measurements of a rubbed C8-PMDA-PDA PI film as a function of the angle of rotation of the film. The film was rubbed with a rubbing density of 180.

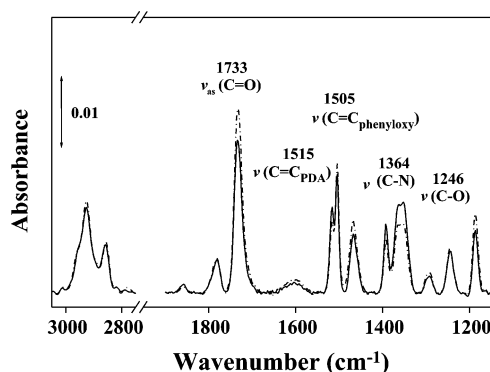


Figure 4. FTIR dichroic spectra from a C8-PMDA-PDA PI film rubbed with a rubbing density of 180. Solid and dashed lines represent the FTIR spectra with the IR light polarized parallel and perpendicular to the rubbing direction, respectively.

To probe the rubbing-induced reorientation of the polymer chains, PI films of thickness ca. 200 nm were rubbed and their optical phase retardation was measured. Figure 3 displays an anisotropic polar diagram of the transmitted light intensity (=in-plane birefringence $\Delta_{xy} \times \text{phase}$) with respect to the angle of rotation of the film measured from a PI film rubbed with a rubbing density of 180; here, Δ_{xy} (in-plane birefringence) = $n_x - n_y$. As seen in the figure, the maximum transmitted light intensity is observed along the rubbing direction, indicating that the optical axes of the polymer chains in the rubbed film plane are preferentially oriented along the rubbing direction. The obtained optical retardation value is 0.98 nm, which is positive. Given that the PI chain is positively birefringent, the director of the anisotropic polar diagram and the positive optical retardation value collectively indicate that the polymer main chains at the rubbed surface are oriented parallel to the rubbing direction. This parallel orientation of the PI polymer main chains at the rubbed surface is further discussed with the IR spectroscopy results in the next section.

Polarized FTIR Spectroscopy. Figure 4 presents representative IR spectra of a C8-PMDA-PDA PI film rubbed at a rubbing density of 180, which were measured with the IR light polarized parallel and perpendicular to the rubbing direction. In these FTIR spectro-

scopic measurements, only modes with in-plane components were observed because only normal incidence spectra were measured. The vibrational modes obtained from the PI film are assigned with the aid of results previously reported for other PIs.⁷ The bands at 1780, 1733, 1515, and 1364 cm^{-1} are assigned 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. Additional bands at 1505 and 1246 cm^{-1} are attributed to the C=C stretching vibration of the phenyloxy unit and the asymmetric C-O-C stretching vibration in the side chain, respectively. Furthermore, the stretching vibrations of CH_3 and CH_2 at the end of the side chain appear in the region 3000–2000 cm^{-1} . The asymmetric CH_3 stretching vibrations are located at 2958 and 2935 cm^{-1} , while the symmetric CH_3 stretching vibration is located at 2872 cm^{-1} ; the asymmetric and symmetric CH_2 stretching vibrational modes are detected at 2923 and 2852 cm^{-1} , respectively.

The unrubbed PI film reveals no IR dichroism dependence (spectra not shown). In contrast, the IR spectra of the rubbed film differ depending on whether the IR light is polarized parallel or perpendicular to the rubbing direction (see Figure 4), indicating that the rubbed PI film is anisotropic in the film plane. Inspection of Figure 4 reveals that some IR bands (1515 and 1364 cm^{-1}) are more intense when the incident beam is polarized along the rubbing direction, whereas other IR bands (1733, 1505, and 1246 cm^{-1}) are enhanced when the polarization is perpendicular to the rubbing direction. When intensity differences are ignored, the spectra measured from the rubbed and unrubbed films are identical. This result suggests that there was no transfer of material from the polymeric fibers of the rubbing velvet fabric to the PI film surface during rubbing.

In addition to the IR spectroscopic studies described above, further IR spectroscopic measurements using a linearly polarized IR light source were conducted on the rubbed PI film as a function of the angle of rotation of the film. These measurements were carried out to elucidate the nature of the reorientation of the polymer chains during the rubbing process. The peak intensities of selected IR bands are plotted in Figure 5 against the angle of rotation of the film as polar diagrams. As seen in parts a and b of Figure 5, 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 polymer chains, to be reoriented parallel to the rubbing direction.

(7) (a) Shin, T. J.; Lee, B.; Youn, H. S.; Lee, K.-B.; Ree, M. *Langmuir* **2001**, *17*, 7842. (b) Hasegawa, R.; Yasushi, M.; Sasaki, H.; Ishibashi, M. *Jpn. J. Appl. Phys.* **1996**, *35*, 3492. (c) Hietpas, G. D.; Sands, J. M.; Allara, D. L. *Macromolecules* **1998**, *31*, 3374. (d) Li, W. S.; Shen, Z. X.; Zheng, J. Z.; Tang, S. H. *Appl. Spectrosc.* **1998**, *52*, 985. (e) Rabolt, J. F.; Burns, F. C.; Schlotter, N. E.; Swalen, J. D. *J. Chem. Phys.* **1983**, *78*, 946.

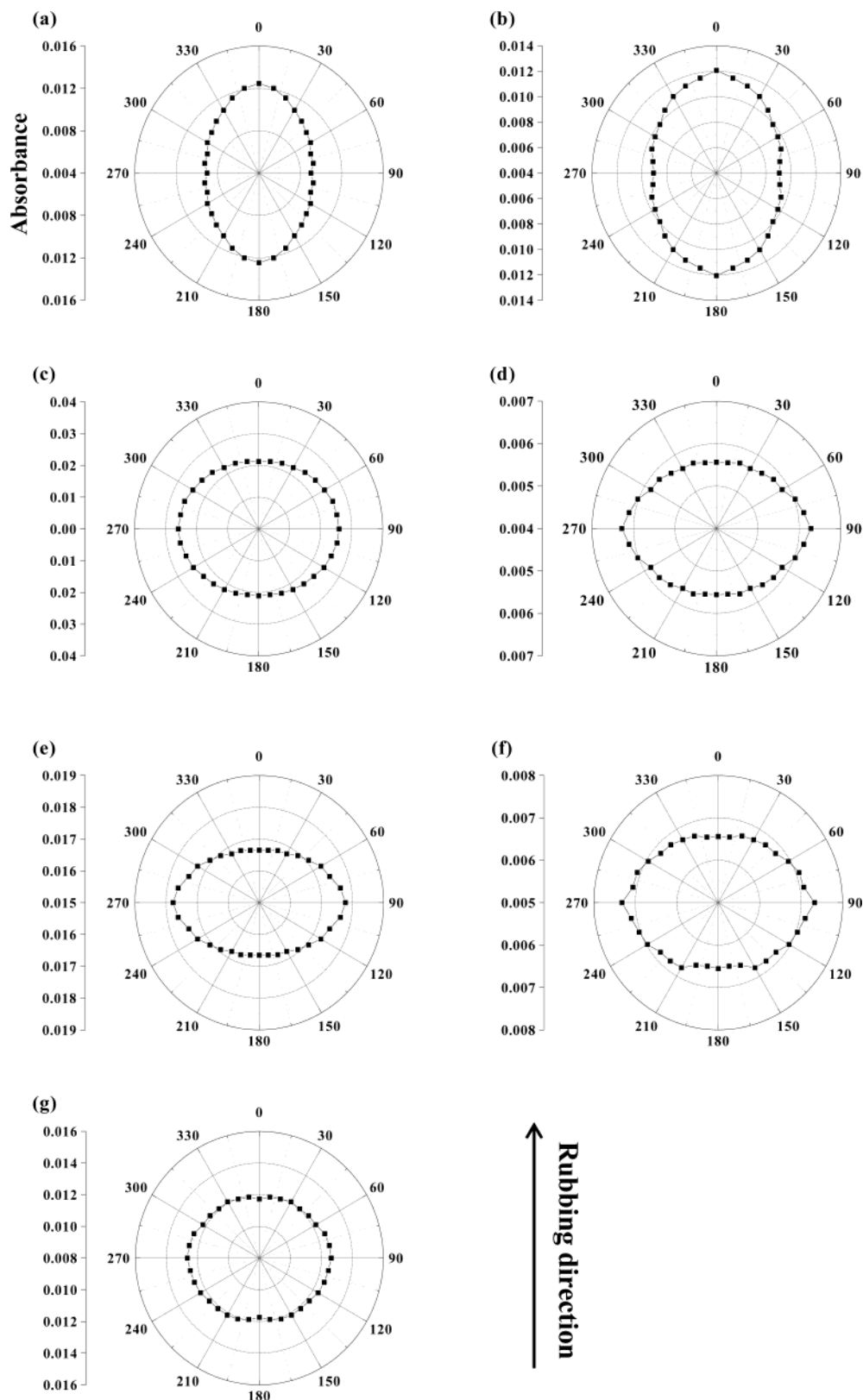


Figure 5. Polar diagrams of the intensities of selected vibrational peaks, measured by linearly polarized IR spectroscopy, of a C8-PMDA-PDA PI film rubbed with a rubbing density of 180 as a function of the angle of rotation of the film: (a) $\nu(\text{C}-\text{N})$ at 1364 cm^{-1} ; (b) $\nu(\text{C}=\text{C}_{\text{PDA}})$ at 1515 cm^{-1} ; (c) $\nu_{\text{as}}(\text{C}=\text{O})$ at 1733 cm^{-1} ; (d) $\nu(\text{C}-\text{O})$ at 1246 cm^{-1} ; (e) $\nu(\text{C}=\text{C}_{\text{phenyloxy}})$ at 1505 cm^{-1} ; (f) $\nu_{\text{as}}(\text{CH}_2)$ at 2923 cm^{-1} ; (g) $\nu_{\text{s}}(\text{CH}_2)$ at 2852 cm^{-1} .

In contrast, the asymmetric $\text{C}=\text{O}$ vibration of the imide ring at 1733 cm^{-1} is slightly enhanced when the polarization of the IR beam is perpendicular to the rubbing direction (see Figure 5c). Overall, the polar diagram indicates that the imide $\text{C}=\text{O}$ bond tends to

be oriented perpendicular to the rubbing direction. However, the enhancement of this mode when the polarization of the IR beam is perpendicular to the rubbing direction is only weak, probably because of the fact that the axis of this $\text{C}=\text{O}$ bond is not exactly

perpendicular to the polymer main-chain axis, as can be seen in the chemical structure shown in Figure 1. The polar diagrams for the C–O–C vibration at 1246 cm^{-1} and the aromatic C=C vibration of the phenyloxy unit at 1505 cm^{-1} show that these modes are enhanced when the beam polarization is perpendicular to the rubbing direction (see Figure 5d,e). This suggests that the long axis of the phenyloxy unit in the side group is aligned perpendicular to the polymer main-chain axis.

Parts f and g of Figure 5 show the polar diagrams for the CH_2 asymmetric and symmetric stretching vibrations at 2923 and 2852 cm^{-1} , respectively. Both of 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*-octyl end of the side group is oriented parallel to the rubbing direction.

Collectively, the IR results indicate that rubbing the film surface causes a reorientation of the polymers to form a structure in which both the polymer main chains and the *n*-octyl side groups are oriented parallel to the rubbing direction, and the phenyloxy side-group units are oriented perpendicular to the rubbing direction.

LC Alignment. We now consider the ability of the rubbed C8-PMDA-PDA PI film to align LC molecules. In these experiments, a mixture of the nematic LC 5CB and the dichroic dye Disperse Blue 1 (1.0 wt % with respect to the amount of the LC) was placed in a cell whose top and bottom surfaces were C8-PMDA-PDA PI films that had been rubbed in opposite directions at a rubbing density of 180; Disperse Blue 1 was chosen as the dichroic dye because it aligns with 5CB. Figure 6a shows a polar diagram of the linearly polarized light absorbance of Disperse Blue 1 in the LC cell as a function of the angle of rotation of the cell. This polar diagram indicates that the LC molecules in the cell are uniformly aligned along the rubbing direction, although their alignment has both homogeneous and homeotropic characteristics.

To understand the observed LC alignment, we consider the chemical structures of the molecules in the PI film and the LC (5CB) molecule, as well as the rubbing-induced polymer segmental reorientations and surface morphology discussed in earlier sections.

First, we examine the chemical structures of the PI chain and the 5CB molecule and consider the possible interactions between these structures. The 5CB molecule has dimensions of approximately 1.8 nm (length) $\times 0.25\text{ nm}$ (diameter). This molecular dimension is comparable to that of the chemical repeat unit of the polymer main-chain backbone and of the [4-*n*-(octyloxy)-phenyl]oxy bristle in the PI chain. Therefore, intermolecular interactions between the phenyl ring components of the polymer and the aromatic mesogen unit of the 5CB molecule are possible. As seen in Figure 1, two phenyloxy bristle units per chemical repeat unit in the C8-PMDA-PDA PI main chain are linked to the 1 and 4 positions of the PMDA unit of the backbone. Consequently, the entire side-group structure per repeat unit of the PI polymer contains one more phenyl ring than the repeat unit of the main-chain backbone. These phenyl rings tend to have π - π interactions with the biphenyl rings (i.e., two phenyl rings) of the 5CB LC

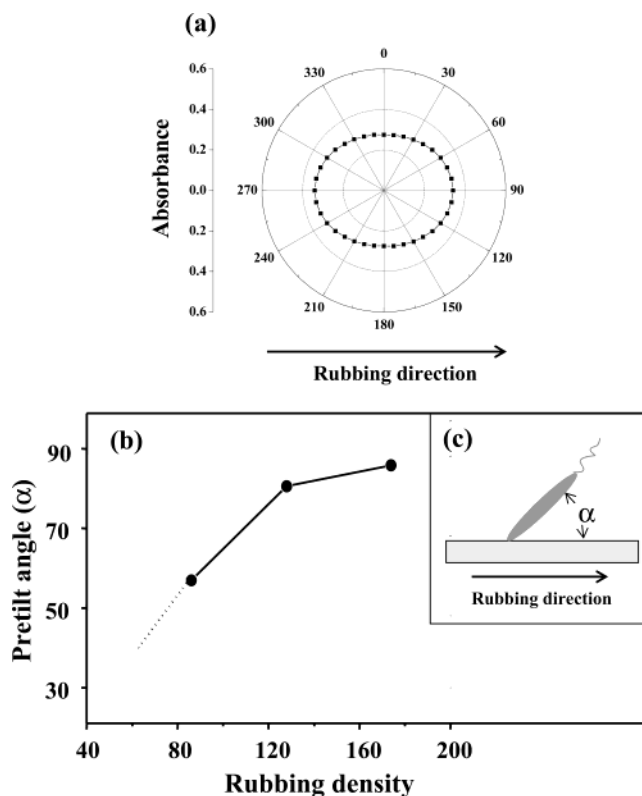


Figure 6. (a) Polar diagram of the linearly polarized light absorbance of the dichroic dye Disperse Blue 1, which aligns parallel to the LC molecules, in a LC cell fabricated with a C8-PMDA-PDA PI film rubbed with a rubbing density of 180, as a function of the angle of rotation of the cell. The light source was a He–Ne laser of wavelength 632.8 nm . (b) Variation of the pretilt angle of the LC molecules in contact with the rubbed film surface as a function of the rubbing density. (c) Pretilt angle of the LC molecules aligned along the rubbing direction.

molecule; the possibility of this kind of interaction has been suggested previously for other PIs and polystyrene.^{8–10} Taking these molecular interactions into account, the entire side-group structure per chemical repeat unit has a better position in the intermolecular interactions with the LC molecules, compared to the main-chain backbone per chemical repeat unit.

Next we consider the contribution of the imide rings to the intermolecular interaction between the PI and LC molecules. The main chain of the PI has two imide rings per chemical repeat unit. For each imide ring, the imide C–N bond forms 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, as described in the earlier Polarized FTIR Spectroscopy section. The imide carbonyl groups have a more polar character than the imide C–N bond; hence, the four carbonyl groups per chemical repeat unit may more favorably interact with LC molecules (in particular, with the polar cyano group of 5CB) than do the two imide C–N bonds. This suggests that the reoriented imide carbonyl groups would also tend to

(8) Sakamoto, K.; Arafune, R.; Ito, N.; Ushioda, S.; Suzuki, Y.; Morokawa, S. *J. Appl. Phys.* **1996**, *80*, 431.

(9) (a) Stohr, J.; Samant, M. G. *J. Electron. Spectrosc. Relat. Phenom.* **1999**, *98*, 189. (b) Stohr, J.; Samant, M. G.; Cossy-Favre, A.; Diaz, J. *Macromolecules* **1998**, *31*, 1942.

(10) Wei, X.; Hong, S.; Zhuang, X.; Goto, T.; Shen, Y. R. *Phys. Rev. E* **2000**, *62*, 5160.

align the LC molecules perpendicular to the rubbing direction.

An additional consideration is that the entire side-group structure has four ether linkages that the main-chain backbone does not have. These ether linkages have a partially polar character and may interact with the LC molecules, influencing these molecules to align perpendicular to the rubbing direction.

To understand the observed LC alignment, we should also consider the reorientation of the *n*-octyl end groups and their role in LC alignment. We have shown in the earlier Polarized FTIR Spectroscopy section that rubbing causes the *n*-octyl end groups to be reoriented parallel to the reoriented main chain rather than to the reoriented phenyloxy units in the bristles. The aliphatic nature of the *n*-octyl end groups may lead to van der Waals interactions between these groups and the aliphatic *n*-pentyl tails of the LC molecules in contact with the rubbed surface, favoring the alignment of LC molecules parallel to the rubbing direction.

Finally, we consider the possible intermolecular interactions of the surface topography with the LC molecules. The microgrooves generated by the rubbing process are a few micrometers in size, and their fine grooves have dimensions of around 100 nm, as discussed in the earlier Surface Topography section. Even taking into account the submicron-sized fine grooves, the dimensions of these surface structures seem too large, compared to that of the LC molecules. This big mismatch of the dimensions may lead to a weak interaction between the fine grooves and the LC molecules. Even though the guiding ability of the grooves to align the LC molecules is expected to be weak, the observed parallel LC alignment, however, suggests the microgrooves and fine grooves developed along the rubbing direction positively contribute to the alignment of the LC molecules along the rubbing direction.

Taking into consideration the factors outlined above, the observation that the LC molecules tend to align along the rubbing direction is believed to be the result of their favorable anisotropic interactions with the reoriented polymer main chains and *n*-octyl bristle end groups along the rubbing direction as well as with the microgrooves and fine grooves developed along the rubbing direction. Moreover, these factors driving the LC molecules to align along the rubbing direction overcome the anisotropic interactions with the perpendicularly reoriented phenyloxy units of the bristles.

In our analysis of the LC alignment, we further tried to determine the pretilt angle (α) of the LC molecules along the rubbing direction, as shown in Figure 6c. The measured α values are plotted in Figure 6b as a function of the rubbing density. Over the rubbing density range of 85–180, the measured α values vary from 55 to 87°. Extrapolation of the data in Figure 6b indicates that the LC pretilt angle should continue to decrease to below 55° as the rubbing density is decreased below 85; however, this could not be confirmed because of the angular detection limit of the measurement technique employed. Conclusively, the LC alignment on the rubbed PI surface has homeotropic to homogeneous characteristics, depending on the rubbing density; homeotropic LC alignment is observed at rubbing densities greater

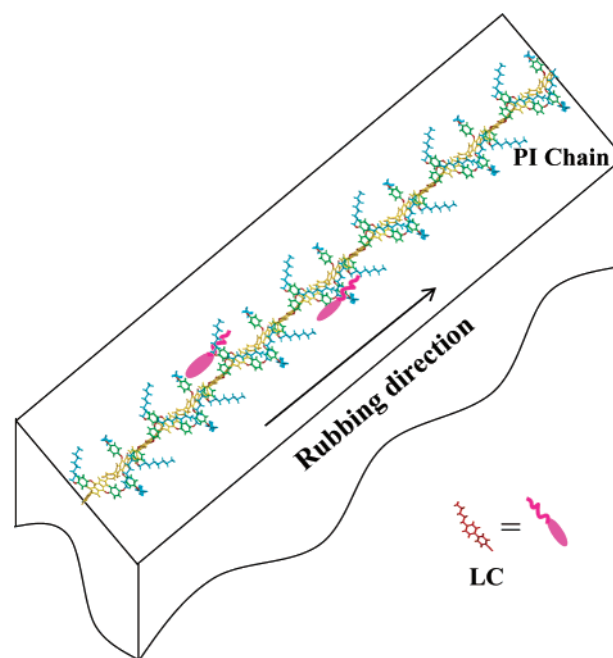


Figure 7. Schematic configuration model of a representative chain of a C8-PMDA-PDA PI molecule at the rubbed film surface and the LC alignment induced by this polymer molecule.

than 80, while homogeneous LC alignment occurs at rubbing densities below 80.

Previous work has shown that, in general, the cyano groups of 4-*n*-alkyl-4'-cyanobiphenyl (*n*CB, *n* = 1–12) LC molecules play a role in keeping these molecules close to a PI surface.¹¹ Moreover, only low pretilt angles are observed for LC molecules at the surfaces of rubbed films of PIs without any side groups.³ Thus, the reoriented main chains and their inclination in the rubbed C8-PMDA-PDA PI film may only make a small contribution to the large pretilt angle of the LCs observed in the present work. These facts suggest that the large pretilt angles reported here are mainly caused by interactions between the reoriented *n*-octyl end groups of the side groups and the aliphatic *n*-pentyl tails of the LC molecules. Consequently, the present results indicate that the preferential reorientation of the alkyl side groups induced by the rubbing process plays a critical role in the generation of the out-of-plane pretilt angle of the LCs.

The present results stand in contrast to the behavior of rubbed films of flexible PIs, which induce large pretilt angles in adjoining LC molecules only when the length of the alkyl side chain exceeds 16 carbons.² Hence, the ability of a rubbed film of C8-PMDA-PDA PI, which has an alkyl side end group of just 8 carbons, to induce very large pretilt angles in adjoining LC molecules represents a novel characteristic of this novel PI.

Taking into account both the LC alignment results and those for the molecular reorientation of the polymer molecules, we generated a molecular configuration model for the C8-PMDA-PDA PI chains reoriented by the rubbing process and for their alignment of LC molecules. Figure 7 displays a schematic configuration model that includes a representative chain of the

(11) Zhuang, X.; Wilk, D.; Marrucci, L.; Shen, Y. R. *Phys. Rev. Lett.* **1995**, *75*, 2144.

reoriented C8-PMDA-PDA PI molecules and two LC molecules aligned by the oriented polymer chain.

Conclusion

C8-PMDA-PDA PI, which is composed of a fully rodlike aromatic backbone and two aromatic–aliphatic bristles per repeat unit of the backbone, was determined to be a positively birefringent brush polymer. Rubbing of the surface of a film of this polymer with a velvet fabric caused the development along the rubbing direction of microgrooves as well as fine grooves whose structure resembled ground beef. The observed surface topography resulted from a combination of two factors: (1) the shear-induced deformation of the polymer film in contact with the fibers of the velvet fabric and (2) the structure of the fibers in the velvet fabric.

Optical retardation measurements showed that rubbing causes the polymer main chains to orient parallel to the rubbing direction. Furthermore, the orientations of the polymer segments at the rubbed surface were quantitatively determined by polarized FTIR spectroscopy; the polymer main chains and the *n*-octyl end groups of the bristles were oriented parallel to the rubbing direction, whereas the phenyloxy units of the bristles were oriented perpendicular to the rubbing direction.

When LC molecules (5CB) were placed in contact with the surface of a rubbed C8-PMDA-PDA PI film, they were found to uniformly align along the rubbing direction. This uniform alignment was attributed to favorable anisotropic interactions with the polymer main chains,

n-octyl end groups of the bristles, and microgrooves and fine grooves, all of which lie parallel to the rubbing direction. These factors favoring LC alignment along the rubbing direction outweighed the anisotropic interactions of the LC molecules with the phenyloxy units of the bristles, which were oriented perpendicular to the rubbing direction. The rubbed PI film surface induced very large LC pretilt angles that ranged from 25 to 87°, depending on the rubbing density. These large pretilt angles were favored despite the relatively short alkyl side end group of C8-PMDA-PDA PI, which contains only half of the 16 carbons generally required to achieve large pretilt angles of LCs. This result suggests that the *n*-octyl end groups of the bristles play a critical role in the generation of large pretilt angles, most likely through favorable interactions between these groups and the aliphatic tails of the LC molecules.

In summary, the present study has revealed the unique LC-aligning ability of C8-PMDA-PDA PI. The properties of this model brush PI make it a promising candidate material for the LC alignment layers used in advanced LC display devices, in particular devices that require large LC pretilt angles or nearly homeotropic LC alignment.

Acknowledgment. This study was supported by KOSEF via the Center for Integrated Molecular Systems and the Center for Advanced Functional Polymers and by the Ministry of Education (BK21 Project).

CM034055M