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Polarized Near Edge X-ray Absorption Fine Structure Spectroscopic Study on Organized Molecular Films of Fluorinated Comb Polymers with Various Chain Lengths

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1. Introduction

The characterization of polymer films by spectroscopy, X-ray diffraction, and scanning microprobe microscopy, particularly with respect to molecular orientation and packing in organized ultrathin films, is currently of great interest. In surface science, lattice structures and binding energies of constituent atoms for solid surfaces such as catalysts have been revealed by analysis based on features in near-edge X-ray absorption fine structure (NEXAFS) spectra.¹ NEXAFS spectroscopy has yet to be widely applied to organic thin films. Some notable recent examples of such applications are the elucidation of hydrocarbon orientation in Langmuir–Blodgett (LB) films of cadmium arachidate² and the discussion of the photopolymerization of long-chain diacetylene in LB films in reference to ultraviolet photoelectron spectroscopy (UPS) observations.³ In addition, oriented poly(tetrafluoroethylene) and perfluorotetracosane films have recently been studied by polarized NEXAFS spectroscopy.^{4–6}

Fluorinated amphiphiles and polymers are expected for providing low-energy surfaces with high tribological,

thermal, and chemical stability.^{7–9} The characteristics of these fluorinated polymers are considered to be primarily related to the orientation of fluorocarbons in films. The present authors previously investigated monolayers at the air/water interface by surface pressure–area isotherm measurements together with Brewster angle microscopy for several acrylates and methacrylates containing fluorocarbons and their comb polymers. We, successfully clarified the structures of those builtup films on solid substrates with scanning electron microscopy, atomic force microscopy, and X-ray diffractions together with their friction behavior.^{10,11}

In the present study, the molecular alignments in transferred films of comb polymers with fluorocarbon side chains of various lengths and various atoms at the ω -position are investigated by polarized NEXAFS spectroscopy for the X- and Z-type monolayers and multilayer films.

2. Experimental Section

Fluorinated comb polymers, poly-2-(perfluoroalkyl)ethyl acrylate and methacrylate $F(CF_2)_n(CH_2)_2O[COC(X)CH_2]_m$ (abbreviated Poly-FF_nEA and Poly-FF_nEMA ($n = 6, 8, 10$) $X = -H$ and $-CH_3$, respectively, and poly-1*H*,1*H*,($n + 1$)*H*-(partial fluoroalkyl) acrylate and methacrylate $H(CF_2)_nCH_2O[COC(X)CH_2]_m$ (abbreviated Poly-F_nA and Poly-F_nMA ($n = 4, 6, 8, 10$) $X = -H$ and $-CH_3$) were used in this work. Syndiotactic (diad: 58% by ¹H NMR)¹² comb polymers were obtained as follows: After ⁶⁰Co γ -ray irradiation of the corresponding monomers at $-196^\circ C$, postpolymerized, the samples were dissolved in acetone or tetrahydrofuran and purified by precipitation in tetrachloromethane.¹³ These fluorinated comb polymers were practically insoluble in common organic solvents without trifluoroacetic acid. The molecular weight of these polymers was estimated to be $(1.5–6.0) \times 10^4$ from the intrinsic viscosity of $[\eta] = 0.12–0.54$ for these trifluoroacetic acid solutions at $30^\circ C$.

Monolayers were spread from the trifluoroacetic acid solutions onto distilled water (Milli-Q Plus, 18.2 M Ω cm), and the spreading solution was allowed to flow down along a small glass rod, according to the method proposed by Trurnit.¹⁴ These monolayers were transferred onto NESA glass coated with three layers of Cd stearate to obtain a hydrophobic surface. Nonalternating X- and Z-type films were prepared at $5^\circ C$ and 25 mN/m by lifting horizontally and by surface-lowering methods,¹⁵ respectively.

NEXAFS spectra were measured on the BL-11A soft X-ray parallel polarized, grazing incidence monochromator station of the Photon Factory at the National Laboratory for High-Energy Accelerator Research (KEK-PF slow-positron facility). F K-edge spectra were measured in the 660–760 eV photon energy region, and in the partial electron yield (PEY) mode with -450 V retarding voltage and 2.0 kV accelerating voltage. These condi-

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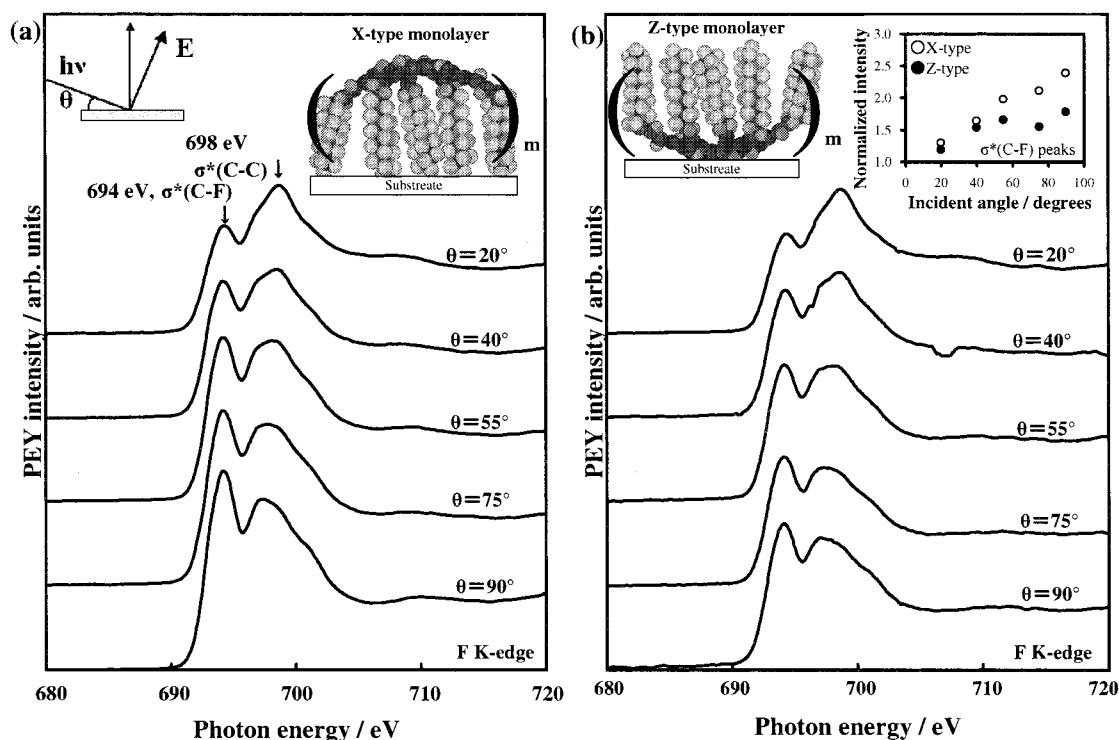


Figure 1. NEXAFS spectra for (a) X- and (b) Z-type monomolecular layers of Poly-FF₁₀EA and on the normalized 694 eV peak intensity vs incident angle.

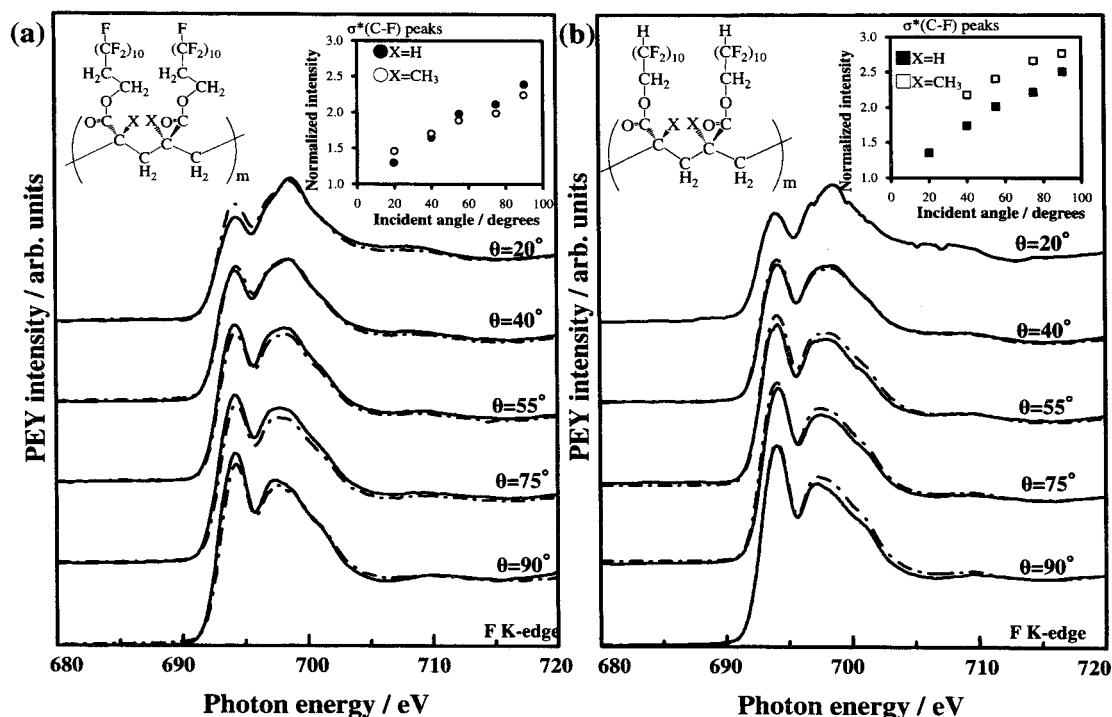


Figure 2. NEXAFS spectra for X-type monolayers of (a) Poly-FF₁₀EA (solid line) and Poly-FF₁₀EMA (dashed line) and (b) Poly-F₁₀A (solid line) and Poly-F₁₀MA (dashed line) and the normalized 694 eV peak intensity vs incident angle (inset).

tions provide clear spectra on the monomolecular level, avoiding slower (secondary) electrons and efficiently collecting electrons in the channeltron. The intensity of the spectra, which exhibits angular dependence, was normalized with respect to the edge-jump of the $\sigma^*(\text{C-F})$ peak.

3. Results and Discussion

Figure 1 shows the F K-edge NEXAFS spectra of the X- and Z-type monomolecular layers for Poly-FF₁₀EA, for various incidence angles. Both spectra were found to be

significantly dependent on the incidence angle at the monolayer level. According to Seki et al.,¹⁶ the peaks at about 694 and 698 eV have been assigned to the transitions from F_{1s} to the $\sigma^*(\text{C-F})$ and $\sigma^*(\text{C-C})$ orbitals, respectively. The relative intensity of the $\sigma^*(\text{C-F})$ peak, attributable to the fluorocarbon side chains, with respect to $\sigma^*(\text{C-C})$ becomes maximum at normal incidence ($\theta = 90^\circ$) and weakened at grazing incidence ($\theta = 20^\circ$) for both films. These results suggest that the transition moments of the

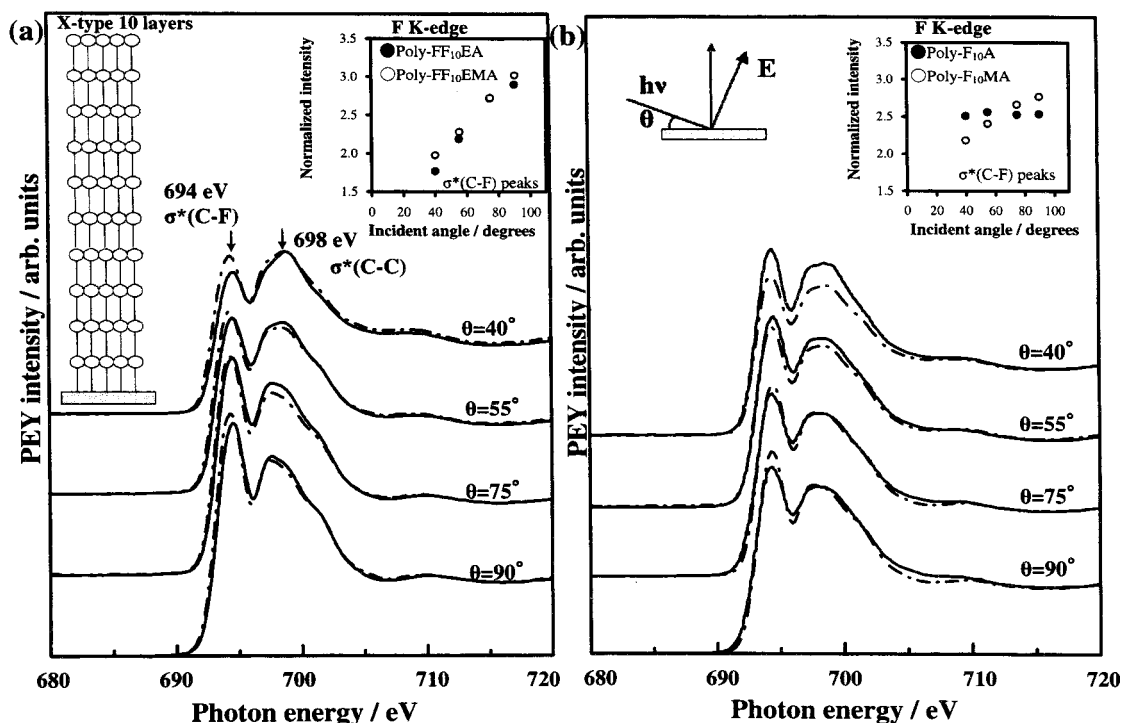


Figure 3. NEXAFS spectra for X-type multilayer films (10 layers) of (a) Poly-FF₁₀EA (solid line) and Poly-FF₁₀EMA (dashed line) and (b) Poly-F₁₀A (solid line) and Poly-F₁₀MA (dashed line) and the normalized 694 eV peak intensity vs incident angle (inset).

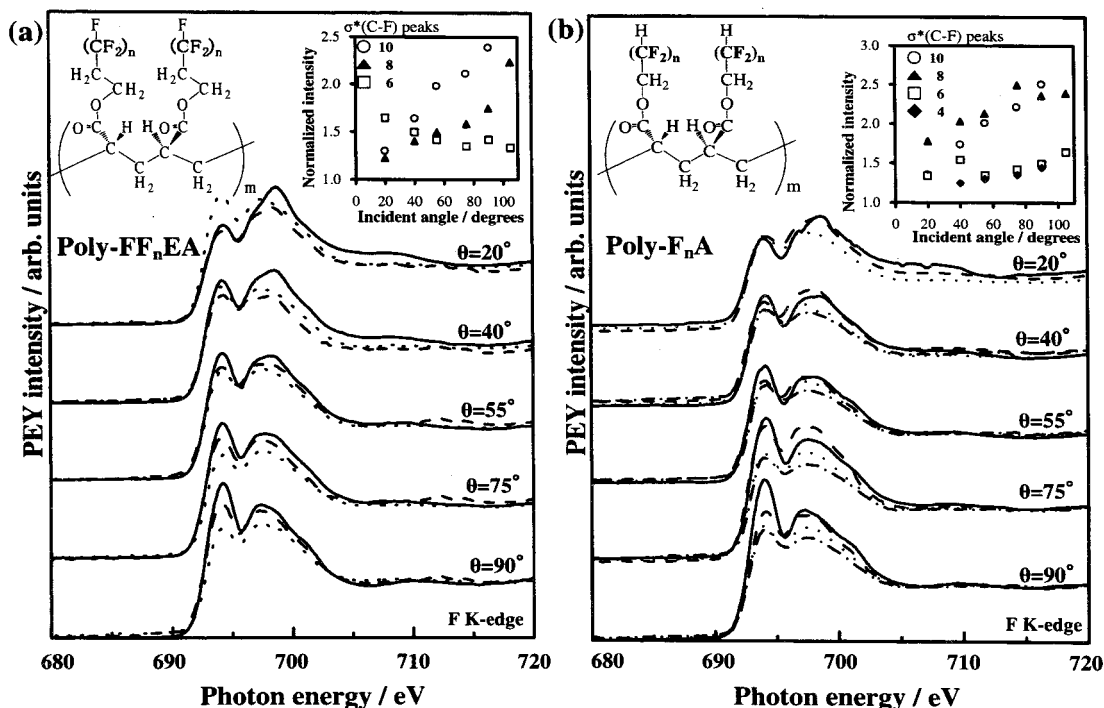


Figure 4. NEXAFS spectra for monolayers of (a) Poly-FF_nEA ($n = 6, 8, 10$) and (b) Poly-F_nA ($n = 4, 6, 8, 10$) ($n = 10$, solid line; 8, dashed line; 6, dotted line; 4, dash-dot line) and the normalized 694 eV peak intensity vs incident angles (inset).

694 eV band were rather parallel to the surface, indicating the nearly perpendicular orientation of the fluorocarbon side chains. Compared to the Z-type film, in which the fluorocarbon chains are exposed to the air, the X-type film, in which the outermost surface consists of the polymer backbones, produces a higher normalized $\sigma^*(\text{C-F})$ in-

tensity, as shown in the inset of Figure 1b. It is therefore plausible that the uniformity of molecular alignments of the fluorocarbons in the outermost layers was degraded during or after deposition, although the toughness of the polymer main-chain remained unchanged at the monomolecular level. Figure 2 shows the change in the NEXAFS spectra for the monomolecular comb polymer films with different α -substitutions of $-\text{H}$ and $-\text{CH}_3$ at the hydrophilic polymer main chains and with hydrogens (H) instead of fluorines (F) atoms at the ω -position of the fluorocarbons.

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A clear angular dependence can be observed, suggestive of highly ordered molecular arrangements in the X-type monomolecular layers of Poly-FF₁₀EA, Poly-FF₁₀EMA, Poly-F₁₀A, and Poly-F₁₀MA. All these films exhibited similar plots of normalized 694 eV peak intensity versus incident angle. The contribution of the $\sigma^*(\text{C}-\text{F})$ orbital (694 eV) attributable to fluorocarbon side chains was largest at normal incidence, whereas the $\sigma^*(\text{C}-\text{C})$ orbital (698 eV) became prominent at grazing incidence. These results indicate that the fluorocarbon side chains stand almost vertically and are anchored to the polymer main chains in the monolayers, irrespective of the chemical structures.

However, subsequent layers of the comb polymers with hydrogen atoms at the ω -position of the side chains of the fluorocarbons in multilayer films exhibited varying degrees of disorder. Figure 3 shows the F K-edge NEXAFS spectra for the X-type multilayer (10 layers) films of Poly-FF₁₀EA, Poly-FF₁₀EMA, Poly-F₁₀A, and Poly-F₁₀MA. The structural information of the top few layers was obtained, taking into account the probing depth of the PEY mode.¹⁶ Again, there is a clear variation with respect to the incidence angle. From the plots of normalized $\sigma^*(\text{C}-\text{F})$ intensity, the upper layers in the X-type multilayer films appear to be well-ordered. In particular, the multilayer Poly-FF₁₀EA and Poly-FF₁₀EMA films were more highly ordered than the monolayer films. However, multilayer film of Poly-F₁₀A, having hydrogen atoms at the ω -position of the fluorocarbon side chains, was notably disordered and the normalized intensity of the $\sigma^*(\text{C}-\text{F})$ peak remained constant irrespective of the incident angle. This disordering of the molecular alignments is probably due to formation of the intermolecular hydrogen bonding between the ω -position hydrogen and carbonyl groups of hydrophilic head of the comb polymers, which reflects in the effect of the spreading solvents on the monolayer.¹¹

Figure 4 shows the F K-edge NEXAFS spectra for X-type monolayers of Poly-FF_{*n*}EA and Poly-F_{*n*}A with

various fluorocarbon side-chain lengths. There is no clear dependence of the incident angle in the relative intensity of the 694 and 698 eV peaks at $n = 4$ and 6, suggesting that the comb polymers form random conformations of the main chains with the shorter fluorocarbon side chains. The $\sigma^*(\text{C}-\text{C})$ bands in the spectra changed slightly, reflecting the change in conformation and inductive effect of the fluorocarbons. Although molecular orbital and band calculations have been employed in previous studies in an attempt to interpret features in the high-energy region of NEXAFS spectra,^{5,16} the high-energy bands observed in the present study are not interpretable.

4. Conclusion

Minor changes in the chemical structure of the fluorinated comb polymers, such as changing the α -methyl substituents on the polymer backbone and inserting hydrogen rather than fluorine at the ω -position of the fluorocarbons, were found to affect the NEXAFS spectra of the transferred films. The hydrogen substitution at the ω -position of the fluorocarbons is thought to allow the formation of hydrogen bonds with carbonyl groups and distort the molecular orientation of films. The NEXAFS spectra, related to the uniformity and/or the disorder of the molecular orientation in the films, were also observed to vary according to the film types (X or Z) and the number of layers in the multilayer films.

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