**NEXAFS Studies in Molecular Organized Films of Fluorinated Comb-Polymer**

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**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(CF₂)₁₀(CH₂)₂OCO(CHCH₂)₈ [PFF₁₀ EA] and poly-1H,1H,1H-(icosafuoro-undecyl) acrylate, H(CF₂)₁₀CH₂OCO(CHCH₂)₈ [PHF₁₀ 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 PFF₁₀ EA and PHF₁₀ 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 PFF₁₀ 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 PFF₁₀ EA and the PHF₁₀ A monolayer films, however, in the PHF₁₀ 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 PHF₁₀ A and PFF₁₀ EA films (X-type, 10 layers).](image)

![Fig. 2 Incident angle dependence of C-F intensity for PHF₁₀ A (X-type, 1 layer): open circle, PHF₁₀ A (X-type, 10 layers): solid circle, PFF₁₀ EA (X-type, 1 layer): open rectangle, PFF₁₀ EA (X-type, 10 layers): solid rectangle, respectively.](image)

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