11A/2000G282

NEXAFS Studies in Molecular Organized Films of Fluorinated Comb-Polymer

Tohru ARAKI*[1], Atsuhiro FUJIMORI[1], Hiroo NAKAHARA[1], Eisuke ITO[2], Masahiko HARA[2],
Hisao ISHII[3], Yukiko OUCHI[3], Kazuhiko SEKI[3, 4], and Yoshinori KITAJIMA[5]
[1]Department of Chemistry, Faculty of Science, Saitama University, Saitama 338-8570, Japan
[2]Local Spatio-Temporal Functions Laboratory, FRS, RIKEN, Saitama 351-0198, Japan
[3]Department of Chemistry, Graduate School of Science, Nagoya University, Nagoya 464-8602, Japan
[4]Research Center for Materials Science, Nagoya University, Nagoya 464-8602, Japan
[5]KEK-PF, Tsukuba, Ibaraki 305-0801, Japan

Introduction

The fluorinated amphiphiles including the comb-polymers containing fluorocarbon side-chains are known to have low energy surface as well as the characteristic thermal behavior and chemical stability. We have reported the monolayer formation at the air/water interface and the surface structures of their built-up films for the monomers and the corresponding polymers with several acrylates of amphiphiles containing fluorocarbon studied by the surface pressure-area (π-A) isotherms and AFM. In this work, we applied F K-edge NEXAFS spectroscopy on investigating the molecular packing and orientation in the organized molecular films of these comb-polymers.

Experimental

The newly synthesized fluorinated amphiphilic comb-polymers, poly-2- (perfluorodecyl)ethyl acrylate, $F(CF_2)_{10}(CH_2)_2OCO(CHCH_2)_n$ [$PFF_{10}EA$] and poly-1H,1H,11H-(icosafluoro-undecyl) acrylate, $H(CF_2)_{10}CH_2OCO(CHCH_2)_n$ [$PHF_{10}A$] having the hydrogen atom at the ω-position were used. The monolayers of the comb-polymers were spread onto the sub phase water flowing down along a small glass rod from the trifluoroacetic acid solutions. These monolayers were transferred onto NESA glass at 5 °C and 25 mN/m by a horizontal lifting method at various surface pressures to obtain the non-alternating X-type films. F K-edge NEXAFS spectra were measured at BL-11A in the partial electron yield mode (PEY) with -450 V retarding voltage under the vacuum of 10^{-8} Torr range.

Results and Discussion

Figure 1 shows the dependence of incident angle for the F K-edge NEXAFS spectra for the X-type 10 layers of $PFF_{10}EA$ and $PHF_{10}A$. The lowest energy peak at about 694 eV was assigned to the transitions from F 1s to σ*(C-F) orbital. Comparing the peak intensity at different incident angles, we can determine the molecular orientation qualitatively. In the case of $PFF_{10}EA$, σ*(C-F) peak intensity for the normal incidence is stronger than that for the grazing incidence, indicating that the resonance of the σ*(C-F) orbital is parallel to the substrate surface; the fluorocarbon chains are almost perpendicular to the surface. On further discussion, we show σ*(C-F) peak intensity to the incident angles which normalized by the same edge-jump at Fig. 2. The apparent strong angular-dependence is seen and the normalized peak intensity takes a maximum at θ=90° in the $PFF_{10}EA$ and the $PHF_{10}A$ monolayer films, however, in the $PHF_{10}A$ 10 layers film that is weak and implies that there is no molecular ordering in the film.

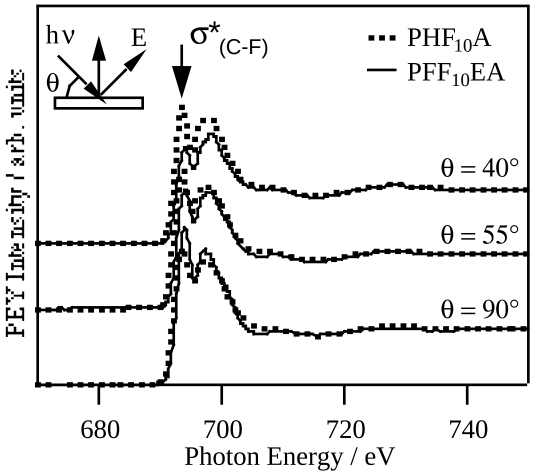

Fig. 1 F K-edge NEXAFS spectra of $PHF_{10}A$ and $PFF_{10}EA$ films (X-type, 10 layers).

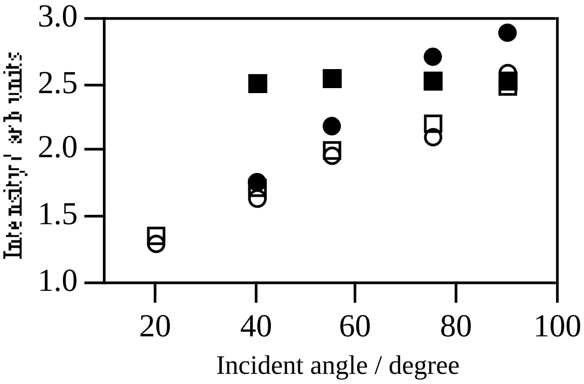

Fig. 2 Incident angle dependence of C-F intensity for $PHF_{10}A$ (X-type, 1 layer): open circle, $PHF_{10}A$ (X-type, 10 layers): solid circle, $PFF_{10}EA$ (X-type, 1 layer): open rectangle, $PFF_{10}EA$ (X-type, 10 layers): solid rectangle, respectively.

* araki@chem.saitama-u.ac.jp