

## Formation and Structure of Organized Molecular Films for Fluorinated Comb Polymers with Various Chain Lengths

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The molecular orientation in mono- and multilayer films of fluorinated comb polymers with various side-chain lengths were characterized by in-plane X-ray diffraction, polarized near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, and atomic force microscopy (AFM) at molecular level resolution. Those two-dimensional lattices of fluorinated side-chain were significantly changed, depending on the slight difference of the chemical such as the  $\alpha$ -methyl group at the polymer main-chains and the exchange of atoms at the  $\omega$ -position of the side-chains. The NEXAFS spectra were found to vary with respect to the incidence angle, the number of layers in organized molecular films as well as the chemical modification. And further, the dependence of fluorinated side-chain lengths to the molecular orientation for the comb polymers was exhibited by AFM observation at molecular resolutions.

Key words: fluorocarbon, comb polymer, organized molecular film, NEXAFS, in-plane XRD

### 1. INTRODUCTION

Fluorinated polymers and amphiphiles have been already used practically in thin films thanks to their physical behavior of low friction coefficient<sup>1, 2</sup> and chemical-resistance. The molecular orientations of fluorocarbon chains in addition to the characteristics of a large van der Waals radius and electronegativity of the fluorine atom, seem to be indispensable to such functions.<sup>3</sup> Fluorocarbon chains  $(-\text{CF}_2-)_n$  of poly(tetrafluoroethylene)<sup>3, 4, 5</sup> take some helical conformations with rigid rod-like forms which are clearly different from the normal hydrocarbon chains with the *trans* zig-zag planar structure. For fabrication of well-defined molecular alignments controlled at the monomolecular level, the monolayer assembling method could be applied to the fluorinated comb polymers. And structural characterizations of those films have been carried out using the *in situ* Brewster angle microscopy, the scanning electron microscopy, the atomic force and friction force microscopies (AFM and FFM) and X-ray diffractions.<sup>6, 7, 8</sup> Recently, the mono- and multilayers of fluorinated amphiphiles have been characterized by *in situ* X-ray diffraction and reflection methods which are considered to be a powerful tool because of the higher scattering power of fluorine atom.<sup>9, 10</sup> On the other hand, near-edge X-ray absorption fine structure (NEXAFS) studies have given the information on the molecular orientation of perfluorotetracosane [ $n\text{-CF}_3(\text{CF}_2)_{22}\text{CF}_3$ ] and poly(tetrafluoroethylene) [PTFE,  $(-\text{CF}_2-)_n$ ] films.<sup>11, 12</sup>

In the present investigation, structures of the transferred monomolecular films of the comb polymers containing various fluorocarbon side-chains on solids and the surface morphologies of the outermost layers have been investigated by the *in-plane* X-ray diffractions, polarized near-edge X-ray absorption fine structure (NEXAFS) spectroscopy and the atomic force microscopy (AFM).

### 2. EXPERIMENTAL

#### 2.1 Materials

Fluorinated amphiphiles with vinyl groups as monomer materials, 2-(perfluoroalkyl)ethyl acrylate and methacrylate,  $\text{F}(\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OCOC}(\text{X})=\text{CH}_2$  [ $n = 6, 8, \text{ and } 10$ ; abbreviated by  $\text{FF}_n\text{EA}$  and  $\text{FF}_n\text{EMA}$  for  $\text{X} = -\text{H}$  and  $-\text{CH}_3$ , respectively], and also 1H, 1H, 11H-icosafuoroalkyl acrylate and methacrylate,  $\text{H}(\text{CF}_2)_n\text{CH}_2\text{OCOC}(\text{X})=\text{CH}_2$ , [ $n = 4, 6, 8, \text{ and } 10$ ; abbreviated by  $\text{F}_n\text{A}$  and  $\text{F}_n\text{MA}$  for  $\text{X} = -\text{H}$  and  $-\text{CH}_3$ , respectively] were purchased from Daikin Fine Chemicals Co. Ltd. and purified by recrystallization repeated several times from *n*-hexane solutions. These analogous monomers containing the fluorocarbon with various chain lengths sealed in Pyrex glass tubes in a vacuum were irradiated with <sup>60</sup>Co  $\gamma$ -ray (1.0 Mrad in liq.-N<sub>2</sub>) at  $-196^\circ\text{C}$ , and the post-polymerizations were carried out in the range of  $-83 \sim 50^\circ\text{C}$ . The obtained comb polymers were dissolved in a little acetone or tetrahydrofuran and purified by precipitation through pouring into tetrachloromethane.<sup>13, 14</sup> These fluorinated

comb polymers were practically insoluble in common organic solvents without trifluoroacetic acid. The tacticity of these polymers was obtained to be almost syndiotactic (Diad: 57.4 %) by  $^1\text{H-NMR}$  analysis according to the reference.<sup>15</sup> Their molecular weights were estimated to be  $1.5 \sim 6.0 \times 10^4$  from the intrinsic viscosity of  $[\eta] = 0.12 \sim 0.54$  for these trifluoroacetic acid solutions at 30 °C. These fluorinated comb polymers are abbreviated as Poly-FF<sub>n</sub>EA, Poly-FF<sub>n</sub>EMA [ $n = 6, 8, \text{ and } 10$ ], Poly-F<sub>n</sub>A, and Poly-F<sub>n</sub>MA [ $n = 4, 6, 8, \text{ and } 10$ ].

## 2.2 Procedures

These polymers were dissolved in trifluoroacetic acid as a good solvent, and spread on the distilled water to allow the spreading solution to flow down a small glass rod projecting from the surface of the subphase in the trough according to the Truinit's suggestion.<sup>16</sup> These monolayers were deposited onto the solid substrates at 5 °C by a horizontal lifting or a surface lowering method and a Langmuir-Blodgett (vertical dipping) method at various surface pressures to obtain the non-alternating X- or Z-type and the alternating Y-type films, respectively. Surface morphologies of the transferred films were observed by an electron scanning microscope (Hitachi, model 4100) and an atomic force microscope (Seiko Instruments SPA300 with SPI3800 probe station; spring constant of 0.09  $\text{Nm}^{-1}$ ). And further, the in-plane spacing of the two-dimensional lattice of the films were determined by analysis of an X-ray diffractometer with different geometrical arrangements<sup>17</sup> (Bruker AXS, MXP-BX,  $\text{CuK}_\alpha$  radiation, 40 kV, 40 mA, an article specially made to order) equipped with a parabolic graded multilayer mirror. The monomolecular level resolution of this in-plane XRD apparatus was realized by applying incident angle of the X-ray is 0.2°, and slow scanning at 0.05° / 150 min (multilayers : 0.05° / 20 min scan). NEXAFS spectra were measured on BL-7A and 11A soft X-ray beamline at the Photon Factory in the National Laboratory for high-energy accelerator research organization (KEK-PF) with synchrotron radiation from a bending-magnet source. The F K-edge spectra were measured in the photon energy regions of 660 – 760 eV, and in the partial electron yield mode (PEY<sup>12, 18</sup>) with –450 retarding voltages, respectively and 2.0 kV accelerating voltage under the vacuum of  $10^{-8}$  Torr.

## 3. RESULTS AND DISCUSSION

### (1) Structure of two-dimensional lattice for the side-chains of fluorinated comb polymer films studied by in-plane X-ray diffraction.

Figure 1(a) shows the in-plane X-ray diffractions for the Poly-FF<sub>10</sub>EA, Poly-FF<sub>10</sub>EMA, Poly-F<sub>10</sub>A and Poly-F<sub>10</sub>MA, together with the estimated lattice structures for molecular packing of the fluorocarbon side-chains in the X-type

films, as indicated in Fig. 1(b).<sup>7</sup> The powder diffractions of these fluorinated comb polymers all provided the single peak with the lattice spacing of 5.0, 5.0, 4.9, and 4.8 Å for Poly-FF<sub>10</sub>EA, Poly-FF<sub>10</sub>EMA, Poly-F<sub>10</sub>A and Poly-F<sub>10</sub>MA, respectively. The similar single spacing for the Poly-FF<sub>10</sub>EA film was obtained to be 4.95 Å. As referred to the results of the *in situ* X-ray diffraction for the monolayers of other fluorinated amphiphiles on the water surface,<sup>9</sup> the above obtained values suggest the hexagonal packing of the fluorocarbons in the two-dimensional lattice. In the case of the Poly-FF<sub>10</sub>EMA film, the additional diffraction was observed with 4.1 Å together with 5.0 Å, whereas the Poly-F<sub>10</sub>MA film provided mainly the peak with 4.15 Å. These facts indicated a kind of the orthorhombic packing of the fluorocarbon side-chains in these polymethacrylate films. Its molecular packing was considered to be enhanced by the interlayer hydrogen bonding between the hydrogen at the  $\omega$ -position of the side-chains and the carbonyl groups of the esters on the main-chain of the comb polymer in the multilayered films. And further, the similar interlayer hydrogen bonding in the Poly-F<sub>10</sub>A multilayered film seemed to induce the further distorted molecular packing of the fluorocarbon side-chains, resulting in nearly to the triclinic form with the relatively small lattice value of 3.75 Å together with 4.9 Å and 4.1 Å. These interlayer hydrogen bonding were appeared in the effect of the spreading solvents on the monolayer behavior and confirmed by the IR spectra.<sup>19</sup> From the in-plane X-ray diffraction profiles Poly-FF<sub>10</sub>EA and Poly-F<sub>10</sub>A X-type monomolecular layers (Figure 1(c)), it was confirmed that both Poly-FF<sub>10</sub>EA and Poly-F<sub>10</sub>A monolayers formed same hexagonal packing in the

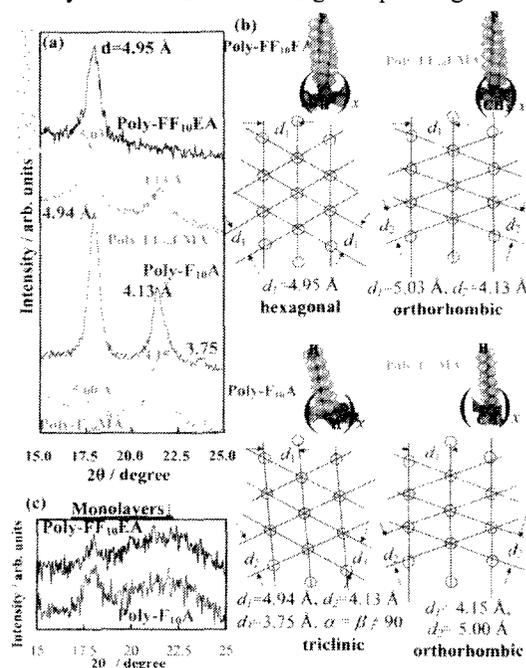


Figure 1. In-plane XRD patterns for X-type multilayers of the fluorinated comb polymers with the estimated lattice structures for molecular packing of the fluorocarbon side-chains in the X-type films.

two-dimensional lattice. This experimental fact was well correspondence to results of NEXAFS measurement which structure of Poly-F<sub>10</sub>A monolayer having hydrogen atom at the  $\omega$ -position was different from that multilayers one.<sup>20</sup>

(2) *Polarized NEXAFS Spectroscopic Study of Organized Molecular Films for Fluorinated Comb Polymers.*

Due to the effect of interlayer hydrogen bonding, subsequent layers of the comb polymers with hydrogen atoms at the  $\omega$ -position of the side-chains of the fluorocarbons in multilayer films exhibited varying degrees of disorder. Figure 2(a) shows the F K-edge NEXAFS spectra for the X-type multilayer (10 layers) films of Poly-FF<sub>10</sub>EA and Poly-F<sub>10</sub>A. The structural information of the top few layers was obtained, taking into account the probing depth of the PEY mode.<sup>12, 18</sup> In the case of multilayers of Poly-FF<sub>10</sub>EA, there is a clear variation with respect to the incidence angle because of formation of highly ordered orientation for the fluorinated side-chains. From the plots of normalized  $\sigma^*(\text{C-F})$  intensity, the upper layers in the X-type multilayer of Poly-FF<sub>10</sub>EA appear to be well-ordered. However, the multilayer film of Poly-F<sub>10</sub>A, having hydrogen atoms at the  $\omega$ -position of the fluorocarbon side-chains, was notably disordered and the normalized intensity of the  $\sigma^*(\text{C-F})$  peak remained constant irrespective of the incident angle.

Figure 2(b) shows the estimation of the orientation angle for Poly-FF<sub>10</sub>EA, Poly-FF<sub>10</sub>EMA, Poly-F<sub>10</sub>A, and Poly-F<sub>10</sub>MA molecules in the X-type 10 layers from the polarized F K-edge NEXAFS spectra. Assuming the uniaxial molecular orientation in the film and taking the tilted angle 14.3° of the -CF<sub>2</sub> plane to the perpendicular direction of the molecular axis of the fluorocarbon, the orientation angles of the fluorinated side-chain were determined by comparison of the polarized dependence of the normalized peak intensity for the

NEXAFS spectra and the ideal orientation angle curves. From these results, the fluorocarbons of Poly-FF<sub>10</sub>EA are almost perpendicular orientation to the surface. This result nearly agreed the value estimated by the previous X-ray diffraction study<sup>7</sup> whereas those of Poly-F<sub>10</sub>A were apparently orientated at the magic angle or their little polarization dependence due to a random conformation. This figure indicated also the orientation of the fluorocarbons of Poly-FF<sub>10</sub>EMA and Poly-F<sub>10</sub>MA molecules in the transferred films, and those are found to be tilted about 20° or 40° to the surface normal. It is considered for the less dependence of the incidence angles *i.e.*, the glancing angles on the normalized intensities of the side-chains of Poly-F<sub>10</sub>A and Poly-F<sub>10</sub>MA to be ascribed to some random orientation in the films due to the hydrogen bonding.

(3) *Dependence on fluorinated side-chain length to the molecular arrangement of monomolecular films estimated by atomic force microscopy.*

The change of AFM images in the nm scales of the Z-type films of Poly-FF<sub>n</sub>EA monolayers at the condensed states with the side-chain lengths is shown in Fig. 3. The anisotropic arrangements of the domains for  $n = 6$  tend to the isotropic with a nearly hexagonal packing of the fine domains with the lower height for  $n = 10$ . Fourier transformations (FT) images of Poly-FF<sub>10</sub>EA Z-type monolayer also exhibited the quasi-hexagonal spots indicating two-dimensional packing system of the fluorinated side-chain, and these FT spots of Poly-FF<sub>n</sub>EA films have a tendency to be unclear with decreasing of the side-chain length. The lattice values of the side-chains in Poly-FF<sub>10</sub>EA Z-type films were about 5.0 Å, which was well corresponding to the results of in-plane diffraction. In the case of Poly-FF<sub>8</sub>EA and Poly-FF<sub>6</sub>EA films, these values appeared to be dispersed a little, being due to some irregular surface morphology based on the increase of

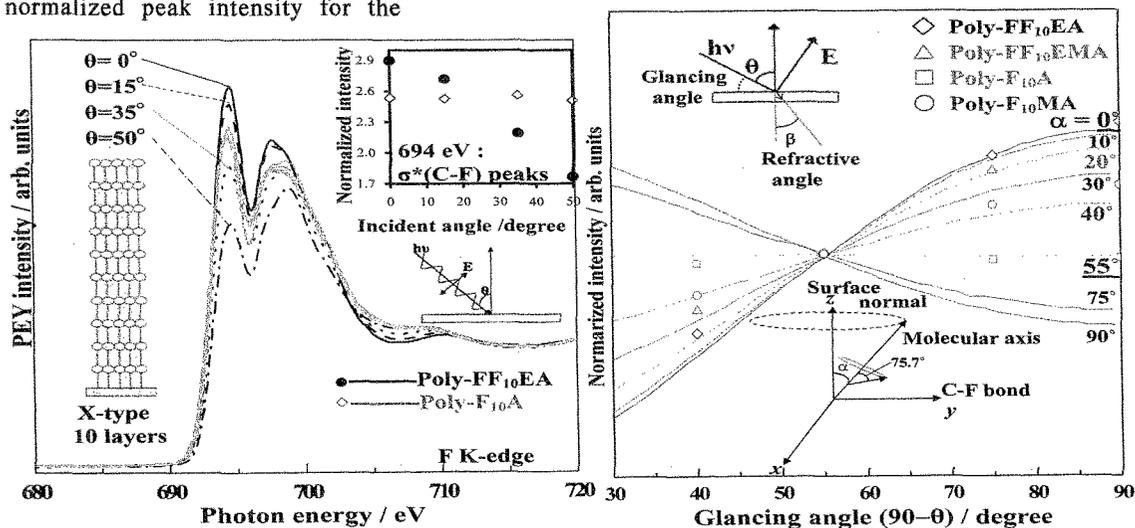


Figure 2. Polarized NEXAFS spectra and Estimation of orientation angle of multilayers for Poly-FF<sub>10</sub>EA and Poly-F<sub>10</sub>A (10 layers, 25 mNm<sup>-1</sup>, 5 °C).

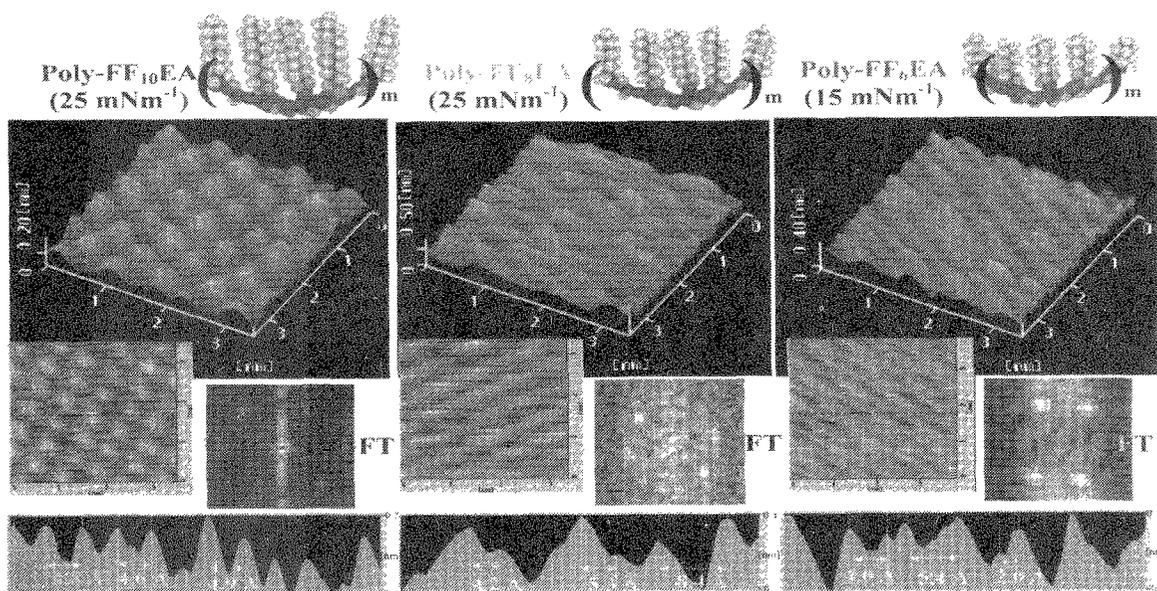


Figure 3. AFM images of Z-type monolayers of Poly-FF<sub>n</sub>EA (5 °C, n=10, 8, 6).

inclination of the side-chains.

#### 4. CONCLUSION

From the in-plane X-ray diffraction as well as the polarized NEXAFS spectroscopy, it has been found that the organized molecular films of fluorinated comb polymers on solids could be formed with the several types of orientation and packing of the fluorocarbon side-chains in the two-dimensional lattice, depending on the slight difference of the chemical such as the  $\alpha$ -methyl group at the polymer main-chains and the exchange of atoms at the  $\omega$ -position of the side-chains. The angular dependence of the incident X-ray on the NEXAFS spectra for fluorinated comb polymer films gives very effective information on the orientation of the fluorocarbon side-chains of those polymers. The hydrogen substitution at the  $\omega$ -position of the fluorocarbons is considered to allow the formation of hydrogen bonds with the carbonyl groups of the esters and distort the molecular orientation in the comb polymer films. And further, it has been confirmed that the heterogeneous domain forms of Z-type monolayers for fluorinated comb polymers gradually disordered with the decrease of the side-chain lengths from the results of molecular resolution AFM and their FT images.

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