To characterize the reorientations of molecular segments in polymer films treated by rubbing, which is critical information for understanding the effects of the rubbing process, the surface structures of rubbed, nanoscaled films of poly[p-phenylene 3,6-bis(4-n-octoxy)phenyloxy]pyromellitimide (C8-PMDA-PDA PI), a well-defined brush polyimide composed of aromatic–aliphatic bristles set into a fully rodlike polymer backbone (two bristles per repeating unit), were extensively investigated as a function of rubbing density by polarized infrared (IR) spectroscopy in transmission mode and by two-dimensional correlation analyses of these IR spectra. The rubbing process was found to strongly cause local reorientations of the rodlike polymer backbones as well as of the bristles on the film surface. On the surface of a rubbed film, the polymer backbones and the aliphatic n-octyl end groups of the bristles are preferentially reoriented along the rubbing direction, but the phenyloxy units of the bristles are preferentially reoriented perpendicular to the rubbing direction; these preferential reorientations are enhanced as the rubbing density increases. The polymer main chains are more strongly influenced by the rubbing process than are the bristles. This study is the first time that the ordering of the rubbing-induced reorientations of the polymer segments in a rubbed film has been determined; the rubbing-induced reorientations were found to occur in the following sequence: PDA phenyl ring, imide ring, phenyloxy unit, imide C–N bond, and aliphatic n-octyl group. Moreover, it was found that in the rubbing process the imide rings (which make up the polymer main chain) undergo biaxial reorientation (i.e., in-plane reorientation along the rubbing direction and out-of-plane reorientation). In particular, the out-of-plane reorientation of the imide rings is enhanced by increasing the rubbing density.

Introduction

The uniform and unidirectional alignment of liquid crystal (LC) molecules is the most important factor determining the optical and electrical performance of LC flat-panel display devices.1 To achieve the uniform alignment of LC molecules, polyimide (PI) films have widely been used as the alignment layer because of their many advantageous properties.2,3 Before PI can be used as an alignment layer, it must be treated to unidirectionally align the polymer molecules at the surface.2 At present, rubbing with a velvet fabric is the only process used to treat PI film surfaces in the mass-production of LC flat-panel display devices because of its simplicity and control of the LC anchoring energy.4 This rubbing process is known to modify the surface morphology and to reorient the polymer chains in the alignment layer film.3 It is, therefore, not only important to examine the modification of the film surface produced by rubbing but also to determine the rubbing density.
understand the mechanism of rubbing-induced molecular reorientation in the polymer film surface. These issues have been examined in a variety of studies. Atomic force microscopy has been used to study rubbed film surfaces. These studies have shown that as the rubbing depth (density) increases, microgrooves are produced in alignment with the rubbing direction. The anisotropically aligned polymer chains have been examined using optical phase retardation measurements, second harmonic generation, near edge X-ray absorption spectroscopy, and grazing incident X-ray scattering, and polarized infrared spectroscopy. These methods provide information about the surface topography of rubbed polymer films, as well as about the molecular orientations within the film and the thickness of the oriented layer. However, the critical information required for understanding the effects of the rubbing process at the surfaces of films is a characterization of the events involved in the reorientation of polymer chains in the rubbed films, and these events have yet to be investigated in detail.

Two-dimensional (2D) correlation spectroscopy enables the enhancement of the spectral resolution by spreading peaks along the second dimension, simplification of complex spectra consisting of many overlapped peaks, establishment of unambiguous assignments of bands selectively coupled by various interaction mechanisms, and identification of the sequence of the spectral intensity changes by an external perturbation. Moreover, 2D correlation spectroscopy can analyze systematic patterns of subtle spectral changes induced by an external perturbation that are not readily noticeable in conventional one-dimensional spectra. As a result of these advantages, 2D correlation spectroscopy has been applied extensively to interpret numerous spectroscopic data for analytical chemistry, complex reaction kinetics, electrochemistry, photochemistry, and so forth.

In 2D correlation spectroscopy, the spectral intensity is generally plotted as a function of two independent spectral variables. The two orthogonal axes of the spectral variables define the 2D spectral plane, and the spectral intensity is obtained along the third axis normal to the spectral plane. The intensity of a synchronous spectrum generally represents the simultaneous or coincidental changes of the spectral intensity variations measured at two independent spectral variables. An autopeak located at a diagonal line represents the overall susceptibility of the corresponding spectral region to change in spectral intensity as an external perturbation is applied to the system. Cross peaks located at the off-diagonal positions represent simultaneous or coincidental changes of the spectral intensities observed at these variables. The sign of synchronous cross peaks becomes positive if the spectral intensities at the two spectral variables corresponding to the coordinates of the cross peak are either increasing or decreasing together as a function of external variable during the observation interval. However, the negative sign of the cross peaks indicates that one of the spectral intensities is increasing while the other is decreasing. On the other hand, the intensity of an asynchronous spectrum represents sequential or successive changes of spectral intensities measured at $v_1$ and $v_2$. An asynchronous cross peak develops only if the intensities of two spectral features change out of phase (i.e., delayed or accelerated) with each other. The sign of an asynchronous cross peak becomes positive if the intensity change at $v_1$ occurs predominantly before $v_2$ in the sequential order of $t$. It becomes negative if the change occurs after $v_2$. This rule, however, is reversed if the synchronous peak is negative.

Adopting this technique, we recently introduced a new method for 2D data representation that depicts the intensities of the first derivatives of the IR absorbance with respect to temperature on a plot of wavenumber versus temperature. We have also reported the potential of this 2D data representation to identify the photochemical processes of a nanoscaled polymer film.

To better understand the influence of the rubbing process on the surfaces of polymer films, in the present study we have attempted to apply 2D correlation spectroscopy to rubbed films of poly(p-phénylene pyromellitimide) derivative containing 4-n-octoxyphenylxy side groups (C8-PMDA-PDA PI), which is a well-defined brush polymer composed of aromatic-aliphatic bristles set into a fully rodlike polymer backbone (two bristles per repeating unit of the polymer backbone), as shown in Figure 1. To characterize the reorientations of the polymer chains produced at different rubbing densities, we measured the surface orientational distributions of both the main chains and the bristles (i.e., the side groups) of the PI films using linearly polarized Fourier transform infrared (FTIR) spectroscopy. Additional information on the molecular reorientations induced by the rubbing process was obtained by means of 2D map representations of the first derivatives of the IR absorbance with respect to the rubbing density, on a plot of wavenumber versus rubbing density. In addition, we determined the reorientation sequence of the molecular segments in the main chain and in the side groups, using 2D correlation analysis of the dichroic difference FTIR spectra of the PI films.

**Experimental Section**

**Materials and Film Preparation.** The soluble poly(amic acid) (PAA) precursor of C8-PMDA-PDA PI shown in Figure 1 was prepared in N-methyl-pyrrolidone (NMP) from the respective dianhydride and 1,4-phenylene diamine (PDA), according to the following method.

![Chemical structure of the fully rodlike poly(p-phénylene pyromellitimide) derivative containing 4-n-octoxyphenylxy side groups (C8-PMDA-PDA PI).](Image)


method described previously. The PAA precursor has an inherent viscosity of 0.95 at a concentration of 0.1 g/dL in NMP at 25 °C. The PI films were prepared by spin-casting the PAA solution onto calcium fluoride (CaF₂) windows [25 mm (diameter) × 2 mm (thickness)] for the FTIR spectral measurements and onto indium tin oxide glass for the optical retardation 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 a dry nitrogen gas flow at 250 °C for 2 h. The resulting PI films had a thickness of about 200 nm, measured using a spectroscopic ellipsometer (J. A. Woollam Company, model M-44) and an alpha-stepper (Veeco Company, model Tektak3). The PI films coated onto the substrates were rubbed using a laboratory rubbing machine (Wande Company) with a roller covered with rayon velvet rubbrcloth (Yoshikawa Company, YA-20-R). The velvet fabric density was 24,000 fibers/cm²; each fiber had dimensions of 1.85 mm (height) × 15 μm (diameter). The rubbing density (L/I) was varied by changing the cumulative rubbing time for a constant rubbing depth (0.35 mm): L/I = N[(2πrn/60v) − 1] where L is the total length of the rubbing cloth that contacts a certain point of the polymer film (mm), I is the contact length of the circumference of the rubbing roller (mm), N is the cumulative number of rubbings, (r and n) are the speed (rpm) and the radius (cm) of the rubbing roller, respectively, and v is the velocity (cm/s) of the substrate stage.

Measurements. Polarized FTIR spectral 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. FTIR spectra were measured with the infrared beam polarized parallel and perpendicular to the rubbing direction and recorded at a 4 cm⁻¹ resolution with a liquid nitrogen cooled mercury cadmium telluride detector under a pressure of approximately 1.0 Torr. To ensure a high signal-to-noise ratio, 256 scans were accumulated. 2D correlation analysis was performed using an algorithm based on the numerical method developed by Noda et al. The 2D correlation analysis was carried out after baseline correction of the FTIR spectra. A subroutine KG2D14 composed in Array Basic language was employed for the 2D correlation analyses. Optical retardation was measured using a phase retardation analyzer as described elsewhere. In these measurements, the He–Ne laser beam (632.8-nm wavelength) was incident normal to the surface of the film and the transmitted light intensity (= in-plane birefringence × phase) was monitored as a function of the angle of rotation of the film with respect to the surface normal.

Results and Discussion

Optical Retardation. Figure 2a shows a polar diagram of the transmitted light intensity with respect to the angle of rotation of the film, measured for a rubbed film of C8-PMDA-PDA PI. The anisotropy of this polar diagram indicates that at the rubbed film surface the C8-PMDA-PDA PI chains, which are positively birefringent, have been reoriented preferentially along the rubbing direction. The optical retardation (i.e., the in-plane birefringence multiplied by film thickness) is a measure of the preferential reorientation of the PI chain along the rubbing direction and was found to be dependent on the rubbing density of the rubbing process. As seen in Figure 2b, the retardation rapidly increases with the rubbing density up to a rubbing density of 60, then increases more slowly with further increases in the rubbing density, and nearly levels off above a rubbing density of 180.

Polarized FTIR Spectroscopic Analysis. Figure 3 presents two representative dichroic FTIR spectra of the PI film rubbed at a rubbing density of 40, both measured in transmission mode, one with the IR beam polarized perpendicular and parallel to the rubbing direction, respectively.
the aid of a previous study\textsuperscript{15,16} and are summarized in Table 1. The rubbed film produces an anisotropy between the two FTIR spectra, which arises from the preferential molecular orientation in the film plane as described above in Optical Retardation.

To obtain information about the rubbing-dependent behaviors of the vibrational bands associated with the molecular segments of the C8-PMDA-PDA PI film, a series of transmission FTIR spectra were obtained with the IR beam polarized perpendicular to the rubbing direction for various rubbing densities. The FTIR results are shown in Figure 4a. In particular, the vibrational bands at 1733, 1515, 1364, and 1246 cm\textsuperscript{-1} exhibit significant intensity changes with variations in the rubbing density, as is evident in the figure. The band at 1733 cm\textsuperscript{-1} corresponds to the C=O asymmetric stretching vibration of the imide ring. The transition dipole moment of this asymmetric C=O vibration is aligned perpendicular to the axis of the polymer main chain, particularly the imide ring units, so variation in this vibrational band can provide information about the reorientation of the polymer main chains as well as about the reorientation of the imide rings on the rubbed film surface. The intensity of this vibrational band increases with increasing rubbing density, up to a rubbing density of around 80, and then slightly decreases with further increases in the rubbing density. These results indicate that the imide rings (i.e., the polymer main chains) become increasingly aligned with the rubbing direction as the rubbing density increases. On the other hand, the peak at 1505 cm\textsuperscript{-1}, which corresponds to the aromatic C=C vibration of the phenyloxy unit in the side group, is also enhanced with increasing rubbing density. In addition, the band at 1246 cm\textsuperscript{-1}, which corresponds to the stretching vibration of the C\textendash O\textendash C bond in the side group, strengthens as the rubbing density increases. These results indicate that the phenoxy units in the side groups become increasingly aligned with the direction perpendicular to the rubbing direction as the rubbing density increases. In contrast, the band at 1515 cm\textsuperscript{-1}, corresponding to the aromatic C=C vibration of the PDA unit in the polymer backbone, weakens as the rubbing density increases. The intensity of the peak at 1364 cm\textsuperscript{-1}, corresponding to the C\textendash N stretching vibration of the imide bond in the polymer backbone, also decreases with increasing rubbing density. These polarized IR results lead to the conclusion that the reorientation of the polymer main chains to an alignment parallel to the rubbing direction becomes more favorable as the rubbing density increases, which is consistent with that derived from the variation of the intensity of the C=O vibrational band with rubbing density discussed above. Collectively, the polarized IR results lead to the conclusion that, on the surface of the rubbed film, the fully rodlike polymer backbones are preferentially reoriented along the rubbing direction, but the side groups (i.e., the phenoxy unit) are preferentially reoriented perpendicular to the rubbing direction, and that these preferential reorientations are enhanced as the rubbing density increases.

The degree of reorientation of each molecular segment in the polymer film can be determined by presenting the first derivatives of the IR spectral absorbance of Figure 4a with respect to the rubbing density, on a plot of wavenumber versus the rubbing density. As shown in Figure 4b, the intensities of the IR absorption bands change rapidly for rubbing densities near 60, then change more slowly with a further increase of the rubbing density. The transition dipole moments of the vibrational modes at 1505 and 1246 cm\textsuperscript{-1} (originating from the side group) are aligned perpendicular to the rubbing direction, and the intensities of their bands rapidly increase on initial rubbing and then increase more slowly with a further increase of the rubbing density. These results reveal the rubbing-induced reorientation behavior of the side groups on the film surface. On the other hand, the transition dipole moments of the vibrational modes at 1515 and 1364 cm\textsuperscript{-1} (originating from the polymer backbone) are aligned parallel to the rubbing direction, and the intensities of their bands rapidly decrease on initial rubbing and then slowly decrease with further increase of the rubbing density. These results reveal rubbing-induced reorientation behavior of the polymer main chains that is consistent

\begin{table}[h!]
\centering
\caption{Characteristic Vibrational Bands of C8-PMDA-PDA PI}
\begin{tabular}{ll}
\hline
C8-PMDA-PDA PI & assignment \\
\hline
2958 & $\nu_\text{as}(\text{CH}_3)$ \\
2935 & $\nu_\text{s}(\text{CH}_3)$ \\
2923 & $\nu_\text{s}(\text{CH}_2)$ \\
2872 & $\nu_\text{s}(\text{CH}_2)$ \\
2852 & $\nu_\text{s}(\text{CH}_2)$ \\
1770 & $\nu_\text{C}=\text{C}_{\text{PDA}}$ \\
1733 & $\nu_\text{s}(\text{C} = \text{O})$ \\
1515 & $\nu_\text{C}=\text{C}_{\text{phenyloxy}}$ \\
1471 & $\delta(\text{CH}_2)$ \\
1364 & $\nu_\text{C} = \text{N}$ \\
1246 & $\nu_\text{C} = \text{O}$ \\
\hline
\end{tabular}
\end{table}

\begin{figure}[h!]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{(a) Polarized FTIR spectra of a rubbed C8-PMDA-PDA PI film for an IR beam alignment perpendicular to the rubbing direction for various rubbing densities. (b) 2D map of the first derivatives of the polarized FTIR spectra with respect to variation of the rubbing density (a). Solid and dashed lines indicate $+\Delta A/\Delta R D$ and $-\Delta A/\Delta R D$ at a given wavenumber, respectively. $\Delta A$ and $\Delta R D$ denote the absorption difference in the spectrum and the rubbing density difference, respectively.}
\end{figure}

\begin{thebibliography}{10}
\end{thebibliography}
First, consider the rubbing-dependent orientation of the asymmetric C=O vibrational mode (1733 cm$^{-1}$) in the film plane. For this band, an orientation function $F$ can be calculated using normalized uniaxial orientation distributions, where $F = \text{dichroic difference, } \Delta A_{\text{xy}} = A_x - A_y / \text{total absorbance obtained before rubbing, } A$, if the transition dipole moment of the asymmetric C=O vibration is oriented parallel to the rubbing direction, $F = 1.0$, and if the transition dipole moment is oriented perpendicular to the rubbing direction, $F = -0.5$. As shown in Figure 5a, the orientation function $F$ for the asymmetric C=O vibration is negative over the rubbing density range considered, again confirming that the transition dipole moment of the C=O vibration is oriented perpendicular to the rubbing direction, which means that the imide rings (i.e., the polymer main chains) are oriented along the rubbing direction. However, the value of $F$ increases slightly from $-0.048$ to $-0.025$ as the rubbing density increases from 40 to 160. The PI chains are reoriented toward the rubbing direction by the rubbing process, as already seen from the optical retardation results (Figure 2b), so the orientation function $F$ should always decrease toward the value $-0.5$ as the rubbing density increases. When this point is taken into account, the obtained orientation function results, therefore, suggest that the rubbing-dependent reorientation of the transition dipole moment of the asymmetric C=O vibration does not occur uniaxially in the film plane.

Second, we consider a rubbing-induced biaxiality of the asymmetric C=O vibration as an alternative to the uniaxial orientation approach discussed above by assuming that the imide ring is not distributed isotropically in the out-of-plane direction. The preferred reorientations into the plane (xy plane) and out of the plane (z plane) are then expressed by the orientation functions defined by $F_{\text{xy}}(\text{plane}) = [3 \times \text{total absorbance obtained before rubbing, } A_x]/[(A_x + A_y + A_z)/3]$ and $F_{\text{yz}}(\text{plane}) = [\text{dichroic difference, } \Delta A_{\text{yz}} = A_x - A_z] / \text{total absorbance obtained before rubbing, } A$. When these relationships are used, the $F_\text{xy}$ and $F_\text{yz}$ of the C=O band (1733 cm$^{-1}$) have been estimated for various rubbing densities, and the resulting values are presented in Figure 5b. The value of $F_\text{xy}$ (i.e., the in-plane component of the orientation function) gradually decreases up to a rubbing density of 80 and then drops more slowly to $-0.055$ with further increases in the rubbing density. This indicates that the transition dipole moment of the asymmetric C=O vibration is reoriented toward an alignment perpendicular to the rubbing direction in the film plane with increasing rubbing density and that this directional in-plane reorientation only occurs to a small extent for rubbing densities in the range 80–160. On the other hand, the value of $F_\text{yz}$ (i.e., the out-of-plane component of the orientation function) rapidly decreases ($-0.16$ to $-0.084$) for rubbing densities up to 160. There are two possible molecular reorientation behaviors that might explain the rubbing-dependent out-of-plane reorientation produced by the rubbing process. The first possible factor is the inclination behavior of the polymer chains reoriented along the rubbing direction. If inclination of the reoriented polymer chains takes place during the rubbing process, it should be detectable in the optical retardation measurements as a gradual or slight decrease of the optical retardation with rubbing density. However, no such decrease was observed in the plot of optical retardation versus rubbing density (Figure 2b). Thus, the contribution of such an inclination to the drop in intensity of the asymmetric C=O vibration in the rubbing density range 80–160 is negligible. The second possible factor is the rubbing-induced out-of-plane reorientation of the transition dipole moment of the asymmetric C=O vibrational mode (i.e., the rubbing-induced rotation of the imide ring about the C–N imide bond). Such a rubbing-induced out-
of-plane reorientation of the transition dipole moment of the C=O vibrational mode is in good agreement with the observed variation in $F_o$ as well as with the measured optical retardations. Therefore, the $F_o$ variation with rubbing density shown in Figure 5b is mainly due to the out-of-plane reorientation of the asymmetric C=O vibration (i.e., the out-of-plane reorientation of imide rings, the components of the polymer main chains) whose transition dipole moment is reoriented perpendicular to the rubbing direction by the rubbing process. Consequently, the drop in Figure 4 of the intensity of the asymmetric C=O vibration band for rubbing densities greater than 80 is caused by the rubbing-induced biaxial reorientation characteristic (in-plane reorientation along the rubbing direction and out-of-plane reorientation) of the imide rings; the out-of-plane reorientation is particularly enhanced for rubbing densities greater than 80. This biaxial reorientation of the imide rings is strongly coupled with the preferential reorientation of the polymer main chains along the rubbing direction.

The biaxial reorientation of the imide rings produced by rubbing may be strongly related to high pretilt angles ($25°-87°$, depending on the rubbing density) of nematic LC (4-n-pentyl-4′-cyanobiphenyl) molecules in contact with the rubbed film surface. As shown in Figure 1, the two imide rings in the chemical repeat unit of the polymer chain are chemically bonded to the phenyl ring with two 4-(n-octoxy)phenyloxy side groups at the 3 and 6 positions. Thus, the rubbing-induced biaxial reorientation of the imide ring should be accompanied by the out-of-plane rotation of the side groups. The out-of-plane reoriented side groups may significantly contribute to the high pretilt angle of LC molecules on the film surface.

**2D Polarized FTIR Correlation Analysis.** In the previous sections, we discussed the examination of rubbing-induced molecular reorientation using optical retardation and polarized FTIR dichroism. However, these techniques do not enable the determination of the sequence of reorientations of the main chains and side groups on the PI film surface. We have, therefore, analyzed the polarized FTIR dichroism difference spectra with the 2D correlation approach to obtain detailed information about the sequence of reorientations of the polymer segments. Figure 6 shows the variations in the synchronous and asynchronous 2D FTIR correlation spectra of a C8-PMDA-PDA PI film with variation of the rubbing density, in the range 1300–1760 cm$^{-1}$. A power spectrum extracted along the diagonal line of the synchronous 2D correlation spectrum is also shown at the top of Figure 6a. The 2D correlation spectra were constructed from five spectra measured at intervals of 40 in the rubbing density range 0–160.

The synchronous 2D FTIR correlation spectrum in Figure 6a provides the following information. First, 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 side groups and the main chains in the PI film, respectively. These autopeaks reflect the local reorientations of both the main chains and the side groups. The changes in intensity of the 1364 and 1733 cm$^{-1}$ bands suggest that the imide ring is strongly influenced by the rubbing process. According to the power spectra, 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 backbones are more strongly influenced by rubbing than the phenyloxy units in the side groups. These observations additionally suggest that the rubbing process strongly causes local reorientations of the rodlike polymer backbones on the PI film surface.

Second, several cross peaks appear in the synchronous 2D FTIR correlation spectrum in the spectral region 1300–1760 cm$^{-1}$ that are associated with the molecular segments of the polymer film (Figure 6a). Positive cross peaks are observed at (1505, 1733), (1505, 1471), and (1515, 1364) cm$^{-1}$. Positive cross peaks reveal that the relative reorientation directions of the transition dipole moments of the vibrational modes fall into two groups (i.e., those of the main chains and those of the side groups) and provide information about the cooperative reorientation between IR bands. The positive cross peak at (1515, 1364) cm$^{-1}$ shows not only the reorientation direction of the transition dipole moments of the vibrational modes originating in the main chains (which lies parallel to the rubbing direction as shown in Figure 3) but also that the rubbing process cooperatively reorients the rodlike polymer backbones. The positive cross peak at (1505, 1733) cm$^{-1}$ shows that these two bands correspond to vibrations with transition dipole moments aligned in the same direction.

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**Figure 6.** (a) Synchronous and (b) asynchronous 2D correlation spectra in the region 1760–1300 cm$^{-1}$ obtained from the IR spectra of a C8-PMDA-PDA PI film rubbed with varying rubbing densities. Solid and dashed lines indicate the positive and negative cross peaks, respectively.
that is, perpendicular to the rubbing direction, as was observed in Figure 3. The positive cross peak at (1505, 1471) cm\(^{-1}\) indicates that the band for the phenyloxy units in the side groups is strongly correlated with the band for the n-octyl end groups in the side groups. This suggests that the aliphatic n-octyl end groups in the side groups undergo cooperative reorientation with the aromatic units (i.e., the phenyloxy units) in the side groups as a result of the rubbing process. In fact, the transition dipole moment of the CH\(_2\) deformational mode 1471 cm\(^{-1}\) is aligned perpendicular to the chain axis of the extended n-octyl end group. When this fact is taken into account, it is suggested that the aliphatic n-octyl end groups in the side groups are reoriented perpendicular to the phenyloxy units in the side groups by rubbing and so lie parallel to the polymer main chains as well as to the rubbing direction.

Third, the negative cross peaks at (1505, 1515), (1505, 1364), (1733, 1515), (1733, 1364), and (1471, 1515) cm\(^{-1}\) show that the reorientation direction of the transition dipole moments of the first vibrational mode of each pair is perpendicular to that of the other vibrational mode of the pair. The negative cross peaks imply that the reorientation direction of the polymer main chains is perpendicular to that of the aromatic side groups. These results are in good agreement with those of the 2D map in Figure 4b.

From the asynchronous 2D FTIR correlation spectrum in Figure 6b, the IR bands assigned to molecular segments within the polymer film can be differentiated. The sequence of reorientations of the molecular segments in the main chains and of the side groups was determined according to a rule proposed by Noda et al.\(^{10}\)

Initially, we determine the reorientation order of the main chains and side groups. 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 imidiering bands at 1733 and 1364 cm\(^{-1}\) in the main chain indicate that the PDA phenyl ring reorients more rapidly than the imidiering, although the backbone is reoriented as a rigid rod. The cross peak at (1733, 1364) cm\(^{-1}\) due to asymmetric C=O stretching and C=N stretching in the imide ring indicates that the C=O group reorients more rapidly than the C=N group in the imide ring. For the side groups in the PI film, the cross peak at (1505, 1471) cm\(^{-1}\) between the phenyl ring vibration at 1505 cm\(^{-1}\) of the phenyloxy unit and the aliphatic end group at 1471 cm\(^{-1}\) indicate that the phenoxy unit reorients more rapidly than the aliphatic n-octyl end group. Further, the cross peak at (1505, 1364) cm\(^{-1}\) between the phenyl ring vibration at 1505 cm\(^{-1}\) of the phenyloxy unit and the C=N stretching vibration of the main chain at 1364 cm\(^{-1}\) indicate that the phenoxy unit of the side group reorients more rapidly than the C=N bond in the main chain. In both the main chains and the side groups, the more rigid segments such as the imide rings and the aromatic rings reorient more rapidly than the flexible segments such as the aliphatic n-octyl end group. The reorientation order for the main chain and the side groups can be determined from the cross peaks between the phenyl ring vibration of the PDA unit and the vibrational modes of the side groups (i.e., the aromatic and aliphatic side groups), which indicate that the main chain units reorient more rapidly than the side groups. These observations collectively lead to the conclusion that the rubbing-induced reorientations of the polymer segments occur in the following sequence: (1) PDA phenyl ring (main chain; at 1515 cm\(^{-1}\)), (2) imide ring (main chain; at 1733 cm\(^{-1}\)), (3) phenoxy unit (side group; at 1505 cm\(^{-1}\)), (4) imide C=N bond (main chain; at 1364 cm\(^{-1}\)), and (5) aliphatic n-octyl end group (side group; at 1471 cm\(^{-1}\)).

**Conclusion**

The rubbing-dependent behaviors of the vibrational bands associated with the molecular segments of C8-PMDA-PDA PI, a well-defined brush PI composed of aromatic–aliphatic bristles on a fully rodlike backbone, were investigated in detail as a function of the rubbing density by using polarized FTIR spectroscopy in transmission mode with a particular focus on 2D map representations and 2D correlation analysis of the resulting spectra.

It was found that, at the surface of the rubbed film, the fully rodlike polymer backbones are preferentially reoriented along the rubbing direction but the side groups (i.e., the phenoxy unit) are preferentially reoriented perpendicular to the rubbing direction and that these preferential reorientations are enhanced with increasing rubbing density. In particular, the rubbing process was found to cause significantly local reorientations of the rodlike polymer backbones on the PI film surface, in which the segments of the polymer backbones reorient in a cooperative manner. Of course, rubbing also causes the cooperative reorientation of the segments of the side groups, although the PDA units in the polymer backbones are more strongly influenced by the rubbing process than the phenoxy units in the side groups. In addition, this is the first time that the ordering of the rubbing-induced reorientation of the polymer segments has been determined; rubbing-induced reorientation was found to occur in the following sequence: PDA phenyl ring (main chain), imide ring (main chain), phenoxy unit (side group), imide C=N bond (main chain), and aliphatic n-octyl group (side group).

Moreover, from the 2D map representation and orientation function analyses of the asymmetric C=O vibrational mode, which has a different rubbing density dependence from those of the other vibrational modes, it was found that in the rubbing process the imide rings (which can be taken to represent the polymer main chain) undergo biaxial reorientation (in-plane reorientation along the rubbing direction and out-of-plane reorientation). In particular, the out-of-plane reorientation of the imide rings in the polymer main chains that reorient along the rubbing direction is always enhanced with increasing rubbing density. This biaxial reorientation of the imide rings is strongly coupled with the preferential reorientation of the polymer main chains along the rubbing direction. Such biaxial reorientation of the imide rings is necessarily accompanied by the out-of-plane rotation of the side groups, perhaps contributing to the high pretilt angle of LC molecules on the film surface. In contrast, inclination of the reoriented imide rings (i.e., the polymer chains) was not found to occur on PI films rubbed with various rubbing densities.

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