Structural control of organized molecular films for comb polymers and its structural estimation

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The molecular orientation in mono- and multilayers of fluorinated comb copolymers with various monomer ratios were characterized by in-plane and out-of plane X-ray diffraction (XRD), near-edge X-ray absorption fine structures (NEXAFS) spectroscopy at the C K-edges, and atomic force microscopic (AFM) observation. Furthermore, the fine structure in the solid state and phase transition behavior of these newly synthesized comb copolymers having fluorocarbon and hydrocarbon side-chains were investigated by temperature controlled wide angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC). From the WAXD profiles, two kinds of short spacing peaks which were assigned to the sub-cells for fluorinated and hydrogenated side-chains were confirmed at 5.0 and 4.1 Å, respectively. Furthermore, two kinds of endothermic peaks, which corresponded to melting peaks of the both side-chain crystals, appeared in the heating process of the DSC thermograms. From these experimental findings, the phase-separated structure having the independently packed immiscible side-chain crystals formed in the whole polymer crystal. In addition, it was found that these comb polymers formed highly ordered (double) layer structure on the basis of WAXD and small angle X-ray scatting (SAXS). These fluorinated comb copolymers form the monolayer on the water surface and their transferred films adopt phase-separated structures at the nanometer length scale on solids. Hydrogenated domains of about 30 nm in diameter form in these phase-separated surface structures of monolayers. From these experimental results, these copolymer monolayers are expected to be used as new molecular devices such as nano-lithography using surface patterning of polymer nano-materials.

Key words: Comb copolymer, Organized molecular film, Side-chain crystal, In-plane XRD, AFM

1. INTRODUCTION

Fluorinated compounds including fluoro-polymers have attracted wide interested in the basic material sciences and applied technologies for the last fifty years,[1] since the fluorinated surface is effective on the tribological behavior due to the low energy surface[2] and negative surface potentials[3] in addition to their excellent thermal stability and chemical resistance. For the last quarter of a century, fluorinated functional materials have been synthesized to compare with corresponding hydrocarbon derivatives.[4, 5] Surfactants with fluorocarbons in solutions are known to exhibit behaviors different from those of the corresponding amphiphiles with hydrocarbons.[6] Fluorinated amphiphiles and polymerizable lipids were synthesized for formation of biomembrane models.[7] Recently, the polymers with fluorocarbon side-chains were reported for the practical utilization in the lubricant at low temperatures.[8] Molecular orientation of the partially fluorinated amphiphiles in the monolayers at the air/water interface and the wettability of those adsorbed films were examined early in comparison with those of the hydrocarbon derivatives.[3]

In addition, the surface patterning[9] is also an important subject for development of new molecular devices as lithography. It is well known that characteristic phase separation occurs in the mixed materials containing fluorocarbons

and hydrocarbons because of the lack of miscibility.[4] Since H. J. Güntherodt, et al. reported studies on mixed monolayer system containing fluorinated compounds estimated by friction force microscopy,[5] several mixed systems of fluorinated and hydrogenated compounds in the three-dimensional composites and two-dimensional organized molecular films were widely examined by many investigators. However, the surface patterning at the nanometer length scales is impossible in this phase-separated system still now, because the hydrogenated domains in the phase-separated structure are generally of the size of a few μm.[10] This phenomenon may be caused by the expand phase (sea region) formed by unoriented fluorinated compounds. The two-dimensional micro phase separation itself in the mixed monolayer is caused by line tension of domains or by two-dimensional spinodal decomposition. However, whichever process may occur, the 'sea region' is generally an expanded phase. It seems that existence of commonly oriented island and sea phase is a key to the realization of nano-patterning using mixed system of fluorocarbons and hydrocarbons. In order to solve this proposition, there are many possibilities of utilizing the micro phase separation in three-dimensional block copolymers. If phase separation of this type is used for the surface patterning at the nanometer length scale and can be controlled by changes in the monomer ratio on the co-polymerization, it is interesting in

the scopes of not only basic science but also nano-technology.

Recently, instead of the hydrocarbon chains, monomers of acrylates and methacrylates containing various fluorocarbon chains with different lengths and fluorine atoms at the ω-position were used to form monolayers formation at the air/water interface.[11] Furthermore, the comb polymers containing various fluorocarbon side-chains with different lengths and atoms at the ω-position were obtained using post-polymerization of these corresponding monomers by irradiation of ^{60}Co γ-ray at -196 °C in *liq.* $-N_2$.[12] Stabilities of the monolayers and the multilayer formation of the fluorinated monomer amphiphiles with the vinyl groups were studied,[13] and the monolayer assemblies of the corresponding fluorinated comb polymers were also reported.[14] In the present paper, the fine structure in the solid state of newly synthesized fluorinated comb copolymers obtained from several acrylic and methacrylic monomer ratios were investigated by wide-angle X-ray diffraction (WAXD) and small angle X-ray scattering (SAXS). Furthermore, phase transition behavior of these block comb copolymers was examined by differential scanning calorimeter (DSC) and temperature controlled WAXD measurements.

These synthesized fluorinated comb copolymers are expected to be utilized as the new molecular devices such as nano-lithography using the surface patterning of polymer nano-materials, which is based on the formation of the monolayer at the air/water interface and their Langmuir-Blodgett (LB) films.

2. EXPERIMENTAL

2.1 Materials

Fluorinated comb copolymers were obtained by copolymerization of octadecyl acrylate (OA) and methacrylate (OMA) 2-(perfluorodecyl)ethyl acrylate (FF₁₀EA) and methacrylate (FF₁₀EMA) at several monomer ratios. Copolymerizations were carried out in a solution of $CHCl_3$ at 50 °C for 48 hours using 1 mol% azobisisobutyronitrile (AIBN) as initiator. The precipitated polymers were washed with acetone till they were free of monomers. The syndiotactic Poly-FF₁₀E(M)A homopolymer were obtained only by ^{60}Co γ-ray irradiated post-polymerization according to the same procedure given in the previous work.[12] Comb copolymer compositions were determined by ^1H NMR spectroscopy. The tacticity of fluorinated homopolymer was obtained to be almost syndiotactic (Diad; 58 %) by ^1H NMR analysis according to the reference.[15] The molecular weights of several copolymers with higher ratios of OA units were estimated to be about Mw = 2.0 × 10⁴ ($\overline{Mw}/\overline{Mn} \approx 1.5$) on the basis of GPC measurements (see table). The molecular weights of fluorinated homopolymer and copolymers with higher ratio of FF₁₀EA units were estimated to be above a thousand from the

intrinsic viscosity of $[\eta] = 0.12 \sim 0.54$ for these trifluoroacetic acid solutions at 30 °C by applying the relation $[\eta] = KM^{\alpha}$, where $K = 0.24 \sim 0.25 \times 10^{-4}$, $\alpha = 0.75 \sim 0.78$ were assumed from results of viscosity-averaged molecular weight for poly-alkyl acrylate and methacryalte.[18]

Table 1 GPC data of individual acrylic copolymers used in this study.

FF₁₀EA : OA ratio	$\overline{Mn}$ ($/10^4$)	$\overline{Mw}$ ($/10^4$)	$\overline{Mw}/\overline{Mn}$
0:1	1.04	1.54	1.49
1:8	1.56	2.38	1.52
1:5	1.62	2.51	1.54
1:3	1.26	1.79	1.42
1:2	1.63	2.47	1.51
1:1	1.10	1.65	1.50

The copolymerization procedure in this work is generally used to synthesize random copolymers. However, according to the results of ^1H NMR measurements, there is a great possibility of formation of the block copolymer obtained by immiscible monomers. Probably, it can not form many bonding points in the solution during the co-polymerization because immiscible monomers are hard to approach each other and form the bonding.

2.2 Structural estimation of bulk copolymers

The thermal analyses were carried out by using a Seiko Instruments model DSC200 differential scanning calorimeter. The DSC measurements were performed with a scanning rate of 10.0 °C min⁻¹ as standard. Sample mass of ca. 2.00 mg was used for all DSC measurements. As usual scanning of DSC measurements, heating and cooling cycle was repeated twice, in order to examine the difference of the peak position and the transition enthalpy between the 1st heating and the next.

The packing modes of the several copolymers in crystalline phase were examined by X-ray powder diffraction measurements using a Rigaku Rad-rA diffractometer with $CuK\alpha$ radiation, which was equipped with a graphite monochrometer at 40 kV and at 200 mA. And structural changes together with phase transition of several copolymers were examined by temperature controlled X-ray diffraction measurement using a Mac Science MXP18VA diffractometer with $CuK\alpha$ radiation at 40 kV and at 200 mA. In the case of *in situ* elevating temperature measurements, the temperature range from 25 to 65 °C was adopted with reference to the results of DSC measurements.

2.3 Formation of copolymer monolayers on the water surface and estimation of molecular arrangement in the films

The monolayers of the fluorinated comb copolymer were spread from the chloroform / trifluoroacetic acid = 90/10 (v/v) mixed solutions (about 10^{-4} M) onto the distilled water (about 18 MΩ·cm). The surface pressure − area (π − A)

isotherms of the polymers were measured on a Lauda film balance at different temperatures. These fluorinated comb copolymers formed extremely condensed monolayers. These monolayers were deposited onto the solid substrates at r. t. by a surface lowering method at 25 mNm⁻¹ to obtain non-alternating Z-type film. The outermost surface of Z-type film was orient the hydrophobic side-chains to the air.

Surface morphologies of the transferred films were observed by a scanning probe microscope (Seiko Instrument, SPA300 with SPI-3800 probe station), using microfabricated rectangular Si_3N_4 cantilevers with integrated pyramidal tips with a constant force of 0.09 N/m). The long-spacings of the layered structures of the films on glass plates were measured by an out-of plane X-ray diffractometer (Rigaku, Rad-rA, CuKα radiation, 40 kV, 100 mA) equipped with a graphite monochromator. 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[17] (Bruker AXS, MXP-BX, CuKα 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.[18] 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.[19] The NEXAFS spectra were measured without any pre-annealing and no contribution from the substrate of conductive SnO_2 courted glass (NESA glass) could be detected.

3. RESULTS AND DISCUSSION
Estimation of fine structures of fluorinated block comb copolymers

Figure 1 shows X-ray powder diffraction profiles of Poly-FF₁₀E(M)A, Poly-O(M)A and FF₁₀E(M)A : O(M)A comb copolymers. From these WAXD profiles of each homopolymers, short spacing peaks based on the sub-cell of side-chains were confirmed at 4.1 and 5.0 Å. According to the Platé's review, these peaks correspond to (100) reflection.[20] In the case of copolymers, two kinds of short spacing peaks of side-chains were commonly confirmed at 4.1 and

5.0 Å. In the present work, these peaks were defined as H(100) and F(100) reflections, because these peaks were based on the structure in the different region of fluorinated copolymer crystal. In other words, since these values agree well with the in-plane lattice spacing of sub-cells for the each homopolymers, it means that fluorinated and hydrogenated side-chains are separately packed in the phase-separated domains.
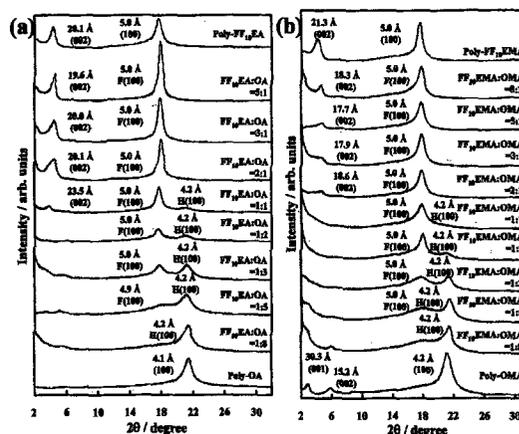
Fig.1 WAXD profiles of (a) acrylic and (b) methacrylic fluorinated comb copolymers.

In the small angle region, the long spacing peaks are positioned at about 20.1 and 23.5 Å in the profiles of Poly-FF₁₀EA and FF₁₀EA : OA = 1:1 copolymers. These polymers form the layer structure along the direction of c-axis. According to the previous work, it seems that these long spacing peaks were defined at (002) reflection, because Poly-FF₁₀EA form the double layer structure, and also because the calculated length of fluorocarbon side-chain are estimated about 20 Å. The *d*-spacing from (001) reflection peak of Poly-OA was estimated at about 50 Å by computer simulation although Poly-OA did not form the layer structure. The expected value of double layered c-axis length for FF₁₀EA : OA = 1:1 copolymers having OA side-chain parts was about 47 Å. It seems that this subtle difference came from the tilted conformation of hydrocarbon side-chain.

From these profiles, interesting systematic changes were also confirmed in both long and short spacing region, which depended on the monomer ratio. With an increase of OA or OMA ratio, the intensity of (002) and F(100) reflection gradually decreased, and H(100) reflection appeared and grew from FF₁₀EA : OA =1:1 copolymer to Poly-OA in the acrylic system. These XRD profiles indicate the possibility of structural control of side-chain crystals and its crystallinity which is reflected in peak. This result will be very important information on the size and on the control of the dispersion degree for each domain related to surface pattering on the occasion of formation for the organized molecular films as following discussion.

In order to confirm the actual formation of
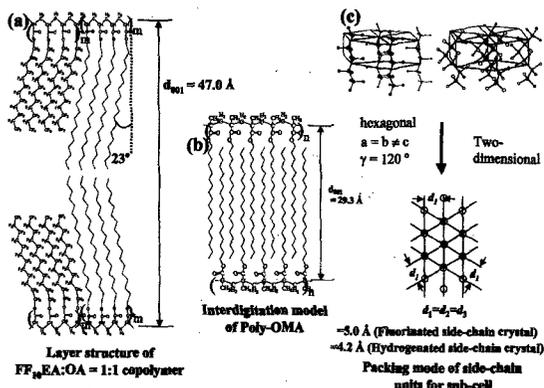
Fig. 2 Schematic illustration of layer structure for the (a) $FF_{10}EA$: OA = 1:1 copolymer and (b) Poly-OMA. (c) Sub-cell structure and two-dimensional lattice of hydrogenated and fluorinated side-chain crystals.

double layer structure, small angle X-ray scattering measurements were carried out. From the results of SAXS measurements, (001) reflection clearly appeared in the low angle region, which positive evidence to the formation of the highly ordered double layer structure of $FF_{10}EA$: OA= 1 : 1 copolymer.

From the results of WAXD and SAXS measurements, the models of molecular arrangement and packing of fluorinated comb copolymers are shown in Fig. 2. The hydrocarbon side-chain parts of $FF_{10}EA$: OA =1:1 copolymer are tilted at about 23°, although the tilt angle of fluorocarbons having shorter side-chain length than hydrocarbons by can not be decided only XRD measurements. However, taking into consideration of incompressibility constraint of main-chain, we adopt the tilted model for the fluorocarbon with almost the same tilt angle with hydrocarbons since it is improbable to allow for the empty space between fluorinated and hydrogenated units. It seems that the side-chains of both hydrocarbons and fluorocarbons of all polymers synthesized in this work are two-dimensionally in hexagonal sub-cells.

Thermal behavior of comb copolymers with fluoro- and hydrocarbon side-chains

Figure 3 displays 2nd-heating process of DSC thermograms for each homopolymer and copolymer (scanning rate; 10 °C min⁻¹). Two kinds of endothermic peaks can be seen in the heating process and other exothermic peaks can be seen in the cooling process. This supports the existence of two kinds of side-chain crystals. These transition peaks show the melting and crystallization peaks of fluorinated and hydrogenated side-chain crystals exhibiting different melting temperatures. In comparison with general crystalline polymers, the melting peaks of Poly-OA and Poly-FF$_{10}$EA in the DSC thermograms are sharp and they appear in relatively low temperature regions (about 50 °C and 130 °C, respectively) because these side-chain crystals packed like a structure of
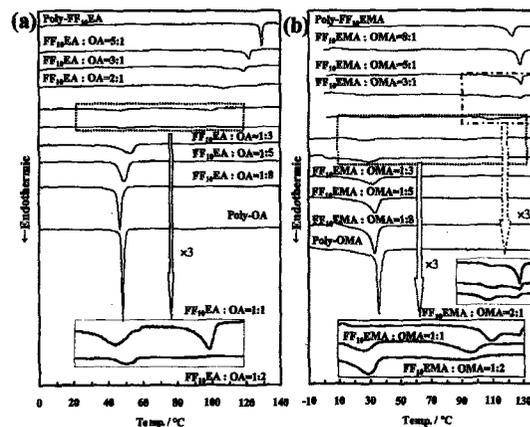
Fig. 3 DSC thermograms of (a) $FF_{10}EA$: OA and (b) $FF_{10}EMA$: OMA copolymers with various copolymerization ratio at 2-nd heating.

corresponding monomers (or general long-chain compounds with low molecular weight). Therefore, it is predict that the transition peaks at higher and lower temperature region are corresponded to those of fluorocarbon and hydrocarbon side-chain crystal.

On going from Poly-OA to $FF_{10}EA$: OA = 1:1 copolymer, the peak positions in the low temperature side hardly move with a variation in $FF_{10}EA$ ratio, whereas the peaks in the high temperature side gradually shift to the low temperature region with an increase of OA ratio. Since copolymers with the exception of 1:1 copolymer also shown the two kinds of peaks at much faster scanning rate (20 ~ 100 °C min⁻¹), this tendency is essentially invariable.

In order to get accurate supported data of the existence of two kinds of side-chain crystals and to draw an inference from the thermal behavior, the temperature controlled X-ray diffraction was carried out. These profiles of $FF_{10}EA$: OA =1:1 copolymer on elevating and cooling processes are shown in Fig. 4. Temperature controlled XRD measurements were carried out at three stages. At first, it was measured at room temperature. The primary peak in the low angle side (d_{002}) is caused by hydrocarbon units. On the basis of our previous work, long period along the c-axis of fluorinated units alone dose not explain the value 22.7 Å since the maximum value of single layer length for fluorinated units is 20.5 Å. At 65 °C, the H(100) reflection disappears together with the melting of hydrogenated side-chain crystal, and long spacing peaks shift to the small angle side. The increase in interlayer spacing is probably due to the fact that the tilt angle of hydrocarbons becomes small in the molten state compared with the random arrangement in the two-dimensional plane. Hence, it is suggested that the length of hydrocarbons along the side-chain axis dominates the long spacing between layers even if hydrocarbon units transit the molten state. When the film is cooled down to 25 °C again, the H(100) reflection appears because of crystallization of the hydrogenated side-chain,

Fig. 5 In-plane XRD profiles of multilayers for (a) acrylic and (b) methacrylic comb copolymers.
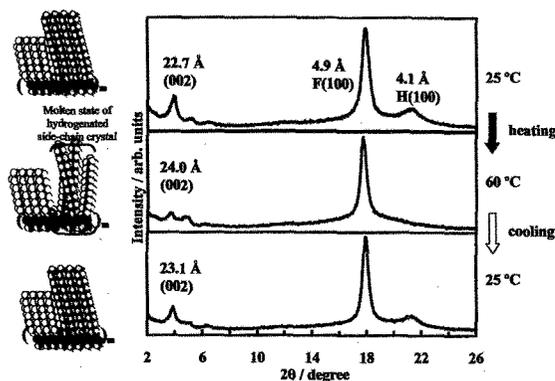
and long spacing peaks shift to the wide angle side due to the tilted arrangement of hydrocarbons. Hence, it is concluded that reversible phase transition occurs in this copolymer system.

Molecular arrangement of organized molecular films for fluorinated comb copolymers

On these experimental results, we try to make use of these fluorinated comb copolymers as the material for formation of monolayers on the water surface. From the surface pressure – area (π-A) isotherms, these phase-separated fluorinated comb copolymers formed extremely stable condensed monolayer at the air/water interface and it was possible to transfer these monolayers on solid substrates.[21] Figure 5 shows the in-plane X-ray diffraction profiles of several transferred films of copolymers. These profiles indicate the packing mode analogues in the organized molecular films of these copolymer system to the bulk state. Furthermore, it is found that $FF_{10}EA$: OA = 1:1 copolymer LB film exhibited almost the same regularity of two kinds of immiscible side-chain crystals though fluorinated side-chain dose not arrange in the $FF_{10}EMA$: OMA comb copolymer films in all composition ratios.

From the results of polarized NEXAFS spectra of monolayers of $FF_{10}EA$ and OA = 1:1 copolymers and Poly-$FF_{10}EA$ 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. Furthermore, 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.

Following the NEXAFS results, it is carried out the estimation of the fluorocarbon side-chain orientation angle for $FF_{10}EA$ and OA = 1:1 copolymer monolayer, Poly-$FF_{10}EA$: Poly-OA = 1:1 mixed monolayer, Poly-$FF_{10}EA$ monolayer and 10 layers, and Poly-$FF_{10E}A$: OA =1:1 mixed monolayer from the polarized F K-edge NEXAFS spectra, as comparable system.
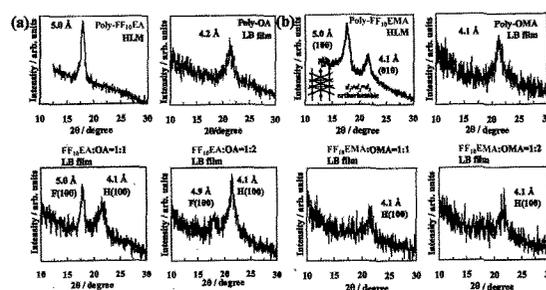
Assuming the uniaxial molecular orientation of fluorocarbon side-chain in the films and taking the tilted angle 14.3° of the $-CF_2$ plane to the perpendicular direction of the molecular axis of the fluorocarbon based on the their helical conformation, we determined the orientation angles of the fluorinated side-chain by comparison of the polarized dependence of the normalized peak intensity for the NEXAFS spectra and the ideal orientation angler curves. These results show that the tilted angle of fluorocarbon side-chain units for $FF_{10}EA$ and OA = 1:1 copolymer monolayer are about 30 degree to the surface normal.

Surface morphology of monolayers on solid for fluorinated comb copolymers

Figure 6 shows AFM images of Z-type monolayers for $FF_{10}EA$: OA and $FF_{10}EMA$: OMA copolymer with various copolymerization ratio on mica at room temperature. In the case of $FF_{10}EA$ and OA = 1:1 copolymer monolayer, nanometer order phase separated structure having about 30 nm diameter hydrogenated domains was confirmed at the scale 1 × 1 μm^2 scales. With the increasing of hydrogenated side-chain ratio, the film surface is gradually covered by hydrogenated island, and fluorinated sea region decrease. In the case of increasing of fluorinated side-chain ratio, the shape and alignment of hydrogenated domains gradually disordered. However, as the overview of formation of surface morphology on this acrylic system, it was possible to control construction of the phase separated structure at nonometer size by method of organized molecular films and copolymerization ratio of fluorinated comb copolymers. While, in the case of methacrylic system, it was confirmed obvious different tendency to the acrylic monolayer. The hydrogenated domain size of these methacrylic monolsyers are corresponded to the micrometer scale. It is supposed that this difference closely relate the orientation regularity of fluorinated side-chain crystal. The result of morphological estimation is summarized in fig. 7. In conclusion, it is supposed to realize the nano-patterning at a few ten nanometer size on fluorocarbons and hydrocarbons system by existing commonly oriented island and sea phase. In the near future, the relationships between
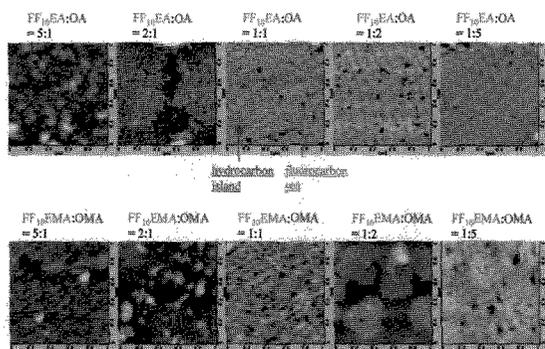
Fig. 6 AFM images of Z-type monolayers on mica for acrylic and methacrylic fluorinated comb copolymers.

surface morphologies and side-chain orientation of fluorinated comb copolymers with several composite ratios in organized molecular films will be reported elsewhere, in detail.

4. CONCLUSION

The solid-state structure and phase transition behavior of fluorinated comb copolymers have been estimated by WAXD, DSC, and temperature controlled WAXD measurements. From the results of these measurements, it is found that fluorinated and hydrogenated side-chain crystals of these comb copolymers were independently packed, and formed hexagonal sub-cell in the two-dimensional lattice. Along the direction of c-axis, these comb polymers form highly ordered (double) layer structure. And further, it was indicated that the phase transition also independently occurred at different temperature region between fluorocarbon and hydrocarbon side-chain crystals on the heating process of DSC measurement. In addition, the phase separation structure with hydrogenated domains at about 30 nm diameter scales were confirmed in $FF_{10}EA : OA =1:1$ copolymer monolayer on solids. From these experimental findings, these fluorinated comb copolymers will be expected to be utilized the newly molecular devices such as nano-lithography based on the surface patterning at a few nanometer sizes of two-dimensional micro phase separated copolymer system.

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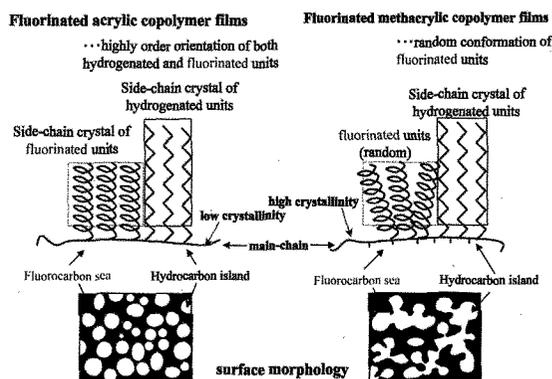
Fig. 7 Schematic illustration of molecular arrangement and surface morphology of acrylic and methacrylic fluorinated copolymer films.

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