

Crystal Structure and Formation of Organized Molecular Films of Fluorinated Comb Copolymers

Atsuhiro Fujimori^{a,*}, Ryosuke Masuya^a, Kouya Kumagai^a, Toru Masuko^a,

Eisuke Ito^b, Masahiko Hara^b, Kaname Kanai^c, Yukio Ouchi^c, and Kazuhiko Seki^{c,d}

^aDepartment of Polymer Science and Engineering, Faculty of Engineering, Yamagata University, Jonan 4-3-16, Yonazawa, Yamagata, 992-8510, Japan. ^bLocal Spatio-Temporal Function, Frontier research system, The Institute of Physical and Chemical Research (RIKEN), Hirosawa 2-1, Wako, 351-0198 Japan. ^cDepartment of Chemistry, Graduate School of Science, Nagoya University. ^dResearch Center for Materials Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan. Fax: +81-238-26-3073, e-mail: fujimori@yz.yamagata-u.ac.jp

The structural estimation in the solid state of the newly synthesized comb copolymers having fluorinated and hydrogenated side-chains were carried out by powder X-ray diffraction (XRD) and differential scanning calorimetry (DSC). And further, monolayer behavior at the air/water interface and the molecular orientation of organized molecular films on the solids for these copolymers, were investigated by surface pressure-area (π -A) isotherm and, in-plane XRD, polarized near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, and atomic force microscopy (AFM), respectively. From these experimental findings, formation of highly ordered molecular orientation in the organized molecular films of these fluorinated block copolymers was confirmed. The phase separated structure in these copolymer monolayers exhibited formation of dispersed hydrocarbon micro-domain at 10 – 20 nm scales.

Key words: Fluorocarbon, Comb polymer, Copolymer, Organized molecular films, NEXAFS spectroscopy

1. INTRODUCTION

The surface patterning is very important subject for development of newly molecular devices.^{1,2} In addition, it is well known that the characteristic phase separation occurs in the fluorocarbon and hydrocarbon mixed monolayers because of very strong aggregation force between fluorocarbon chains.³⁻⁶ If these phase separation behavior and the surface patterning could be controlled by varying the mixed ratio or spreading solvent, it will be very interesting subject at the scope of not only basic science but also the utility in the technology. In the previous work, we investigated the formation of monolayers at the air/water interface for several acrylate and methacrylate derivatives containing fluorocarbon chains and their comb polymers, the structure and friction properties of their organized molecular films,^{7,8} and else studied the polymorphism and the γ -ray irradiated solid state polymerization for these fluorinated amphiphiles.^{9,10} In these fluorocarbon system, several studies managed by many fluorinated amphiphiles were already carried out, however, the investigation using comb polymers containing the fluorocarbons as the side-chains having the properties excellent rubbing-resistant, chemical-resistant and surface activity, was not extensively performed yet. In this study, the phase separation in the monolayers of fluorinated block comb copolymer containing both fluorocarbons and hydrocarbons as the side-chains have been observed by an atomic force microscopy (AFM), together with in-plane

X-ray diffraction (XRD). And further, in order to compare the regularity of molecular orientation between monolayer for comb copolymer and mixed homopolymer monolayer with hydrogenated comb polymer, the polarized C and F K-edge near-edge X-ray absorption fine structure (NEXAFS) spectroscopy were carried out.

2. EXPERIMENTAL

Materials

The fluorinated comb copolymers obtained by copolymerization of 2-(perfluorodecyl)ethyl acrylate $F(CF_2)_{10}(CH_2)_2O(CO)CH=CH_2$ [abbr. by FF₁₀EA] and hydrogenated long-chain compound, octadecyl acrylate $CH_3(CH_2)_{16}(CO)CH=CH_2$ [abbr. OA] having similarly hydrophilic groups of FF₁₀EA in $CHCl_3$ solution with AIBN, were used in this work. The syndiotactic (Diad : 57.4 %) Poly-FF₁₀EA homopolymer only were obtained by ⁶⁰Co γ -ray irradiated post-polymerization as same procedure given in previous works.^{9,10} The molecular weights of several copolymers were estimated to be about 1.5×10^4 ($\bar{M}_w/\bar{M}_n \approx 1.5$) by GPC measurement.

Structural estimation of bulk polymers

The thermal analyses were carried out using a Seiko Instruments model DSC200 differential scanning calorimeter. The DSC measurements were performed with a scanning rate of $10.0 \text{ }^\circ\text{C min}^{-1}$ as standard. Sample mass of ca. 5.00 mg was used for all DSC measurements. As usual scanning of DSC

measurements, heating and cooling cycle was repeated three times, in order to examine for the difference of the peak position and the transition enthalpy between 1-st heating and after that. This phenomenon is caused by the difference of thermal stability of the crystalline phase between that recrystallized from the solution and that recrystallized from the melt by cooling. Transition enthalpy was calculated from the peak area on DSC curve, and the transition entropy was calculated from dividing the enthalpy value by absolute temperature of the phase transition.

The packing modes of the molecules in crystalline phase were examined by X-ray powder diffraction measurement using a Rigaku Rad-rA diffractometer with $\text{CuK}\alpha$ radiation, which equipped with a graphite monochromator, 40 kV, 100 mA.

Formation and structural estimation of organized molecular films

Fluorinated comb copolymers hard to dissolve in the common organic solvents without trifluoroacetic acid. Hence, these samples 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 Trurnit's suggestion.¹¹ These monolayers were transferred onto solid substrates at 25 °C by horizontal lifting and surface-lowering method¹² at 30 mNm^{-1} to obtain the non-alternating X- and Z-type films in which the hydrophobic moieties were oriented toward the air, together with conventional Langmuir-Blodgett (Y-type) films. Morphologies of the surface for the transferred films were observed by an atomic force microscope (Seiko Instruments SPA300 with SPI3800 probe station; spring constant of 0.09 Nm^{-1}). The in-plane spacings of the two-dimensional lattice of the films were determined by analysis of an X-ray diffractometer with different geometrical arrangements^{13, 14} (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 sec. (multilayers : 0.05° / 20 sec. scan). NEXAFS spectra were measured on BL-7A 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 and C K-edge spectra were measured in the photon energy regions of 660 – 760 eV and 275 – 325 eV, and in the partial electron yield mode (PEY) with –450 and –200 V retarding voltages respectively and 2.0 kV accelerating voltage under the vacuum of 10^{-8} Torr.^{15, 16} The optimization of the retarding voltages at both edges was carried out for every

sample. These conditions could provide the clear NEXAFS spectra that contain the structural information of the top few layers of the multilayer films by considering the probing depth of about 50 Å.¹⁷⁻²⁰ The resolution of the spectra was 0.3 eV at the C K-edge. The NEXAFS spectra were measured without any pre-annealing and no contribution from the substrate of conductive SnO_2 coated glass (NESA glass) could be detected. In addition, no drastic structural changes such as bonding scission of fluorocarbons could be found from IR spectroscopy and X-ray diffraction results taken before and after the measurements of NEXAFS spectra.

3. RESULTS AND DISCUSSION

Figure 1 shows wide angle powder X-ray diffraction profiles and DSC thermograms of bulk fluorinated comb copolymers polymerized by several monomer ratio, Poly-FF₁₀EA, and Poly-octadecyl acrylate (POA). In the XRD profiles of copolymers, two kinds of short spacing peaks of side-chains were confirmed at 4.1 and 5.0 Å. Since these values corresponded to in-plane d-spacing of sub-cell for the each homopolymer, it was found that fluorinated and hydrogenated side-chains independently arranged in each phase separated domain. From the results of DSC measurements, it was exhibited that these side-chain crystals melted at the different temperatures. The thermograms of Poly-OA and Poly-FF₁₀EA exhibited melting temperature at about 50 and 130 °C. And further, the FF₁₀EA : OA = 1:1 copolymer have two melting temperature at higher and lower temperature region. These findings mean that hydrocarbon side-chain crystal melt at the 50 °C, and residual fluorocarbon side-chain crystal melted at higher temperature. This hypothesis is also supported by temperature controlled X-ray diffraction measurement.

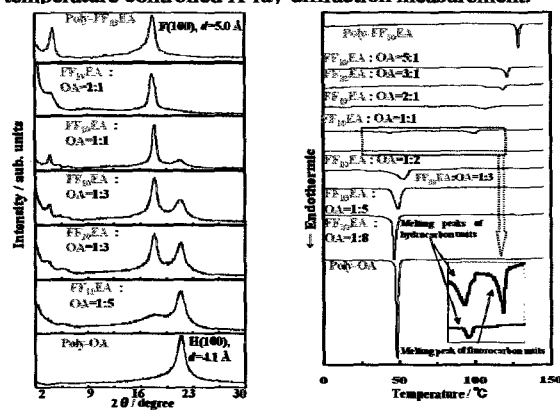


Figure 1 XRD profiles and DSC thermograms of fluorinated comb copolymers.

From the surface pressure – area (π -A) isotherms, these phase separated fluorinated block comb copolymers formed extremely stable condensed monolayer at air/water interface. Figure 2 shows the in-plane X-ray diffraction profiles of several transferred films for FF₁₀EA : OA copolymers on the solid substrate. These profiles were indicated the same packing mode to the bulk state formed in the organized molecular films of

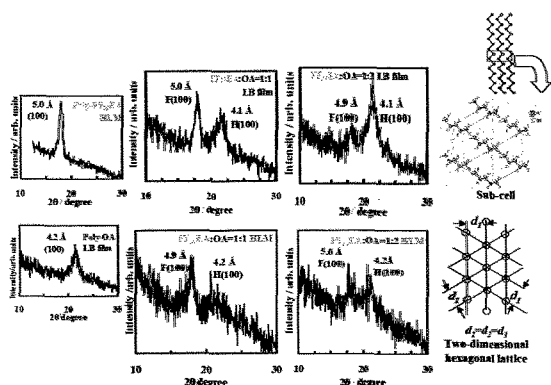


Figure 2. In-plane XRD profiles of multilayers (20 layers, 30 mNm⁻¹, 25 °C) for fluorinated copolymers and illustration of hydrocarbon sub-cell and two-dimensional lattice.

these copolymer system. And further, it is found that FF₁₀EA : OA = 1:1 copolymer LB film exhibited almost same regularity of immiscible two kinds of side-chain crystals. Hence, the estimation of molecular orientation and morphology mainly carry out in the this copolymer film, after that.

Figures 3 show the polarized NEXAFS spectra of monolayers for FF₁₀EA and OA = 1:1 copolymers and Poly-FF₁₀EA and Poly-OA mixed monolayer at C and F K-edges, as comparable system. It is found that the spectra depend significantly on the incidence angle. At F K-edge spectra, the peaks at 694 and 698 eV have been assigned to the transitions from the F1s to the σ*(C-F) and σ*(C-C) orbitals, respectively. And further, the peaks at 293 and 296 eV have been assigned to the transitions from the C1s to the σ*(C-F) and σ*(C-C) orbitals at C K-edge spectra, respectively. The relative intensity of the σ*(C-F) peak, attributable to the C-F bonds of the fluorocarbon chains, with respect to the σ*(C-C) becomes maximum at the normal incidence and weakened at grazing incidence (θ = 70°). These results suggest that the transition moments of the 694 eV band were rather parallel to the surface, indicating the nearly perpendicular orientation of the fluorocarbons.

Figure 4 shows the estimation of the fluorocarbon side-chain orientation angle for FF₁₀EA and OA = 1:1 copolymer monolayer,

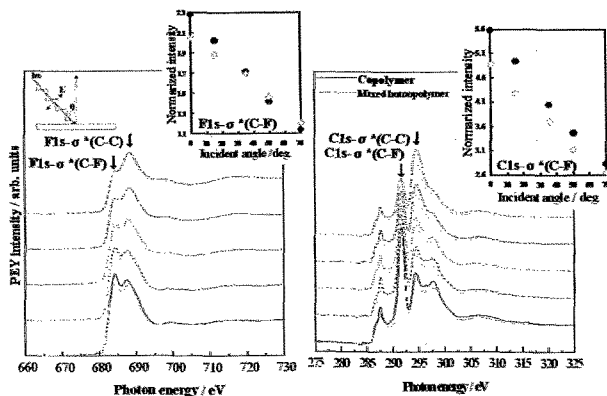


Figure 3. F K-edge and C K-edge polarized NEXAFS spectra for Z-type monolayers of FF₁₀EA and OA = 1:1 copolymer and their 1:1 mixed homopolymers.

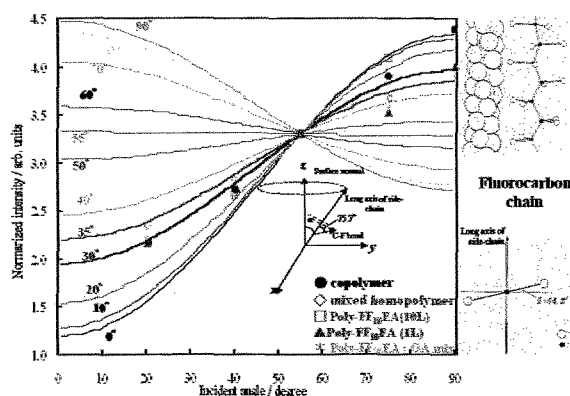


Figure 4. Plots of the normalized σ*(C-F) peaks of NEXAFS spectra vs. the incident angle for various molecular orientations assumed by the uniaxial in the Z-type monolayers of FF₁₀EA : OA = 1 : 1 copolymer and their mixed homopolymer.

Poly-FF₁₀EA : Poly-OA = 1:1 mixed monolayer, Poly-FF₁₀EA monolayer and 10 layers, and Poly-FF₁₀EA : OA = 1:1 mixed monolayer from the polarized F K-edge NEXAFS spectra, as comparable system. Assuming the uniaxial molecular orientation of fluorocarbon side-chain in the films and taking the tilted angle 14.3° of the -CF₂ plane to the perpendicular direction of the molecular axis of the fluorocarbon based on their helical conformation, we determined the orientation angles of the fluorinated side-chain by comparison of the polarized dependence of the normalized peak intensity for the NEXAFS spectra and the ideal orientation angle curves. These results show that the tilted angle of fluorocarbon side-chain units for FF₁₀EA and OA = 1:1 copolymer monolayer are about 30 degree to the surface normal.

Figure 5 shows AFM images of Z-type films for Poly-FF₁₀EA : Poly-OA = 1:1 mixed monolayer, FF₁₀EA and OA = 1:1 copolymer monolayer, and previous reported Poly-FF₁₀EA : OA = 1:1 mixed monolayers²¹ on mica substrate. In the mixed homopolymer monolayer system formed by co-spreading method from CH₃Cl and CF₃COOH solution, several circular hydrocarbon domains in fluorocarbon 'sea' constructed at about micro-meter scales. On the other hand, previous reported fluoropolymer : hydrocarbon monomer mixed system, the domains at 50 – 100 nm diameter scales were confirmed. In addition, many investigators found that there was no miscibility between fluoro- and hydrocarbon chain.^{1,3,4} Hence, it was concluded that these phase separation structure corresponded to the large hill island of aggregated hydrogenated amphiphiles and the sea of fluorinated comb polymers. In the cross section of the surface in molecular resolution images along the dashed line of copolymer system, the distance between fluorocarbon side-chains estimated the range from 4.9 to 5.4 Å, which well corresponded to the value of the two-dimensional short spacing of this

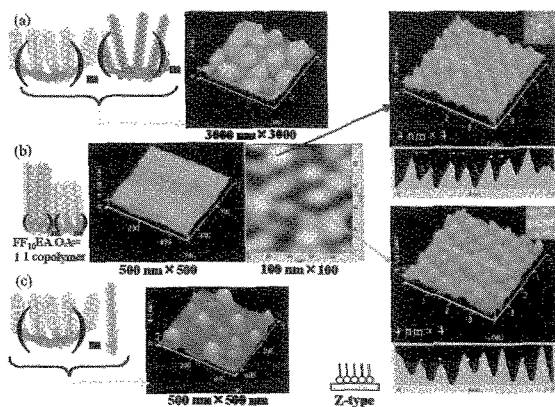


Figure 5. AFM images of several copolymer and mixed Z-type monolayers systems; (a) mixed homopolymer (b) FF₁₀EA and OA =1:1 copolymer (c) Poly-FF₁₀EA and OA.

comb polymer measured by in-plane XRD, whereas the distance between hydrocarbons exhibited the range from 3.9 to 4.3 Å. In the both images of fluorocarbon and hydrocarbon region, two-dimensional Fourier transformations (FT) were also shown. Both FT images exhibited the nearly hexagon spot which was considered the formation of hexagonal systems on two-dimensional packing of molecules. It was supposed that the reason of less clearly FT images of fluorocarbon region than hydrocarbon one was decrease of regularity for the fluorinated side-chain alignments in the 'sea' region.

Hence, the hydrocarbon 'island' region formed homogeneous surface arrangements of the hydrogenated side-chain unit supported by the nearly hexagonal system on the two-dimensional FT spot by the molecular resolution AFM image.

4. CONCLUSION

For the results stated above, the phase separated nano-structure of the organized molecular films for the fluorinated block comb copolymers, have been estimated by in-plane XRD, polarized NEXAFS spectroscopy, and an AFM observations.

In the fluorinated comb copolymer polymerized by several monomer ratio, phase separated structure between hydrocarbon and fluorocarbon side-chain crystals was confirmed. The monolayer behavior at the air/water interface examined by surface $\pi - A$ isotherms which exhibited formation of the extremely stable condensed monolayers. The meso- and microscopic scale observation of transferred Z-type monolayers by AFM exhibited phase transition between hydrocarbon 'island' region and fluorocarbon 'sea' region. These phase separated structures on the Z-type monolayer of FF₁₀EA and OA =1:1 copolymer were observed at 10~20 nm scales. The molecular resolution image of the hydrocarbon 'island' and fluorocarbon 'sea' region commonly exhibited the pseudo-hexagonal spot on the two-dimensional

Fourier transformation which mean homogeneous surface arrangements of the each unit.

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