Molecular Structure Analysis in a Dip-Coated Thin Film of Poly(2-perfluorooctylethyl acrylate) by Infrared Multiple-Angle Incidence Resolution Spectrometry

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Received April 17, 2008; Revised Manuscript Received June 3, 2008

ABSTRACT: Infrared multiple-angle incidence resolution spectrometry (IR-MAIRS) has been employed to study molecular orientation in a thin film of poly(2-perfluorooctylethyl acrylate) (C8FA) coated on a Si substrate. Since the coated C8FA film exhibits a highly effective water and oil repellency, the structure−property relationship has intensively been studied mainly by use of X-ray diffractometry (XRD) thus far. Regardless, XRD provides details of molecular structure only for the crystallized parts in the film, and as a result a limited region of the perfluoroalkyl group is selectively analyzed. To overcome this analytical limitation, IR-MAIRS has first been employed for analysis of a polymer thin film coated on a solid substrate. The discussion after the IR-MAIRS measurements coupled with XRD analysis provided details not only in the polymer thin film but also about structure of the substrate surface, through which a structure determination factor of the polymer film has been revealed.

Introduction

Comb-shaped polymers that have perfluoroalkyl (Rf) groups in their side chains connected to a backbone polymeric chain have attracted much attention due to their unique coexistent properties: low surface free energy,[1] excellent chemical stability,[2] nonfouling behavior,[2] and poor adhesion.[3] Because of these useful properties, poly(fluoroalkyl acrylate)s and poly(fluoroalkyl methacrylate)s (FAs and FMAs) are, in particular, widely recognized to be suitable for industrial coating materials for surface modification.[2] The surface properties of FAs and FMAs are known to depend on the chain length of the perfluoroalkyl group in the polymers. To have an efficient strategy for developing a more powerful coating material on a theorized chemical concept, therefore, understanding of details in molecular structure of the polymer coating films is essentially important.

Thus far, the molecular aggregation structure of the polymers in a coating film has been studied mainly by the use of small-angle X-ray scattering (SAX),[4,5] wide-angle X-ray diffraction (WAXD),[6–10] and grazing-incidence X-ray diffraction (GIXD) techniques.[10–13] Although the X-ray diffraction (XRD) techniques provide molecular information limitedly in crystalline parts, they are commonly used for the thin film analysis, since they enable us to follow changes in polymorphism. In fact, through the XRD analyses of FA and FMA thin films, the crystallinity of the Rf group was found to play an important role in the surface properties of the coated thin films,[4,5] and the crystallinity was also found to have a strong relation to the length of the perfluoroalkyl group.[8,9]

When an annealed film of FA or FMA is prepared on a solid surface, the backbone polymeric chain is extended at least in a short region,[10] and the side chains isotactically connected to the backbone are aligned ordered, which makes a double-layer structure like a Z-type Langmuir−Blodgett (LB) film. Formation of the lamellar structure of the side chains is considered to be a driving force to generate the highly ordered structure. FA and FMA films are in a multilayered structure consisting of the double layers when the length of the Rf group is longer than $-(CF_2)_5CF_3$.[8,9] Through an XRD analysis of the lamellar structure, the long spacing of the layers was compared to the theoretical length of the side chains, which yielded a conclusion that the side chains are perpendicularly oriented to the substrate.[10,11] This further suggests that the polymer chain is entirely aligned parallel to the substrate surface. In this manner, the conventional molecular orientation study has been performed by way of the long-spacing analysis in the crystalline parts. Since the polymer thin films comprise not only crystallines but also amorphous and liquid crystal phases, however, XRD analysis is insufficient to reveal fine molecular structure in a polymer film.

Infrared (IR) spectroscopy is unique that molecular information at a chemical group level can be retrieved no matter what degree the crystallinity is, while the analytical area is macroscopic.[14–20] This means that area-averaged molecular orientation at every chemical group can be analyzed by IR spectroscopy. Another notable point of using IR spectroscopy is that the direction of a group vibration (transition moment) is reflected in a polarized spectrum. The most famous optical geometries for thin-film analyses based on this characteristic are found in transmission and reflection−absorption (RA) spectrometries.

In transmission spectrometry, infrared unpolarized or polarized IR ray is irradiated on the sample film perpendicularly, and the transmitted ray is led to the detector. Since the electric field oscillation is parallel to the film surface, surface-parallel group vibrations are selectively observed, which is the surface selection rule of transmission spectrometry. On the other hand, RA spectrometry is performed on a film deposited on a metallic surface. Since a surface-normal electric field is generated on the surface, surface-normal group vibrations are selectively observed, which is the surface selection rule of RA spectrometry. In this manner, the transmission and RA spectrometries are complementary with each other in terms of surface selection rule, and the combination technique is powerful to reveal orientation of each chemical group. Regardless, this combination technique requires an experimental condition that an identical

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10.1021/ma800850k CCC: $40.75

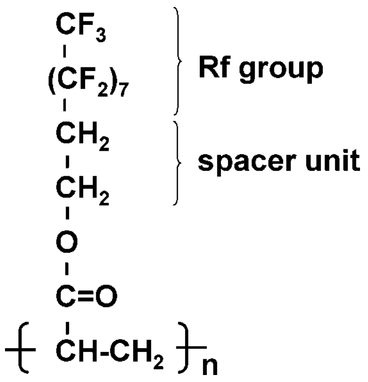

Figure 1. Chemical structure of poly(2-perfluorooctylethyl acrylate), C8FA.

sample must be prepared on two different substrates. In the case of polymer film analysis, this experimental requirement is tough, since preparation of a perfectly identical film of a polymer on two different surfaces is close to impossible.[21] In particular, a dip-coated thin film made from an aqueous polymer solution has poor reproducibility of thickness for a quantitative spectroscopic analysis. Therefore, this powerful technique has limitedly been used only for analysis of LB films.

Recently, infrared multiple-angle incidence resolution spectrometry (IR-MAIRS) has been developed to overcome this experimental limit.[21–24] The new technique simultaneously yields two IR spectra from an identical sample prepared on an IR transparent substrate, which correspond to the conventional transmission and RA spectra, respectively. This technique makes it possible to directly compare the two complementary spectra even for a dip-coated polymer film. In this manner, the MAIRS technique makes the best use of IR spectroscopy for molecular orientation analysis in thin films.

In the present study, a dip-coated thin film of poly(2-perfluorooctylethyl acrylate) (abbreviated as C8FA) on a Si substrate has been subjected to IR-MAIRS. The analytical results have proved that each functional group is highly oriented irrespective of degree of crystallinity, and details in the polymer system have first been revealed. In addition, the surface structure of the substrate of silicon has also been revealed, which can be discussed in relation to the structure of the C8FA film. Through this study, IR-MAIRS has proved to be a powerful and useful technique for polymer thin films.

Experimental Section

The primary chemical structure of C8FA is presented in Figure 1. For details of the synthesis, the reader is referred to elsewhere.[10] C8FA used in the present study was characterized by gel-permeation chromatography with a standard of PMMA for which $M_n = 9.4 \times 10^3$ and $M_w = 1.7 \times 10^4$, and the molecular weight distribution was $M_w/M_n = 1.9$. A powdered sample of C8FA was dissolved in 3,3-dichloro-1,1,1,2,2-pentafluoropropane (HCFC-225, Asahi Glass Co., Ltd.) with an concentration of 0.5 wt % to prepare a coating solution. A double-side-polished silicon (Si) wafer (Ryoko Sangyo Corp., Tokyo, Japan) was cut into a piece with dimensions of 55 mm × 25 mm × 1 mm. After washing the wafer by sonication in pure HCFC-225, it was coated with a C8FA thin film by a dip-coating technique in the coating solution with a withdrawal rate of 0.15 mm s^{-1} at room temperature. One side of the dip-coated films was removed by a soft piece of paper soaked with HCFC-225 to prevent an irregular scattering of the incidental IR ray on a rough surface of the coated film. In other words, the IR ray was irradiated on the very flat backside of the sample, and the transmitted ray through the film was collected by a FT-IR spectrometer. The single-sided C8FA film on Si was thermally incubated at ca. 120 °C as a pretreatment.

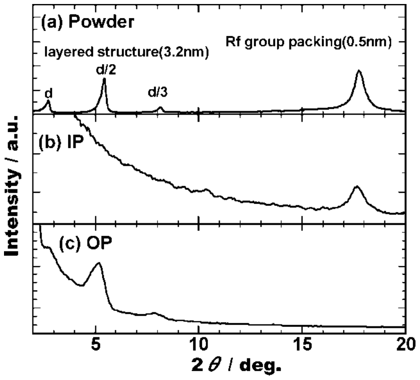

Figure 2. XRD patterns of (a) C8FA powder, (b) IP, and (c) OP diffraction pattern of C8FA coating on Si substrate.

An X-ray diffraction pattern of C8FA powder was measured by a Rigaku (Tokyo, Japan) Ru-200B diffractometer with a Cu Kα X-ray source (50 kV−200 mA) by 0.05° steps with a scan rate of 1 s per a step. In-plane (IP; the scattering vector is parallel to the surface) X-ray diffraction measurements of the C8FA dip-coated film on Si were carried out on a Rigaku (Tokyo, Japan) ATG-X diffractometer. The data were collected using a Cu Kα X-ray source (50 kV−300 mA) by 0.02° steps with a scan rate of 1 s per a step. Out-of-plane (OP; the scattering vector is perpendicular to the surface) X-ray diffraction pattern measurements for the same film were measured on a Rigaku (Tokyo, Japan) RINT 2500 diffractometer with a Cu Kα X-ray source ($\lambda = 0.154\,18$ nm, 50 kV−280 mA). The data were collected as $\theta-2\theta$ scans from 3° to 20° by 0.05° steps with a scan rate of 3 s per a step.

Infrared multiple-angle incidence resolution spectrometry (IR-MAIRS) measurements were performed on a Thermo Fisher Scientific (Madison, WI) Magna 550 FT-IR equipped with a mercury cadmium telluride (MCT) detector. Dry air was running through both the sample compartment and inside the spectrometer for air purge. The IR-MAIRS measurements of the C8FA thin film on Si were performed by collecting single-beam spectra at angles of incidence from 5° to 45° by 5° steps on a Thermo Fisher Scientific (Yokohama, Japan) pulse-motor-controlled MAIRS stage installed in FT-IR, which required no polarizer.[21] The interferogram was accumulated 2000 times to improve the signal-to-noise ratio for each angle of incidence. The spectra obtained were analyzed using the MAIRS algorithm[21,23,24] on MathWorks (Natick, MA) Matlab ver. 7.0.

Normal-incidence IR transmission spectra of the dip-coated C8FA thin film and a KBr pellet involving C8FA powder were measured on a Thermo Fisher Scientific (Madison, WI) Magna 760 FT-IR spectrometer equipped with a deuterated trigycine sulfate (DTGS) detector.

A modeling calculation for optimizing a theoretical structure of C8FA was performed on Winmostar Ver. 3.64 by employing semiempirical molecular orbital method on EigenFollowing algorithm with the AM1 function.[24]

Results and Discussion

Figure 2a presents a XRD pattern of C8FA powder. The peak at $2\theta = 18°$ is assigned to the crystalline domain of the Rf group[10] with the hexagonal packing ($d = 0.5$ nm), which corresponds to the distance between adjacent lamellar units. Three peaks (d, $d/2$, and $d/3$) in the region of $2\theta = 2-9°$ are assigned to the lattice constant of a layered structure[10] ($d = 3.2$ nm), which is the long spacing distance of the double-layer structure in a crystalline

Parts b and c of Figure 2 present the IP and OP XRD patterns, respectively, of the C8FA-coated film on Si. The peaks found for the powder (Figure 2a) are roughly reproduced in the two patterns. The IP and OP patterns are, however, totally different from each other: the Rf packing peak is found in the IP pattern

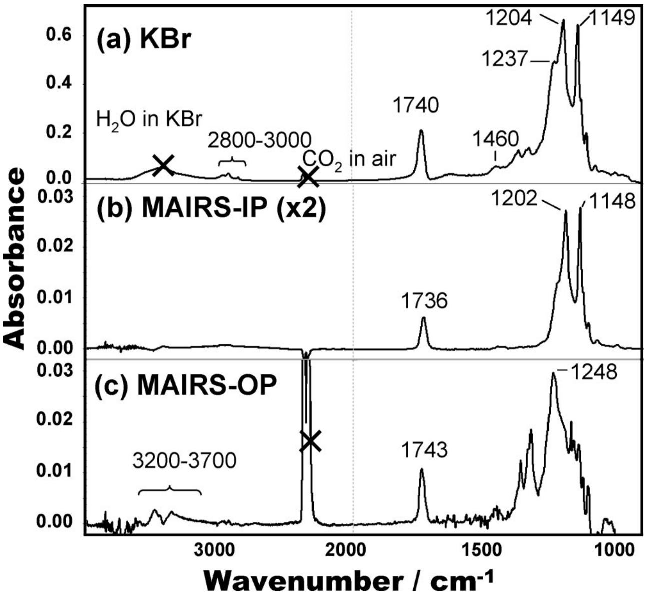

Figure 3. IR spectra of C8FA: (a) transmission spectrum of powder sample (in a KBr pellet), (b) IP × 2, and (c) OP spectra of the film coating on a Si substrate measured by IR-MAIRS.

only, whereas the long-spacing peaks are found in the OP pattern only. This clear separation of the peaks into the IP and OP patterns indicates that the C8FA thin "film" has a layered structure, in which the Rf lamellar units should have a perpendicular stance to the substrate.

With the XRD data, the tilt angle of the side chains to the surface can be calculated by taking the long-spacing distance into account under an assumption that the side chain involving the Rf group has the trans-zigzag conformation. No further discussion, however, can be made with the XRD data only. In addition, the amorphous and liquid-crystal parts in the film are out of discussion. Then, the same sample was subjected to IR analysis.

Figure 3a presents an IR transmission spectrum of C8FA powder dispersed in a KBr pellet, while parts b and c of Figure 3 respectively present the IR-MAIRS IP and OP spectra of the C8FA thin film. Since an OP spectrum greatly responds to noise and a disturbing factor in comparison to a robust IP spectrum, the OP spectrum in Figure 3c has a large carbon dioxide peak, while it is very minor in the IP spectrum (Figure 3b). This is not a result of poor air purge, but minor disturbing peak is enhanced, which is true for the water vapor peaks. At least we have no problem to discuss the fingerprint region.

The KBr pellet spectrum corresponds to an unoriented sample, while the MAIRS spectra reflect molecular orientation in a film. In a low wavenumber region (1000−1500 cm^{-1}), the three spectra are largely different from one another. If the molecules in the thin film are randomly oriented, the three spectra would exhibit an identical shape. Therefore, the largely different shapes clearly indicate that the coated thin film has an anisotropic molecular structure.

Of note is that the bands in the KBr pellet spectrum are separated into the two (MAIRS-IP and OP) spectra. The symmetric and antisymmetric CF_2 stretching vibration bands ($\nu_s(CF_2)$ and $\nu_a(CF_2)$) are, for example, mainly found in the MAIRS-IP spectrum at 1148 and 1202 cm^{-1}, respectively, whereas the antisymmetric C−O−C stretching vibration band (ν_a(COC)) is found at 1248 cm^{-1} in the MAIRS-OP spectrum only. In this manner, IR-MAIRS has a powerful characteristic that overlapping bands may be resolved and appear in the two spectra because of the molecular orientation. In the case of the KBr pellet spectrum, many bands are unresolved, which makes the band location of each mode a little inaccurate. For example, the $\nu_a(CF_2)$ band is found at 1204 cm^{-1}, but the proper position is 1202 cm^{-1} as found in the MAIRS-IP spectrum. This apparent shift is caused by superposition of the adjacent band of the ν_a(COC) mode at 1248 cm^{-1}. The improvement of the band resolution with an aid of the molecular orientation is thus an important benefit of IR-MAIRS particularly for analysis of polymer films, since a polymeric compound generally gives many bands.

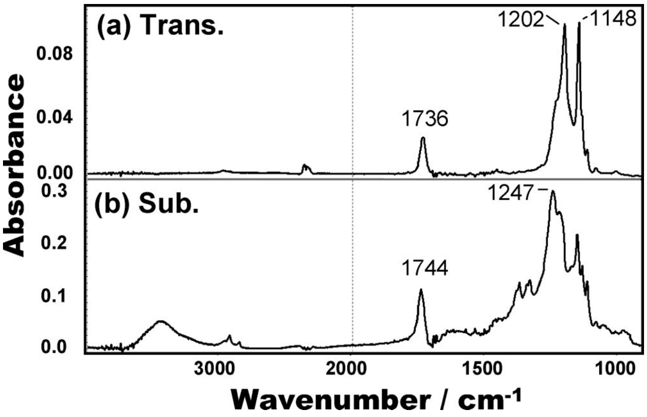

Figure 4. IR spectra of C8FA: (a) transmission spectrum of the sample-coated Si substrate and (b) a differential spectrum: (Figure 3a) − (Figure 4a) × *f*. The coefficient, *f*, was adjusted to cancel the C−F stretching vibration bands.

Before moving on to a further discussion, the reliability of the MAIRS spectra should be examined because this is the first case of MAIRS application to a coated polymer film. The IP spectrum can easily be examined by comparing to a transmission spectrum of the same film. As presented in Figure 4a, the transmission spectrum is found to be almost identical to the MAIRS-IP spectrum, which means that the IP spectrum has no problem.

The OP spectrum can also be examined easily when we remember that the KBr pellet spectrum is roughly a superimposed result of the IP and OP spectra. Then, a subtraction spectrum was calculated by subtracting the transmission spectrum from the KBr pellet spectrum to yield a "quasi"-OP spectrum, which is presented in Figure 4b. As expected, the subtracted spectrum is quite similar to the OP spectrum. The reader may be concerned about minor differences in the fine structure below 1200 cm^{-1} between the subtracted spectrum and the OP one. Note that the subtracted spectrum is a direction to roughly evaluate the OP spectrum, and they do not have to be exactly the same as each other. In addition, IR MAIRS has a low analytical limit at about 1000 cm^{-1}, which makes the OP spectrum noisy near 1000 cm^{-1}. Therefore, the high similarity is enough at this stage. In this manner, the IR-MAIRS spectra have proved reliable. Therefore, let us get back to discussion of the IR-MAIRS spectra.

Both $\nu_s(CF_2)$ and $\nu_a(CF_2)$ bands mainly appear in the MAIRS-IP spectrum, which means that both modes are nearly parallel to the film surface. Since the two modes are both perpendicular to the Rf chain, the Rf chain is thus concluded to have a roughly perpendicular stance to the film surface, which is consistent with a model suggested by the XRD analysis. On the other hand, the ν_a(COC) band appears only in the MAIRS-OP spectrum, which strongly suggests that the C−O−C axis is aligned perpendicularly to the surface. This discussion at a functional group level is thanks to both characteristics of IR spectroscopy and the MAIRS analysis of the anisotropic structure, which is not available with XRD analysis. Of another importance using IR-MAIRS is that the analytical results are true irrespective of its crystallinity in the film.

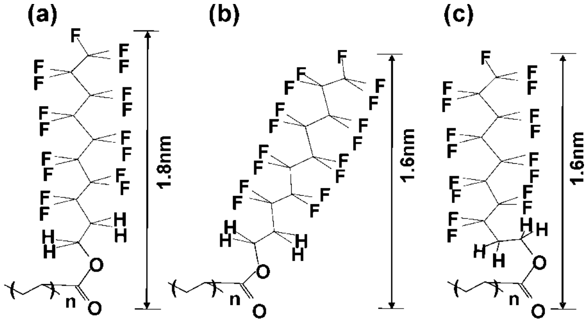

Figure 5. Schematic model of ordered structure of the C8FA dip-coated film in a monomer unit. The Rf group and spacer unit are (a) oriented perpendicular to the surface, (b) obliquely oriented to the surface, and (c) at right angles to each other.

IR-MAIRS enables us to calculate the orientation angle as mentioned later. For the bands of the $\nu_s(CF_2)$, $\nu_a(CF_2)$, and $\nu_a(COC)$ modes, however, the orientation calculation is not a good idea, since the bands are still crowded for measuring absolute band intensities.

On the other hand, the C═O stretching vibration (ν(C═O)) mode in the ester group is of another interest. This mode appears at 1736 and 1743 cm^{-1} in the MAIRS-IP and OP spectra, respectively, whereas it appears at 1740 cm^{-1} in the KBr pellet spectrum. This shows again that the KBr pellet spectrum is a superimposed result of the MAIRS spectra. The clear band shift by 7 cm^{-1} in the MAIRS spectra, which is larger than the resolution (4 cm^{-1}), is considered due to the Berreman effect. The effect is found when a strongly absorbing mode, which has a large absorptivity (the imaginary part of refractive index, *k*), is available in a molecule. The large *k* influences the real part, *n*, which results in an apparent shift. Since the optical dielectric constant (ε_∞) is always larger than the static value (ε_{st}), the longitudinal vibrational mode (ω_L) appears at a higher wavenumber than the transverse mode (ω_T), which is theorized by the Lyddane−Sachs−Teller relation.

$$\frac{{\omega_L}^2}{{\omega_T}^2} = \frac{\varepsilon_{st}}{\varepsilon_\infty} \qquad (1)$$

The anisotropic property is commonly found in a thin film of a dielectric material. Therefore, the higher wavenumber shift by 7 cm^{-1} for the OP spectrum suggests that the longitudinal mode has a surface-perpendicular component.

The orientation angle of a transition moment can be calculated with the use of band intensities appeared in the IP and OP spectra (I_{IP} and I_{OP}) using eq 2.[21]

$$\varphi = \tan^{-1}(2I_{IP}/I_{OP}) \qquad (2)$$

The orientation angle of the ν(C═O) mode is calculated to be 37° from the surface normal. In this manner, the orientation image of the C═O bond has been confirmed.

IR-MAIRS provides information not only about the coated film but also about the substrate surface. The broad bands appeared in a range of 3200−3700 cm^{-1} in Figure 3c are assigned to the O−H stretching vibration modes in the silanol group on the Si substrate. The O−H stretching vibration band is observed mainly in the OP spectrum, which indicates that the silanol group is oriented nearly perpendicular to the surface. The oriented high-density silanol groups are expected to play an essential role for determination of molecular orientation of the coated polymer film.

These analytical results are useful to propose an appropriate molecular model of the thin film. Since the Rf group is known to be stiff, three possible models with a straight Rf group are drawn in Figure 5. Figure 5a is the simplest model, in which a trans-zigzag conformation is employed, and the Rf group has a perpendicular stance to the surface. If this model is true, the thickness of the film should be 1.8 nm, since the optimized structure of the side chain by the calculation is 1.8 nm. As mentioned above, however, the thickness does not agree with the thickness determined by XRD analysis (1.6 nm). In this manner, the first model is denied.

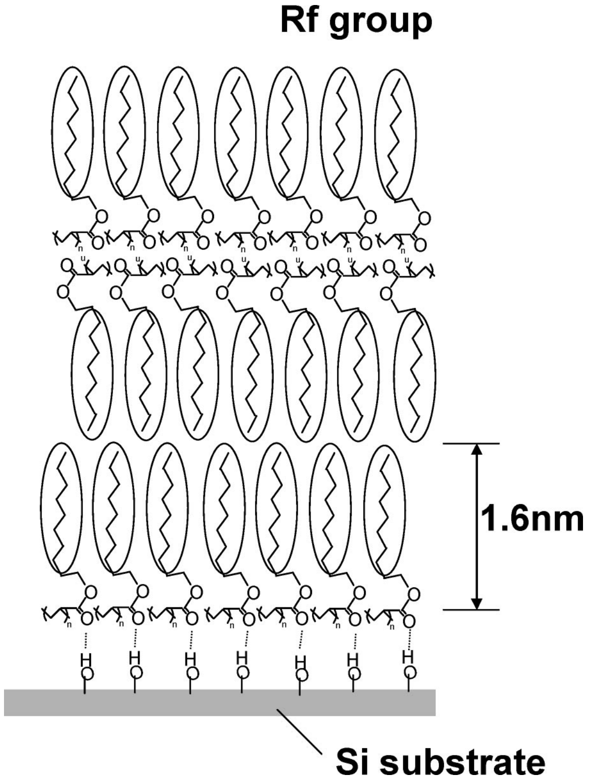

Figure 6. Schematic model of the ordered structure of the C8FA dip-coated film consisting of stratified layers.

The next model presented in Figure 5b has a tilted Rf group, so that the thickness would match the XRD result. For the matching, the Rf group should be tilted with a tilt angle of 27° from the surface normal. In this model, however, both the $\nu_s(CF_2)$ and $\nu_a(COC)$ modes are also tilted largely, which does not match the analytical results by IR-MAIRS. In this manner, the second model has been denied, too.

The third model presented in Figure 5c has a characteristic that the spacer unit of the ethylene group is twisted by introducing the gauche conformation. As a result, the total length of the side chain is 1.6 nm, although the Rf group remains to have a perpendicular stance to the substrate. With this model, transition moments of the $\nu_s(CF_2)$ and $\nu_a(COC)$ modes are parallel and perpendicular to the film surface, respectively, which is consistent with the analytical results by IR-MAIRS. In addition, the tilt angle of the C═O group, 37°, is reasonable when the bond angles about the COC group are taken into account. In this manner, an appropriate schematic model has been determined, which has first been attained by considering both the thickness analysis by XRD based on the molecular modeling calculation and the orientation analysis by IR-MAIRS.

The entire molecular scheme involving the surface structure of the substrate has thus been revealed, which is presented in Figure 6. With the scheme, the silanol groups are considered to interact with the C═O group in the ester group at the root of the side chain. This suggests that the entire molecular orientation of C8FA is determined by this interaction. Therefore, another orientation is expected when C8FA is chemically modified or the film is deposited on another surface, which is underway.

Acknowledgment. A part of the study was financially supported by Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency (JST), to whom the author's great thanks are due.

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MA800850K