# Morphology Related to Phase Separation for the Mixed Monolayer of Fluorinated Comb Polymer and Hydrogenated Long-Chain Compound

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From observations of the atomic and friction force microscopies, it has been found that the mixed monolayers of the comb polymer having the fluorocarbon side-chains and the hydrogenated amphiphile, exhibit a characteristic phase separation behavior at the micro- and mesoscopic resolutions. The regularity for molecular orientation in the mixed film was compared with that in the pure monolayer of the fluorinated comb polymer by using polarized NEXAFS spectroscopy.

The surface patterning[1,2] is an important subject for development of new molecular devices as lithography. It is well known that characteristic phase separation occurs in the mixed monolayers of fluorocarbon and hydrocarbon derivatives because of the lack of miscibility.[3–5] If these phase separation was available for the surface patterning by change of the mixing ratio or spreading solvent for monolayers, it is interesting in the scopes of not only basic science but also nanotechnology. Previously, we have investigated the monolayers at the air/water interface for several acrylate and methacrylate derivatives with various fluorocarbon chains and their comb polymers, the structure and friction properties of their organized molecular films on solids.[6,7] In this study, the phase separation in the mixed monolayers of the fluorinated comb polymer and a hydrogenated long-chain compound has been observed by an atomic force microscope (AFM), together with a friction force microscope (FFM). And further, in order to compare the regularity of molecular orientation of the monolayer for the fluorinated comb polymer with that of mixed monolayer having hydrogenated amphiphile, polarized near-edge X-ray absorption fine structure (NEXAFS) spectroscopy was also applied. The fluorinated comb polymer, poly-2-(perfluorodecyl)ethyl acrylate $[CO(F(CF_2)_{10}(CH_2)_2O)\text{-}CHCH_2]_m$ [abbr.: Poly-$FF_{10}$EA] and hydrogenated long-chain compound, octadecyl acrylate $[C_{18}H_{37}OOCCH{=}CH_2$; OA] having similarly hydrophilic groups of Poly-$FF_{10}$EA, were used in this work. This syndiotactic (Diad: 57.4%) comb polymer was obtained by postpolymerization after $^{60}$Co $\gamma$-ray irradiation as the same procedure in the previous works.[8] Poly-$FF_{10}$EA was hard to dissolve in common organic solvents without trifluoroacetic acid (TFA). The molecular weights were estimated to be above tens of thousands from the intrinsic viscosity of $[\eta] = 0.12$ for these TFA solutions at 30 °C. Samples were dissolved in TFA, a good solvent, and spread completely on distilled water to allow the spreading solution to flow down a small hydrophilic glass rod projecting from the surface of the subphase according to Trurnit's suggestion.[9] These monolayers were transferred onto solid substrates at 5 °C by a surface-lowering method at 25 mN m$^{-1}$ to obtain the non-alternating Z-type films, in which the hydrophobic moieties were oriented toward to air. Morphology of the transferred film surface was observed by an SPM system (SII SPA300; spring constant 0.09 N m$^{-1}$). The NEXAFS spectra were measured on the BL-11A soft X-ray beamline at the Photon Factory in the National Laboratory for High Energy Accelerator Research Organization (KEK-PF, Tsukuba) with synchrotron radiation.

Figure 1 shows the AFM images and the corresponding FFM of the mixed monolayer of Poly-$FF_{10}$EA and OA = 1 : 1 (long-chain ratio) on mica. Figure 1(a) is the AFM image of the mixed monolayer ($500 \times 500\,nm^2$), and (c) and (d) are topo-images of the flat and large hill parts on Figure 1(a) at the molecular resolution ($4.3 \times 4.3\,nm^2$), respectively. In Figure 1(a), many domains with several sizes in the range of about 60–100 nm, were formed in the mixed monolayer. On comparison of the AFM image (Figure 1(a)) and the corresponding FFM image (Figure 1(b)), the higher hill parts exhibited low friction. According to the reports by Lee et al.[10] and Fujihira et al.,[3,4] the microscopic friction force measured by FFM of the fluorinated compounds indicated a larger friction coefficient than the hydrogenated ones owing to the rigid unit of the fluorocarbons. In addition, the height of domains about 2.5 Å corresponds to almost perpendicular orientation of OA molecules. It was considered that the large hill island and the sea parts were corresponding to the close packing of the hydrogenated amphiphiles and fluorinated comb polymers, respectively. Hence, the number of OA molecules in the several domains were in the range of $1.4\text{–}3.9 \times 10^4$. In the cross section of Figure 1(c) image along the dashed line, the distance between fluorocarbon side-chains was estimated to be 5.1 to 5.5 Å, which were well corresponding to the value reported previously for the two- and three-dimensional short spacing of Poly-$FF_{10}$EA measured by X-ray diffractions,[8,11] whereas the distance between hydrocarbons for the OA film homogenously was about 4.3 Å (Figure 1(e)), and was not more than 5.0 Å. Both Fourier transformations (FT) images exhibited the nearly hexagonal systems for two-dimensional packing of the hydrocarbons and a little distorted one of the fluorocarbons. In Figure 1(d), the periodical microscopic friction images in the fluorocarbon region corresponding to AFM images could be achieved by reason of characteristic friction properties of fluorocarbons,[4,8] while in hydrocarbon region, a clear microscopic friction image could not be obtained. Figure 2 shows the AFM images for the mixed monolayers at the several mixing ratio of Poly-$FF_{10}$EA and OA. These monolayers exhibited the systematically structural changes for the shape of the island of the OA molecule. In the case of the Poly-$FF_{10}$EA rich monolayers, the shapes of the hydrocarbon islands were deformed. When the mixed monolayers were consisted of higher mixing ratios of the OA molecules, the circular domains were dispersed with decreasing their size. The difference between the mixing ratio and each observed area was probably due to the change of orientation for several molecules.

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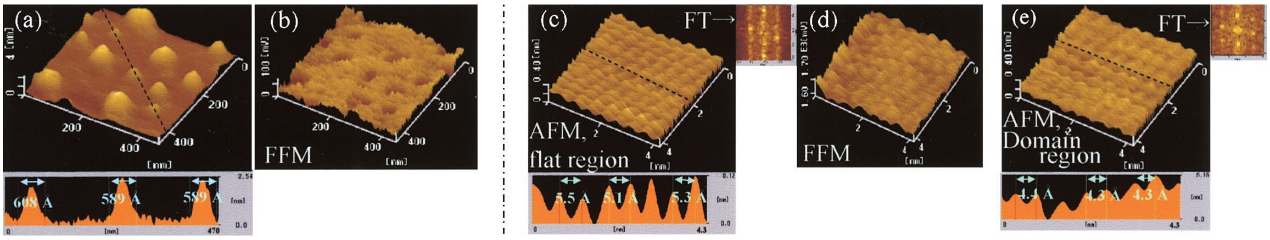

**Figure 1.** AFM and corresponding FFM images of Poly-FF$_{10}$EA : OA = 1 : 1 mixed Z-type monolayer. (a) mixed monolayer (500 × 500 nm$^2$), (b) corresponding FFM images of mixed monolayer, (c) fluorocarbon region (4.3 × 4.3 nm$^2$), (d) corresponding FFM images of fluorocarbon region (e) hydrocarbon region (4.3 × 4.3 nm$^2$) with cross section and two-dimensional Fourier transformation.

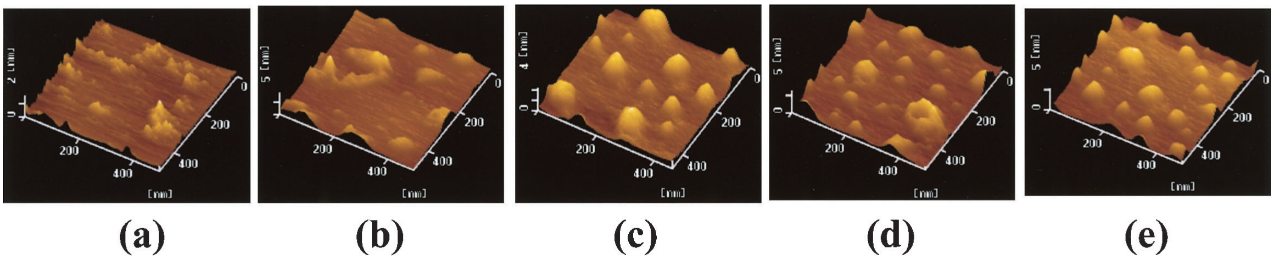

**Figure 2.** AFM images of Poly-FF$_{10}$EA : OA mixed Z-type monolayers on mica at several mixed ratio. (a) 8 : 1, (b) 5 : 1, (c) 1 : 1, (d) 1 : 5, (e) 1 : 8.

Figure 3 shows the dependence of the incidence angle for the F K-edge NEXAFS spectra of the mixed monolayer of Poly-FF$_{10}$EA and OA = 1 : 1. According to Seki et al.,[12] the peaks at about 694 and 698 eV have been assigned to the transitions from F$_{1s}$ orbital to $\sigma^*$(C–F) and $\sigma^*$(C–C) orbital, respectively. The relative intensity ratio of the $\sigma^*$(C–F) to the $\sigma^*$(C–C) peaks is clearly dependent on the incident angle owing to the highly ordered orientation of the fluorocarbons in the film.[13] Although values of the normalized intensity by edge-jump of $\sigma^*$(C–F) peaks for the mixed monolayer were decreased by about 30% to that of the pure Poly-FF$_{10}$EA film which exhibited the remarkably angular dependence, suggesting that the ordered orientation of fluorinated comb polymers in the mixed films to compared the pure Poly-FF$_{10}$EA film can be still obtained by considering the half number of polymer molecules in the same probing area. On assumption of the uniaxial orientation, the tilt angle of fluorinated side-chains in the mixed film was estimated to be about 30°, which maintained the almost same value of the Poly-FF$_{10}$EA monolayer. These results indicate that both molecules independently form the ordered orientation in the two-dimensional sea and island structures of the mixed film.

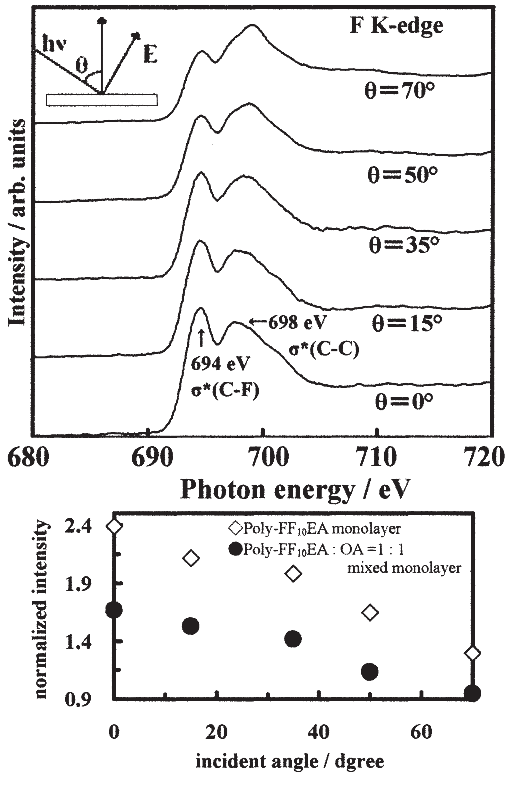

**Figure 3.** Polarized F K-edge NEXAFS spectra and plot of the normalized intensity-incident angle of F1s-$\sigma^*$(C–F) transition peaks for Poly-FF$_{10}$EA : OA = 1 : 1 mixed monolayer.

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