Sequence of Rubbing-Induced Molecular Segmental Reorientations in the Nanoscale Film Surface of a Brush Polymer Rod

Boknam Chae,[†] Seung Woo Lee,[†] Byeongdu Lee,[†] Wooyoung Choi,[†] Seung Bin Kim,*,[†] Young Mee Jung,[†] Jin Chul Jung,*,[‡] Kyung Hoon Lee,[‡] and Moonhor Ree*,[†]

Department of Chemistry, BK21 Program, Division of Molecular and Life Sciences, Center for Integrated Molecular Systems, Polymer Research Institute, and 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: April 10, 2003; In Final Form: August 27, 2003

Poly(*p*-phenylene-3,6-bis(4-(*n*-butoxy)phenyloxy)pyromellitimide) (C4-PMDA-PDA PI), a well-defined model brush polymer composed of a rodlike polymer backbone with two bristles per repeat unit, was the first reported polyimide to align liquid crystals perpendicular to the rubbing direction at the rubbed film surface. In the present study, we used polarized infrared (IR) spectroscopy and 2D correlation analyses of the resulting IR spectra to study nanoscale films of C4-PMDA-PDA PI rubbed at various rubbing densities. The results of these studies allowed us to establish the nature and sequence of the rubbing-induced segmental reorientations that occur in the polymer molecules at the film surface. The rubbing process was found to reorient the fully rodlike polymer backbones and the *n*-butyl bristle end groups such that they lay parallel to the rubbing direction. In contrast, rubbing caused the phenyloxy bristle units to reorient to a direction perpendicular to the rubbing direction. These reorientations of the polymer's main chain and bristles became more pronounced with increasing rubbing density, and the rubbing process had a greater effect on the polymer's main chains than on the bristles. The rubbing-induced reorientations 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. It was additionally evident that the rubbing process reorients the imide rings biaxially, that is, both along the rubbing direction and out of the plane. This biaxial reorientation was found to be accompanied by a biaxial reorientation of the bristles chemically bonded to the PMDA unit that includes the imide rings. In particular, increasing the rubbing density enhanced the out-of-plane reorientation of the imide rings. In contrast, no rubbing-induced inclination of the reoriented imide rings (i.e., the polymer's main chains) was detected.

Introduction

Polyimides (PIs) are widely used as liquid crystal (LC) alignment layers in LC flat-panel display devices because of their many advantageous properties, which include excellent optical transparency, adhesion, heat resistance, dimensional stability, and insulation.[1] At present, the only technique adopted in the LC display industry to treat the surfaces of the PI films used as alignment layers is rubbing with a velvet fabric. This rubbing process generates microgrooves and reorients the PI molecules at the surface of the film such that LC molecules adjacent to the rubbed surface are aligned into a uniform arrangement with a restricted range of pretilt angles.[2] Given the importance of LC alignment in the performance of LC displays, numerous studies have been carried out to develop high-performance alignment layer materials and to understand the mechanism behind the alignment of LC molecules on rubbed polymer surfaces.[1−6] These previous studies have uncovered a number of PI materials that, when fabricated as a film and rubbed, align LC molecules parallel to the rubbing direction. A variety of models have been proposed to explain the surface anchoring and alignment mechanism of the LC molecules.[3−6] Among the models proposed for the alignment process, the microgroove mechanism[3] and the anisotropic polymer chain reorientation mechanism[4,6] have received the most attention. However, the sequence and nature of the molecular events induced by rubbing, which are critical to the rubbing-induced transformation of the film surface, have yet to be investigated in detail.

Recently, we presented the first report of a PI material that can induce the alignment of LC molecules perpendicular to the rubbing direction.[6] This PI, poly(*p*-phenylene 3,6-bis(4-(*n*-butoxy)phenyloxy)pyromellitimide) (C4-PMDA-PDA PI), is a well-defined brush polymer composed of a fully rodlike backbone and two aromatic−aliphatic bristles per repeat unit of the polymer backbone. Atomic force microscopy (AFM) imaging of the surface of rubbed films of C4-PMDA-PDA PI revealed micro- and fine grooves along the rubbing direction, and polarized infrared (IR) spectroscopic analysis showed that rubbing causes the polymer's main chains to reorient along the rubbing direction, as previously observed for the rubbed surfaces of other PI materials.[1−5] However, the aromatic−aliphatic bristles were found to be reoriented perpendicular to the rubbing direction. These reoriented bristles were found to play a major role in the perpendicular LC alignment observed in LC cells fabricated from rubbed C4-PMDA-PDA PI films. The alignment

* To whom all correspondence should be addressed. E-mail: ree@postech.edu, sbkim@postech.edu. Tel: +82-54-279-2120 (M.R.), +82-279-2106 (S.B.K.). Fax: +82-54-279-399.
† Department of Chemistry.
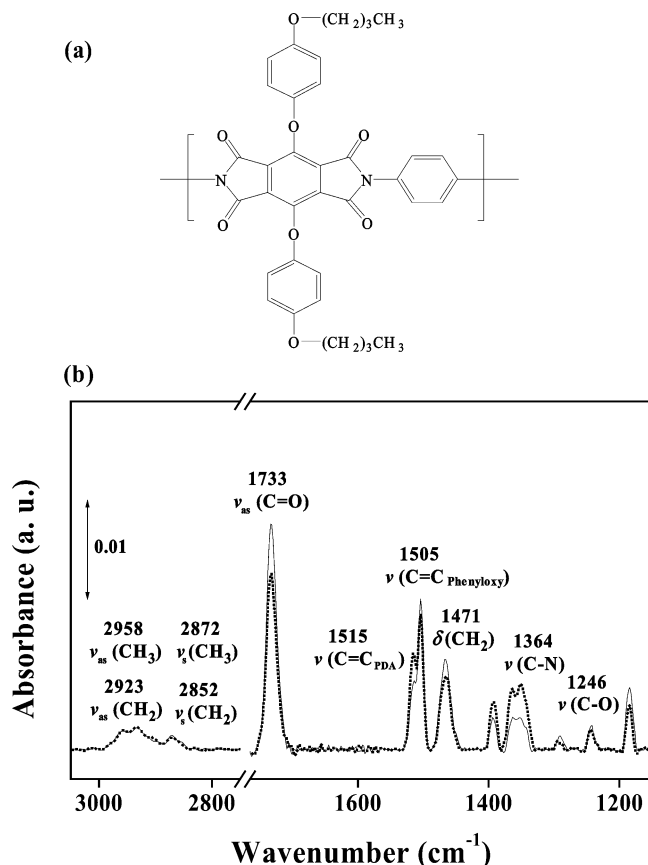‡ Department of Materials Science & Engineering and Center for Advanced Functional Polymers.

Figure 1. (a) Chemical structure of a fully rodlike polyimide containing 4-*n*-butoxyphenyloxy bristles (C4-PMDA-PDA PI). (b) FTIR dichroic spectra measured from a film of C4-PMDA-PDA PI rubbed with a rubbing density of 40. Solid and dashed lines indicate the polarized FTIR spectra perpendicular and parallel to the rubbing direction, respectively.

mechanism proposed on the basis of these results attributes the alignment of LC molecules perpendicular to the rubbing direction to favorable anisotropic interactions with the oriented bristles, which overcome the interactions of the LC molecules with the main chains and micro- and fine grooves that are oriented parallel to the rubbing direction.

In the present study, we extended our investigation of this interesting model brush PI. Specifically, we used polarized IR spectroscopy and 2D correlation analyses of the resulting IR spectra to elucidate the rubbing-induced chain-segment reorientations and their sequence at the surfaces of C4-PMDA-PDA PI films. The polarized IR spectra were further examined by orientation function analysis to get more information on the rubbing-induced chain-segment reorientations.

Experimental Section

A poly(amic acid) (PAA) precursor of C4-PMDA-PDA PI (Figure 1a) was prepared in *N*-methyl-pyrrolidone (NMP) from 3,6-bis(4-(*n*-butoxy)phenyloxy)pyromellitic dianhydride (C4-PMDA) and 1,4-phenylene diamine (PDA), as described previously.[7] The PAA precursor had an inherent viscosity of 0.81 at a concentration of 0.1 g/dL in NMP at 25.0 °C. The PI films were prepared by spin casting of the PAA solution onto calcium fluoride (CaF$_2$) windows (25-mm diameter × 2-mm thickness) for IR spectral measurements, 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 measured to have a thickness

of around 200 nm using a spectroscopic ellipsometer (J. A. Woollam Company, model M-44) and an alpha stepper (Veeco Company, model Tektak3). The PI films coated onto both substrates were rubbed using a laboratory rubbing machine (Wande Company) with a roller covered by a cellulose fabric (Yoshikawa Company, YA-20-R).[1,6] In the rubbing process, the rubbing density (*L/l*) was varied by changing the cumulative rubbing time at a constant rubbing depth (0.35 mm): $L/l = N[(2\pi r n/60v) - 1]$ where *L* is the total length of the rubbing cloth that contacts a certain point of the polymer film (mm), *l* is the contact length of the circumference of a rubbing roller (mm), *N* is the cumulative number of rubbings, *n* and *r* are the speed (rpm) of and the radius (cm) of the rubbing roller (rpm), respectively, and *v* is the velocity (cm/s) of the substrate stage.[1,6]

Fourier transform infrared (FTIR) spectral measurements were carried out on a Bomem DA8 FTIR spectrometer equipped with a polarizer (single diamond polarizer, Harrick Scientific). PI samples were installed perpendicular to the incident beam direction. FTIR spectra were measured with the infrared beam polarized parallel or perpendicular to the rubbing direction and were recorded at 4-cm^{-1} resolution with a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector under a pressure of approximately 1.0 Torr. To ensure a high signal-to-noise ratio, 256 scans were coadded. 2D correlation analysis was performed using an algorithm based on the numerical method developed by Noda.[8] The 2D correlation analysis was carried out after baseline correction of the FTIR spectra. The subroutine KG2D,[9] composed in Array Basic language (GRAMS/386; Galactic Inc., Salem, New Hampshire), was employed for the 2D correlation analyses.

Results and Discussion

Dichroic FTIR Spectroscopy and 2D Map Representation. Figure 1b presents dichroic FTIR spectra of a film of C4-PMDA-PDA PI rubbed at a rubbing density of 40, which were measured in transmission mode with the IR-polarized beam parallel and perpendicular to the rubbing direction, respectively. The assignments of the vibrational modes indicated on the spectra were made according to results previously reported for the PI[6] and other conventional PIs.[10] The FTIR spectrum of the rubbed film recorded with the IR beam polarized parallel to the rubbing direction differs from that recorded with the beam polarized perpendicular to the rubbing direction; this anisotropy arises from the preferential orientation of molecules in the film plane, as described previously in a report of the results of prism coupling, optical retardation, and polarized IR spectral measurements.[6]

To obtain information on the rubbing-dependent behaviors of vibrational bands associated with particular molecular segments in the C4-PMDA-PDA PI film, transmission FTIR spectra were measured with the IR beam polarized parallel or perpendicular to the rubbing direction at various rubbing densities. Figure 2a shows polarized FTIR spectra of PI films rubbed at a range of rubbing densities, recorded with the IR beam polarized perpendicular to the rubbing direction. In these spectra, the vibrational bands at 1733, 1515, 1505, 1364, and 1246 cm^{-1} show significant intensity changes as the rubbing density is varied. The degree of reorientation of moieties giving rise to the individual vibrational bands observed in Figure 2a can be more readily seen by means of a 2D map representation in which the first derivative of the IR spectrum with respect to the rubbing density is plotted over the space of wavenumber and rubbing density, as shown in Figure 2b.

The 2D map in Figure 2b clearly shows that the intensities of the vibrational modes at 1515 and 1364 cm^{-1}, which originate

Segmental Orientations in Brush Polymer Rod Films

J. Phys. Chem. B, Vol. 107, No. 43, 2003 **11913**
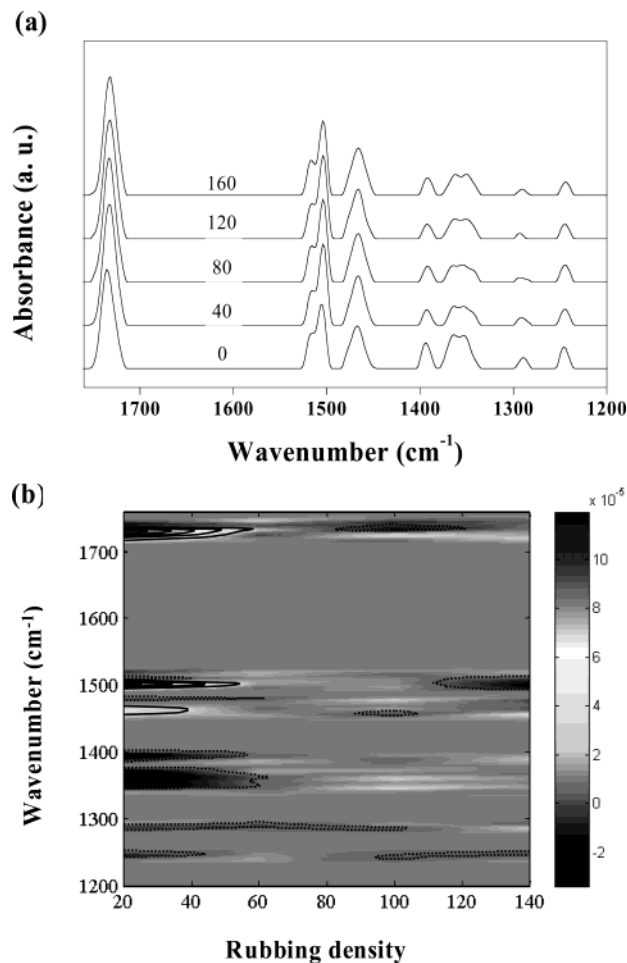
(a)

(b)

Figure 2. (a) Polarized FTIR spectra of a rubbed C4-PMDA-PDA PI film for an alignment perpendicular to the rubbing direction with rubbing density. (b) 2D map of the first derivative with respect to rubbing density ($\Delta A/\Delta$RD) of the polarized FTIR spectra in a, where ΔA and ΔRD denote the absorption difference in the spectrum and the rubbing density difference, respectively. Solid and dashed lines indicate positive and negative $\Delta A/\Delta$RD at a given wavenumber, respectively.

from the phenyl ring and C−N bond of the polymer's main chain, respectively, whose transition dipole moments are parallel to the rubbing direction, rapidly decrease with the commencement of rubbing and then slowly decrease with further increases in the rubbing density. In particular, the intensity drop of the band at 1515 cm^{-1} is still discernible at rubbing densities greater than 115. These variations in band intensity indicate that the preferential reorientation of the rodlike polymer's main chains along the rubbing direction is mainly brought about by rubbing at rubbing densities up to around 60 and that further increases in the rubbing density lead to a very gradual enhancement of the main chain reorientation. This observation is consistent with previous results derived from optical retardation measurements.[6]

Additional information on the reorientation of the polymer's main chain can be obtained from the asymmetric C=O stretching band of the imide ring at 1733 cm^{-1} because the transition dipole moment of this vibrational mode is perpendicular to the polymer's main chain. As seen in Figure 2b, the intensity of this vibration rapidly increases on initial rubbing, reaches a maximum at a rubbing density of 60, and then slowly increases with further increases in the rubbing density up to around 80. This indicates that the preferential reorientation of the polymer's main chain along the rubbing direction is significantly improved over the rubbing density range up to 80,

which is consistent with the behavior of the vibrational modes at 1515 and 1364 cm^{-1}. However, at rubbing densities higher than 80, the intensity of the asymmetric C=O vibrational band slowly decreases with increasing rubbing density, which is quite different from the behaviors of the other vibrational bands.

In fact, a previous study of C4-PMDA-PDA PI films[6] showed that the optical retardation of these films rapidly increases with rubbing density up to a rubbing density of 60 and then more slowly increases with further increases in the rubbing density, finally leveling off above a rubbing density of 210. This result would lead us to expect an increase in the intensity of the C=O asymmetric vibrational mode with increasing rubbing density, which is not the case in the results presented here. Thus, the observation in the present work that the intensity of this mode decreases at rubbing densities greater than 80 must be accounted for in any explanation of the rubbing-dependent reorientation of the imide ring; this matter is investigated in detail in the next section by means of an orientation function analysis.

The intensity of the vibrational mode at 1505 cm^{-1} (originating from the phenyl ring of the bristle), whose transition dipole moment is perpendicular to the rubbing direction, rapidly increases on initial rubbing over the rubbing density range of 0 to 40 and then slowly increases with further increases in rubbing density up to 115. This trend in the IR intensity indicates that the preferential reorientation of the bristles perpendicular to the rubbing direction is mainly achieved by rubbing at rubbing densities up to around 40 and that further increases in the rubbing density give rise to only a gradual consolidation of the bristle reorientation. However, at rubbing densities greater than 115, the IR intensity decreases slightly with increasing rubbing density. This intensity variation may shed additional light on the reorientational behavior of the bristles and is discussed further in the next section.

Orientation Function Analysis. To understand the intensity drops of the asymmetric C=O vibrational mode at rubbing densities greater than 80, as observed in Figure 2, this band was examined in detail using orientation function analysis as follows. We first apply a uniaxial orientation function analysis to the rubbing-dependent reorientation of the asymmetric C=O vibrational mode, which is assumed to occur in the film plane. The reorientation distributions of the vibrational band can be expressed by the uniaxial orientation function **F** = (dichroic difference, $\Delta A_{xy} = A_x - A_y$)/(total absorbance obtained before rubbing, A).[11] This function takes on a value of **F** = 1.0 when the transition dipole moment of the asymmetric C=O vibrational mode is parallel to the rubbing direction and a value of **F** = −0.5 when the transition dipole moment is perpendicular to the rubbing direction. As seen in Figure 3a, the value of **F** for the asymmetric C=O vibrational band is negative over the entire rubbing density range considered, confirming that rubbing causes the C=O vibrational mode is be reoriented perpendicular to the rubbing direction. This orientation of the C=O group indicates that the imide ring (i.e., the polymer's main chain) is aligned along the rubbing direction. Given the observation presented above that increasing the rubbing density always enhances the alignment of the polymer's main chains along the rubbing direction, we would expect the orientation function **F** to decrease monotonically with increasing rubbing density. Contrary to this prediction, however, the **F** value increases slightly on increasing the rubbing density from 40 to 160 (Figure 3a). Consequently, the uniaxial orientation function approach employed here is inappropriate for analyzing the rubbing-dependent orientation of the asymmetric C=O vibrational mode.
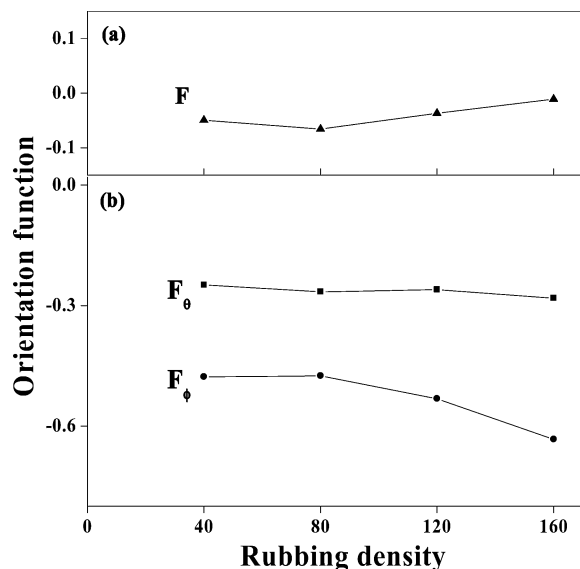
Figure 3. (a) Uniaxial and (b) biaxial orientation functions of the $\nu_{as}(C=O)$ band at 1733 cm^{-1} determined from C4-PMDA-PDA PI films rubbed at various rubbing densities.

To overcome the shortcomings of the uniaxial orientation function approach, we turn to biaxial orientation function analysis as a superior alternative. Assuming that the imide ring is not distributed isotropically in the out-of-plane (z) direction, the preferred reorientations to the in-plane (xy) plane and the out-of-plane (z) plane of the asymmetric C=O vibrational mode are expressed by the orientation functions[12]

$$\mathbf{F}_{\theta(xy\,plane)} = \frac{\left\{ \begin{array}{l} 3 \times (\text{absorbance along the rubbing direction, } A_x)/ \\ (\text{total absorbance obtained before rubbing, } A) - 1 \end{array} \right\}}{2}$$

and

$$\mathbf{F}_{\phi(z\,plane)} = \text{dichroic difference, } \Delta A_{yz} = \frac{A_y - A_z}{A_y + A_z}$$

where A_i is the absorbance of IR radiation polarized in the i direction. These functions have the following properties: (1) when the transition dipole moment of the asymmetric C=O vibration mode is parallel to the rubbing direction (x axis) in the film plane, $\mathbf{F}_\theta = 1$ and $\mathbf{F}_\phi = 0$; (2) when the transition dipole moment is parallel to the y axis in the film plane, $\mathbf{F}_\theta = -0.5$ and $\mathbf{F}_\phi = 1$; and (3) when the transition dipole moment is parallel to the z axis, $\mathbf{F}_\theta = -0.5$ and $\mathbf{F}_\phi = -1$. In this study, A_z is determined by subtracting absorbances A_x and A_y from the total absorbance A. Using the above relationships, $\mathbf{F}_\theta$ and $\mathbf{F}_\phi$ of the C=O band (1733 cm^{-1}) were calculated at various rubbing densities. As shown in Figure 3b, both $\mathbf{F}_\theta$ and $\mathbf{F}_\phi$ are negative at all of the rubbing densities considered.

The value of $\mathbf{F}_\theta$ (the in-plane component of the overall orientation function) decreases on initial rubbing and then varies very little with further increases in the rubbing density (Figure 3b) This result suggests that the initial rubbing at a rubbing density of less than 80 caused the asymmetric C=O vibrational mode to reorient in the film plane to a direction perpendicular to the rubbing direction and that the reorientation achieved during the initial rubbing is not further enhanced with further increases in the rubbing density.

The value of $\mathbf{F}_\phi$ (the out-of-plane component of the overall orientation function), however, is approximately -0.48 for rubbing densities of 40 and 80 but thereafter rapidly decreases with increasing rubbing density. This trend in the out-of-plane reorientation could potentially originate from two types of molecular reorientation behavior during the rubbing process. The first possibility is the inclination of the polymer chains reoriented along the rubbing direction. However, this possibility can be ruled out because such an inclination of the polymer chains would cause a decrease in the optical retardation with increasing rubbing density, which has previously been shown not to occur.[6] The second possibility is the rotation of the asymmetric C=O vibrational mode toward the out-of-plane direction (i.e., rubbing-induced rotation of the imide ring about the C−N imide bond). This rubbing-induced rotation of the C=O vibrational mode would cause a decrease in the $\mathbf{F}_\phi$ value and also an intensity drop of the C=O vibration mode. Therefore, the decrease in $\mathbf{F}_\phi$ with rubbing density, shown in Figure 3b, is attributed to the out-of-plane reorientation of the imide rings, with the components of the polymer's main chains reoriented along the rubbing direction through the rubbing process.

Consequently, the intensity drop of the asymmetric C=O vibration at rubbing densities greater than 80, as observed in Figure 2, is caused by the rubbing-induced biaxial orientation that is characteristic of the imide ring (i.e., the reorientation of the imide rings along the rubbing direction and the rotation about the C−N bond axis). Furthermore, the out-of-plane reorientation (i.e. rotation) of the imide rings, which strongly accompany the rubbing-induced reorientation of the polymer's main chains along the rubbing direction, is always enhanced with increasing rubbing density.

Taking into account the effect of the rubbing-induced biaxial reorientation discussed above, the intensity drops of the phenyl ring vibration (1505 cm^{-1}) of the bristle observed at rubbing densities greater than 115 might also be attributed to the rotation (i.e., out-of-plane orientation) of the phenyl ring in addition to the reorientation perpendicular to the rubbing direction.

We now consider the effect of the out-of-plane orientation characteristic of the asymmetric C=O vibration on the pretilt angle of LC molecules in contact with the rubbed film surface. At the rubbed PI film surface, the pretilt angle of 4-n-pentyl-4′-cyanobiphenyl (nematic LC) molecules ranged from 25 to 55°, depending on the rubbing density; in fact, pretilt angles outside of this range could not be measured because of the measurement limits of the tool employed. The large pretilt angles of the LC molecules may be linked to the biaxially reoriented imide rings. As seen in Figure 1, the two imide rings in the chemical repeat unit of the polymer chain are chemically bonded to the phenyl ring that has two bristles (i.e., 4-(n-butoxyphen-yloxy) side groups), one at the 3 position and the other at the 6 position. Thus, the rubbing-induced biaxial reorientation of the imide ring would cause the bristles to rotate toward the out-of-plane direction, and the out-of-plane bristles may induce the LC molecules to have large pretilt angles.

2D-Polarized FTIR Correlation Analysis. To obtain detailed information about the sequence of events involved in the reorientations of the polymer segments, we analyzed the polarized FTIR dichroism difference spectra using a 2D correlation approach. The 2D correlation spectra were constructed from five spectra measured at rubbing density intervals of 40 over the rubbing density range of 0 to 160. Figure 4 shows variations in the synchronous and asynchronous 2D FTIR correlation spectra of the PI film with rubbing density in the range of 1300 to 1760 cm^{-1}. A power spectrum extracted along
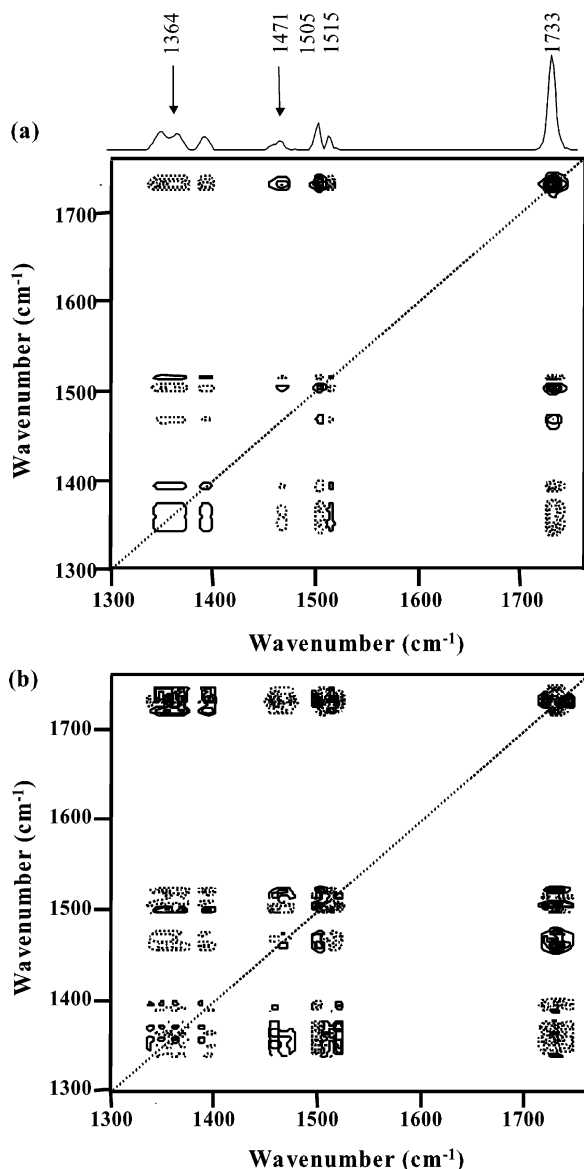
Segmental Orientations in Brush Polymer Rod Films

J. Phys. Chem. B, Vol. 107, No. 43, 2003 **11915**

Figure 4. (a) Synchronous and (b) asynchronous 2D correlation spectra in the region from $1300-1760$ cm^{-1} constructed from IR spectra of C4-PMDA-PDA PI films rubbed at various rubbing densities. Solid and dashed lines indicate positive and negative cross peaks, respectively.

the diagonal line of the synchronous 2D correlation spectrum is shown at the top of Figure 4a.

In the synchronous 2D FTIR correlation spectrum (Figure 4a), the autopeaks at 1471 and 1505 cm^{-1} and those at 1364, 1515, and 1733 cm^{-1} originate from the bands corresponding to the vibrational motions of the bristles and the main chain in the PI film, respectively. The intensity changes of the 1364- and 1733-cm^{-1} bands with changing rubbing density suggest that the imide ring is strongly influenced by the rubbing process. According to the power spectrum, the band at 1515 cm^{-1} is more strongly influenced by the rubbing process than that at 1505 cm^{-1}, suggesting that the PDA units in the polymer backbone are more strongly influenced by the rubbing process than the phenyloxy units in the bristles. These observations collectively suggest that the rubbing process strongly induces local reorientational motions in the segments of the main chain and the bristles, despite the fully rodlike nature of the polymer backbone.

In addition to the autopeaks, the synchronous 2D FTIR correlation spectrum contains several cross peaks in the spectral

region from $1300-1760$ cm^{-1}, which is associated with the molecular segments of the PI film. Positive cross peaks appear at (1505, 1733), (1505, 1471), and (1515, 1364) cm^{-1}. The positive cross peak at (1515, 1364) cm^{-1} shows not only the reorientation direction of these two vibrational modes originating from the main chain (which is parallel to the rubbing direction) but also that the rubbing process cooperatively reorients the polymer backbone. The positive cross peak at (1505, 1733) cm^{-1} shows that these two modes (phenyl ring of the bristle and asymmetric C═O) are aligned in the same direction; from the analysis given earlier in this paper, we know that they are aligned perpendicular to the rubbing direction. The existence of a positive cross peak at (1505, 1471) cm^{-1} indicates that the motion of the phenyloxy unit in the bristle strongly correlates with that of the *n*-butyl end group in the bristle. This suggests that the rubbing-induced reorientation of these groups is cooperative. Given that the CH$_2$ deformational mode of 1471 cm^{-1} possesses a dipole moment vector perpendicular to the *n*-butyl chain axis, we additionally conclude that the *n*-butyl bristle end is reoriented parallel to the rubbing direction that coincides with the reorientation direction of the polymer's main chain but is perpendicular to the reorientation direction of the phenyloxy bristle unit.

The synchronous 2D FTIR correlation spectrum additionally contains negative cross peaks at (1505, 1515), (1505, 1364), (1733, 1515), (1733, 1364), and (1471, 1515) cm^{-1}, indicating that, for each of these pairs of modes, the reorientation direction of one vibrational mode is perpendicular to that of the other vibrational mode. Given that each of the negative cross peaks arises from the correlation between one mode from the polymer's main chain and one from the aromatic ring in the bristle, we conclude that the reorientation direction of the polymer's main chain is perpendicular to that of the aromatic ring in the bristle. These results are in good agreement with those from the 2D map in Figure 2(b).

Figure 4(b) shows the asynchronous 2D FTIR correlation spectrum. In this spectrum, the bands of the polymer chain segments can be differentiated. The sequence of the rubbing-induced reorientations of the molecular segments in the main chain and in the bristles was determined according to a procedure reported previously.[8] The cross peaks at (1515, 1733) and (1515, 1364) cm^{-1} between the phenyl ring vibration at 1515 cm^{-1} in the PDA unit and the imide ring modes at 1733 and 1364 cm^{-1} in the main chain indicate that the PDA phenyl ring is more sensitive to changes in rubbing density than the imide ring. The cross peak at (1733, 1364) cm^{-1} between the asymmetric C═O stretching and C─N stretching modes of the imide ring indicates that the C═O group is more sensitive to changes in rubbing density than the C─N group in the imide ring. The cross peak at (1505, 1471) cm^{-1} between two groups in the bristles, the phenyl ring vibration in the phenyloxy unit at 1505 cm^{-1}, and the vibration of the aliphatic end group at 1471 cm^{-1} indicate that the phenyloxy unit is more sensitive to changes in rubbing density than the aliphatic *n*-butyl end group. Furthermore, the cross peak at (1505, 1364) cm^{-1} between the vibration of the phenyl ring in the phenyloxy unit at 1505 cm^{-1} and C─N stretching in the main chain at 1364 cm^{-1} indicates that the phenyloxy unit of the bristle is more sensitive to changes in rubbing density than the C─N bond in the main chain. Collectively, the above results indicate that segments in the main chain and bristles that have greater rigidity, such as the imide ring and aromatic rings, tend to change more rapidly with reorientation at lower rubbing densities than flexible segments such as the aliphatic *n*-butyl end group. The sequence of

reorientations in the main chain and bristles can be established by examining the cross peaks between the phenyl ring vibration of the PDA unit and the vibrational modes in the bristles, which indicate that the main chain unit changes more rapidly than the bristles. Taken together, the observations presented above suggest that the rubbing-induced reorientations of the polymer segments occur in the following sequence: PDA phenyl ring (main chain), imide ring (main chain), phenyloxy unit (bristle), imide C−N bond (main chain), and aliphatic *n*-butyl end group (bristle).

Conclusions

To elucidate the molecular rearrangements induced by rubbing the surface of a film of the well-defined brush polyimide C4-PMDA-PDA PI, we carried out a detailed study of the vibrational bands associated with the molecular segments of this PI as a function of rubbing density using polarized FTIR spectroscopy and 2D correlation analyses.

We found that at the surface of the rubbed film the fully rodlike polymer backbones are preferentially reoriented along the rubbing direction but the bristles are preferentially reoriented perpendicular to the rubbing direction and that these preferential reorientations are enhanced as the rubbing density increases. In particular, we found that the rubbing process strongly induces local segmental reorientations of the PI polymer, despite its rodlike nature, and that this rubbing-induced rearrangement of the polymer segments is cooperative. The rubbing process was found to have a greater effect on the PDA units in the polymer backbone than on the phenyloxy units in the bristles. In addition, the polymer segments undergo rubbing-induced reorientation in the following sequence: PDA phenyl ring (main chain), imide ring (main chain), phenyloxy unit (bristle), imide C−N bond (main chain), and aliphatic *n*-butyl group (bristle).

Additional studies using 2D-polarized FTIR correlation analysis and orientational function analysis showed that the response of the asymmetric C=O vibrational mode to rubbing differs from that of the other vibrational modes considered. Specifically, the rubbing process causes the imide rings (which represent the polymer's main chain) to undergo out-of-plane reorientation in addition to the preferential reorientation along the rubbing direction in the film plane, with this out-of-plane reorientation becoming more pronounced with increasing rubbing density. This biaxial reorientation of the imide rings should be accompanied by a rotation of the bristles toward the out-of-plane direction; this may correlate to the high pretilt angle of LC molecules at the film surface. No evidence of an inclination of the reoriented imide rings (i.e., polymer chains) was found at any of the rubbing densities considered.

References and Notes

(1) (a) Lee, K.-W.; Paek, S.-H.; Lien, A.; During, C.; Fukuro, H. *Macromolecules* **1996**, *29*, 8894. (b) Kim, S. I.; Ree, M.; Shin, T. J.; Jung, J. C. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2909. (c) Kim, S. I.; Pyo, S. M.; Ree, M.; Park, M.; Kim, Y. *Mol. Cryst. Liq. Cryst.* **1998**, 316, 209. (d) Sato, Y.; Sato, K.; Uchida, T. *Jpn. J. Appl. Phys.* **1992**, *31*, L579.

(2) (a) *Liquid Crystals*; Collings, P. J., Ed.; IOP Publishing, Ltd.: Bristol, England, 1990. (b) Collings, P. J.; Patel, J. S., Eds., *Handbook of Liquid Crystal Research*; Oxford University Press: Oxford, England, 1997.

(3) (a) Berreman, D. W. *Phys. Rev. Lett.* **1972**, *28*, 1683. (b) Berreman, D. W. *Mol. Cryst. Liq. Cryst.* **1973**, *23*, 215. (c) Flanders, D. C.; Shaver, D. C.; Smith, H. I. *Appl. Phys. Lett.* **1978**, *32*, 597. (d) Pidduck, A. J.; Bryan-Brown, G. P.; Haslam, S.; Bannister, R.; Kitely, I.; McMaster, T. J.; Boogaard, L. *J. Vac. Sci. Technol., A* **1996**, *14*, 1723. (e) Mahajan, M. P.; Rosenblatt, C. *Appl. Phys. Lett.* **1999**, *75*, 3623.

(4) (a) Oh-e, M.; Hong, S.; Shen, Y. R. *J. Phys. Chem. B* **2000**, *104*, 7455. (b) Toney, M. F.; Russell, T. P.; Logan, J. A.; Kikuchi, H.; Sands, J. M.; Kumar, S. K. *Nature* **1995**, *374*, 709. (c) Miyano, K. *Phys. Rev. Lett.* **1979**, *43*, 51. (d) Ge, J. J.; Li, C. Y.; Xue, G.; Mann, I. K.; Zhang, D.; Wang, S.-Y.; Harris, F. W.; Cheng, S. Z. D.; Hong, S.-C.; Zhuang, X.; Shen, Y. R. *J. Am. Chem. Soc.* **2001**, *123*, 5768. (e) Stöhr, J.; Samant, M. G.; Cossy-Favre, A.; Diaz, J.; Momoi, Y.; Odahara, S.; Nagata, T. *Macromolecules* **1998**, *31*, 1942. (f) Feller, M. B.; Chen, W.; Shen, Y. R. *Phys. Rev. A.* **1991**, *43*, 6778.

(5) (a) Castellano, J. A. *Mol. Cryst. Liq. Cryst.* **1983**, *94*, 33. (b) Becker, M. E.; Killan, R. A.; Kosmowski, B. B.; Mlynski, D. A. *Mol. Cryst. Liq. Cryst.* **1986**, *132*, 167. (c) Nazarenko, V. G.; Lavrentovich, O. D. *Phys. Rev. E* **1994**, *49*, R990. (d) Johannsmann, D.; Zhou, H.; Sonderkaer, P.; Wierenga, H.; Myrvold, B. O.; Shen, Y. R. *Phys. Rev. E* **1993**, *48*, 1889. (e) Durand, G. *Physica A* **1990**, *163*, 94. (f) Barbero, G.; Evangelista, L. R.; Madhusudana, N. V. *Eur. Phys. J.* **1998**, *1*, 327.

(6) Chae, B.; Kim, S. B.; Lee, S. W.; Kim, S. I.; Choi, W.; Lee, B.; Ree, M.; Lee, K. H.; Jung, J. C. *Macromolecules* **2002**, *35*, 10119.

(7) (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.

(8) (a) Noda, I. *Appl. Spectrosc.* **1993**, *47*, 1329. (b) Noda, I.; Dowrey, A. E.; Marcott, C.; Story, G. M.; Ozaki, Y. *Appl. Spectrosc.* **2000**, *54*, 236A. (c) Shin, H. S.; Jung, Y. M.; Oh, T. Y.; Chang, T.; Kim, S. B.; Lee, D. H.; Noda, I. *Langmuir* **2002**, *18*, 5953. (d) Jung, Y. M.; Shin, H. S.; Czarnik-Matusewicz, B.; Noda, I.; Kim. S. B., *Appl. Spectrosc.* **2002**, *56*, 1568. (e) Chae, B.; Lee, S. W.; Ree, M.; Jung, Y. M.; Kim, S. B. *Langmuir* **2003**, *19*, 687.

(9) The program is available from the home page of Professor Yukihiro Ozaki of Kwansei Gakuin University, Sanda, Japan (http://science.kwansei.ac.jp/~ozaki/).

(10) (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.

(11) Buffeteau, T.; Pezolet, M. *Macromolecules* **1998**, *31*, 2631.

(12) (a) Wiesner, U.; Reynolds, N.; Boeffel, C.; Spiess, H. W. *Makromol. Chem. Rapid Commun.* **1991**, *12*, 457. (b) Kaito, A.; Nakayama, K.; Kanetsuna, H. *J. Macromol. Sci., Phys.* **1987**, *26*, 281.