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NEXAFS studies on the structure of perfluoroalkyl carbonic acid Langmuir Blodgett films

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We examined Langmuir Blodgett (LB) films of PFODA (perfluorooctadecanoic acid) prepared at various surface pressures with NEXAFS (Near Edge X-ray Absorption Fine Structure) spectroscopy. Experimental results revealed that the sample without the rubbing treatment possesses (1) no anisotropy along the dipping direction with almost vertical alignment to the substrate surface, (2) higher degree of order of the chain for the sample prepared under the higher surface pressure. Moreover, it was found that the rubbing process induces a uni-directional tilt angle of the chain without changing the magnitude of the degree of order.

Keywords: fluorinated compounds, LB films, NEXAFS, rubbing process, molecular orientation

1. Introduction

Controlling of the molecular orientation and its quantitative characterization have been the subject of recent interest in demand for molecular devices. Particularly, fluorinated compounds have been attracted much attention because of their wide applicability to electronics, coatings and lubrications. By controlling fluorinated compounds high-orderly, we would be able to drag the properties of this compounds to the full. Although their surface structure may strongly affect their properties as a film, quantitative analysis and hence the detailed understanding is still lacking. In this study, we applied NEXAFS (Near Edge X-ray Absorption Fine Structure) spectroscopy to the study of Langmuir Blodgett (LB) films of PFODA (perfluorooctadecanoic acid: $CF_3(CF_2)_{16}COOH$), and examined (1) its molecular orientation, and (2) the change in the molecular orientation through a rubbing process. NEXAFS spectroscopy is recognized as a convenient tool to study the orientation of adsorbates on a solid surface.

2. Experimental

We prepared three types of PFODA LB films on Si substrates at surface pressures of 40, 20, and 5mN/m. Ultrapure water produced in a Milli-Q system from deionized water was used as a subphase. We also prepared another three films through a rubbing process (rubbing pressure is $20g/cm^3$) to the above samples. The structure of the LB films with/without the rubbing process was separately checked with an atomic force microscope. F K-edge NEXAFS spectra were measured on the BL-11A of Photon Factory at Institute of Materials Structure Science for High Energy Accelerator Research Organization (KEK-PF) with a Grasshopper monochromator (2400 lines/mm grating). Measurements were performed in the total-electron yield mode under the vacuum of 10^{-8} Torr range. In order to investigate the orientation of molecules, we examined the incident angle dependence of the spectra. We also measured F K-edge NEXAFS spectra of PFT (perfluorotetracosane: n-$C_{24}F_{50}$) to estimate the linear polarizability of the incident X-ray beam and to be 0.88.

3. Result and Discussion

Figure 1 shows a typical example of F K-edge NEXAFS spectra of a PFODA LB film (40mN/m) at normal (90°) and grazing

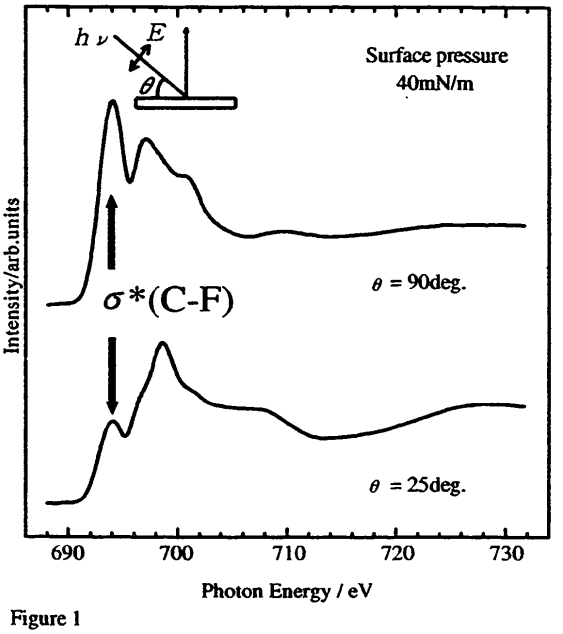

Figure 1
F K-edge NEXAFS spectra of PFODA LB film made at 40mN/m

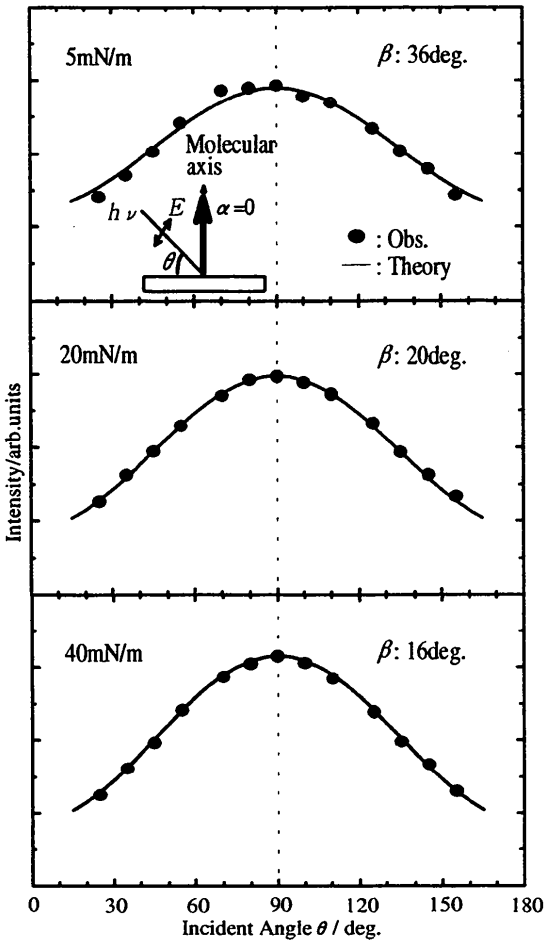

Figure 2
The summaries of incident angle dependence of the σ *(C-F) peak for the PFODA LB films without rubbing process

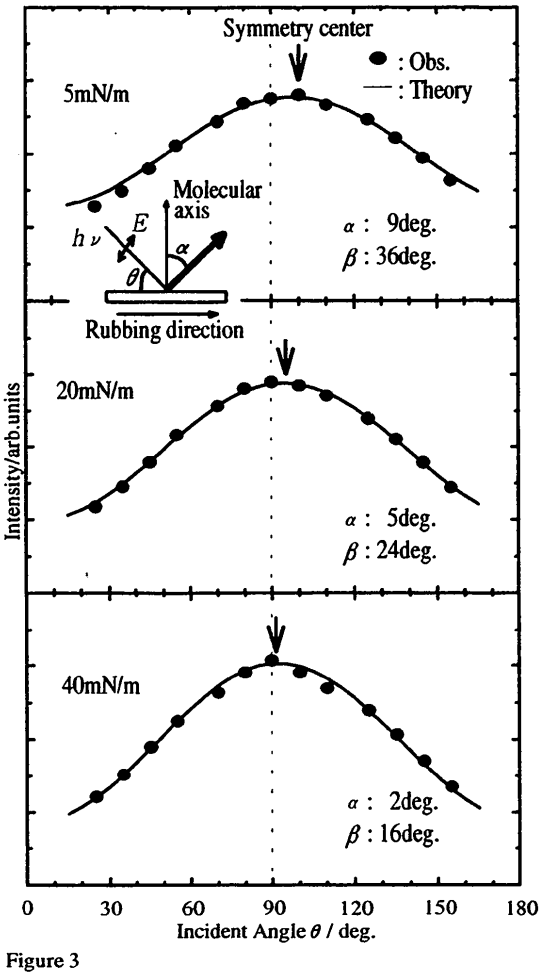

Figure 3
The summaries of incident angle dependence of the σ *(C-F) peak for the PFODA LB films with rubbing process

(25°) incidence. θ is defined as the angle between the substrate surface and the incident X-ray beam (see inset of figure 1). The lowest energy peak was assigned to $F_{1s} \rightarrow$ σ*(C-F) resonance (Ågren, *et al.*, 1995). It is found that this spectra indicates the polarization dependence by comparing the intensities of the peak for normal and grazing incidence. We could also gain similar spectra about PFODA LB films of 20 and 5mN/m.

Figure 2 shows the summaries of incident angle dependence of the σ*(C-F) peak for the LB films made at 5, 20, 40mN/m without rubbing process. We performed the peak deconvolution by using the fitting procedure applied to the NEXAFS spectra (Bunn *et al.*, 1954; Nelder *et al.*, 1965; Stöhr, 1992). The maximum peak position of each sample is the surface normal (90°), indicating that each sample possess no anisotropy along the dipping direction with almost vertical alignment to the substrate surface. The orientational distribution FWHM (β) is increasing with the decrease of the surface pressure, where the Gaussian distribution function is assumed (Stöhr, 1992), indicating that films prepared under the higher surface pressure possess narrower distribution-width.

Similarly, figure 3 shows the summaries of incident angle dependence of the σ*(C-F) peak for the LB film made at 5, 20, 40mN/m with rubbing process. The maximum peak position of each sample is shifted by 9° from the surface normal for the sample at 5mN/m, 5° for 20mN/m, and 2° for 40mN/m, respectively. β is almost the same as those without rubbing process. This indicates that films prepared at lower surface pressure are influenced more strongly by the rubbing process without changing distribution-width.

The results obtained above are schematically illustrated in figure 4. The sample without the rubbing treatment possesses, (1) no anisotropy along the dipping direction with almost vertical alignment to the surface, and (2) higher degree of order of the chain for the sample prepared under the higher surface pressure. Moreover, the rubbing process induces a uni-directional tilt angle of the chain without changing the magnitude of the degree of order and the samples prepared under the lower surface pressure possess larger tilt angle.

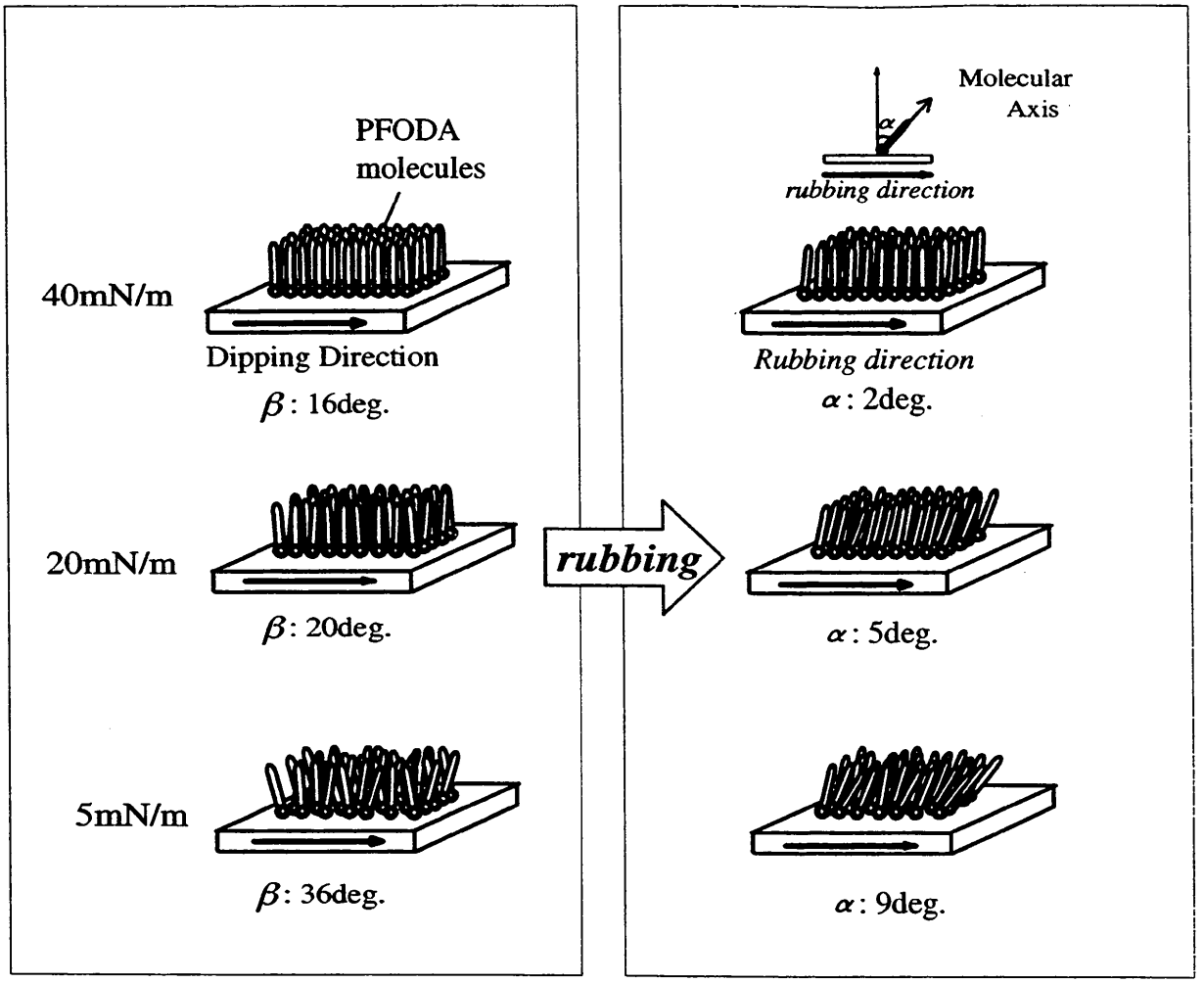

Figure 4
Molecular orientation of PFODA LB films with/without rubbing process

4. Conclusion

With use of NEXAFS spectroscopy, we examined LB films of PFODA on its molecular orientation and the change in the molecular orientation through a rubbing process. The molecular orientation of each film without rubbing process is normal to the substrate surface, and that with rubbing process orients toward the rubbing direction.

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