

Solid-state structure of fluorinated comb copolymer and molecular orientation of its organized molecular film

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Molecular orientation and surface morphology of monolayers related to solid-state structure for methacrylate comb copolymers having fluorocarbon and hydrocarbon side-chains were investigated using X-ray diffraction (XRD), differential scanning calorimetry (DSC), and atomic force microscopy (AFM). From the XRD profiles, two kinds of short spacing peaks were confirmed at 5.0 and 4.2 Å, which assigned the sub-cells for both side-chains. Further, two kinds of endothermic peaks, which corresponded to melting peaks of the both side-chain crystals, appeared in the thermograms. From the AFM observation of their monolayers, it was found that there were hydrogenated domains at a few hundred nm diameters in their monolayers, whereas corresponding acrylate copolymer monolayers form the phase-separated structure with the domains at 10-30 nm diameters.

Key words: Fluorinated comb copolymer, Phase transition, Phase-separated structure, Side-chain crystal, Size-control of hydrogenated domains

1. INTRODUCTION

It is essential to control the molecular arrangement at the monomolecular level and their morphology at mesoscopic scale in order to drive the functionality of these organic molecular devices in an efficient manner. Fine structure of fluorinated polymers and their derivatives have attracted wide interested in the fundamental material sciences and applied technologies for the past half of century,^{1,2} since the surface of fluorinated thin films exhibit the characteristic friction behavior due to the low energy surface³ and negative surface potentials⁴ in addition to their excellent thermal stability and chemical resistance.

On the other hand, the micro-lithography technique^{5,6} based on surface patterning is an important subject for construction of new molecular devices. It is known that characteristic phase separation occurs in the mixed materials containing fluorocarbons and hydrocarbons because of the lack of their miscibility.³⁻⁸ Since Overney, *et al.* reported studies on mixed monolayer system containing fluorinated compounds estimated by friction force microscopy,^{5,6} 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 scale is impossible in this phase-separated system still now, because the hydrogenated domains in the phase-separated structure are generally size of a few μm .⁹ This may be caused by the expanded phases formed by irregularly ordered 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 fluorinated 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-technological industry.

In the present paper, the fine structure in the solid state of newly synthesized fluorinated methacrylate comb copolymers was investigated using XRD. Furthermore, phase transition behavior of these comb copolymers was examined using differential scanning calorimeter (DSC) and temperature controlled XRD measurements. In addition, these methacrylate comb copolymers are formed extremely condensed monolayers on the water surface. Their transferred films on mica are exhibited phase separated surface at μm ~ sub-micron scales whereas previous reported corresponding acrylate monolayers form the patterned structure at 10-30 nm scales. Generally, since poly-methacrylic acids exhibit the higher glass transition temperature than poly-acrylic acids, the reason of those differences of surface morphology is suggested influence of packing hindrance for fluorinated side-chain by arrangement of low mobility methacrylate main-chain.

2. EXPERIMENTAL

2.1 Materials

Fluorinated comb copolymers were obtained by co-polymerization of octadecyl methacrylate (OMA) and 2-(perfluorodecyl)ethyl methacrylate (FF₁₀EMA) at several monomer ratios. Co-polymerizations were carried out in a

solution of CHCl_3 at 50 °C for 48 hours using 1 mol% azobisisobutyronitrile (AIBN) as an initiator. These monomers and initiator were purchased from Tokyo Kasei Co. Ltd. and Daikin Fine Chemicals Co. Ltd., and used without further purification. The precipitated polymers were washed with acetone till they were free of monomers. The syndiotactic poly- FF_{10}EMA homopolymer were obtained only by 1 M rad ^{60}Co γ -ray irradiated post-polymerization according to the same procedure given in the previous work.¹⁰ The γ -ray irradiation was carried out at the Japan Atomic Energy Institute at Takasaki. Comb copolymer compositions were determined by ^1H NMR (Nihon densi Co Ltd. EX270 NMR) spectroscopy. The tacticity of the fluorinated homopolymer was obtained to be almost syndiotactic (Diad; 57.4 %) by ^1H NMR analysis according to the reference.¹¹ The molecular weights of several copolymers with higher ratios of OMA units were estimated to be about $\overline{M}_w = 3.5 - 5.0 \times 10^4$ ($\overline{M}_w/\overline{M}_n \approx 2.2$) on the basis of GPC (JASCO-860-CO) measurements (see table 1). The molecular weights of fluorinated homopolymer and copolymers with higher ratios of FF_{10}EMA 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 $[\eta] = K\overline{M}^\alpha$, 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 methacrylate.¹²

The co-polymerization procedure in this work is generally easy to synthesize the random copolymer. According to the results of ^1H NMR measurements, there is a great possibility of formation of the block-type random copolymer obtained by immiscible monomers. That is to say, it was confirmed the shift to the high magnetic field side of chemical shift in ^1H NMR spectra originated by existence of adjacent hydrogen atoms to the fluorocarbon block unit. It seems that there are considerably fluorinated and hydrogenated block units. Probably, it cannot 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.

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 $\text{CuK}\alpha$ radiation, which was equipped with a graphite monochromator at 40 kV and at 200 mA.

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

arrangement in the films.

The fluorinated comb copolymer were spread from chloroform / trifluoroacetic acid = 90/10 (v/v) mixed solutions (about 10^{-4} M) onto distilled water (about 18 $\text{M}\Omega\text{-cm}$). Surface pressure - area ($\pi - A$) isotherms of the polymers were measured on a film balance (Kyowa Kaimen Kagaku Co. Ltd., compression speed; 5 $\text{Å}^2/\text{repeating units} \cdot \text{min}$) at 15 °C. These fluorinated comb copolymers formed extremely condensed monolayers. These monolayers were deposited onto the solid substrates at r. t. by a surface lowering method¹³ at 25 mNm^{-1} to obtain non-alternating Z-type film. For the outermost surface of Z-type films, the hydrophobic fluorocarbon side-chains were exposed 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 Nm^{-1} . The long-spacing of the layered structures of the films on glass substrates were measured by an out-of plane X-ray diffractometer (Rigaku, Rad-rA, $\text{CuK}\alpha$ radiation, 40 kV, 100 mA) equipped with a graphite monochromator. The in-plane spacing of the two-dimensional lattice of the films were determined by analysis of an X-ray diffractometer with different geometrical arrangements¹⁴ (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° / 20 sec.

3. RESULTS AND DISCUSSION

Estimation of fine structures for fluorinated comb copolymers.

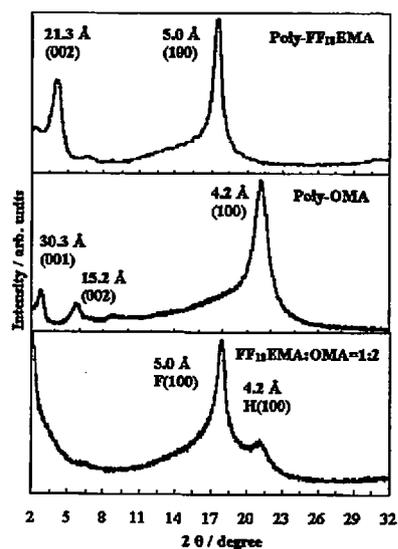


Fig. 1 XRD profiles of poly- FF_{10}EMA , Poly-OMA, and $\text{FF}_{10}\text{EMA} : \text{OMA} = 1:2$ copolymer.

Figure 1 shows X-ray powder diffraction profiles of poly-FF₁₀EMA, poly-OMA and FF₁₀EMA : OMA = 1:2 fluorinated comb copolymer. From the WAXD profiles of each homopolymer, short spacing peaks based on the sub-cell of side-chains were confirmed at 4.2 and 5.0 Å. According to the Platé's review, these peaks correspond to (100) reflection.¹⁵ In the case of copolymers, two kinds of short spacing peaks of side-chains were commonly confirmed at 4.2 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 homopolymers, it means that fluorinated and hydrogenated side-chains are separately packed in the phase-separated domains.

In the small angle region, the long spacing peaks are positioned at about 21.3 or 30.3 and 15.2 Å in the profiles of poly-FF₁₀EMA and poly-OMA. These polymers form the layer structure along the direction of *c*-axis. According to the previous work, it seems that this long spacing peak in the profile of poly-FF₁₀EMA were defined at (002) reflection, because poly-FF₁₀EMA form the double layer structure, and also because the calculated length of fluorocarbon side-chain are estimated about 21 Å. The *d*-spacing from (001) reflection peak of poly-OMA was estimated at 30.3 Å. This value is smaller than double layer structure of poly-OMA, which is estimated the length along the *c*-axis at about 25 Å. According to the previous reports, the reason of smaller *c*-axis length is formation of interdigitated structure for poly-OMA layers.^{16,17} It was supported that FF₁₀EMA : OMA = 1:2 copolymer could not form the layer structure on this side-chain ratios.

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

Figure 2 displays 2nd-heating processes of DSC thermograms for each homopolymer and copolymers. On going from poly-OMA to FF₁₀EMA : OMA = 1:1 copolymer, the peak positions in the low temperature side hardly move with a variation in FF₁₀EMA ratios. In the case of peaks in the high temperature side, those don't shifted with OMA ratios except the one of FF₁₀EMA : OMA = 1:1 and 1:2 copolymers, although these peaks split within the region of 90 - 130 °C, which mean the existence of different thickness of 'lamellae' (in this case, this term is able to exchange to the 'layers'). It is supposed that the melting peak shift to the low temperature side of fluorinated side-chain crystal of FF₁₀EMA : OMA = 1:1 and 1:2 copolymers means a subtle miscibility of both side-chain crystals on these composition. Although copolymers with the exception of 1:1 and 1:2 copolymer also show the two kinds of peaks at much faster scanning rates (20 ~ 100 °C min⁻¹), this tendency is essentially invariable.

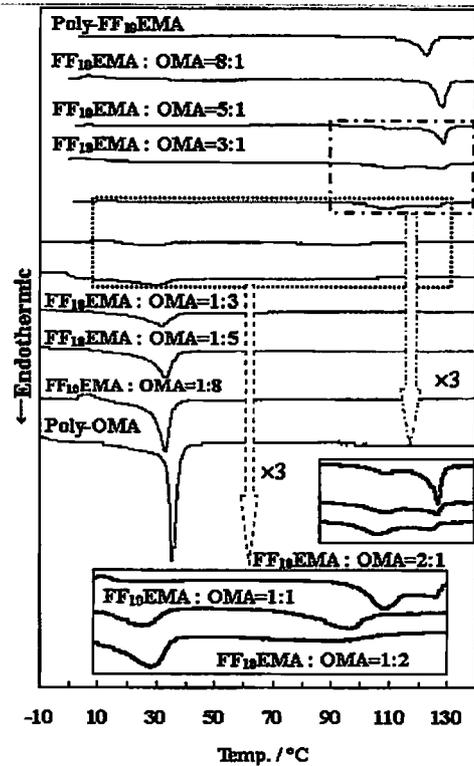


Fig. 2 DSC thermograms of fluorinated comb copolymers with several ratios (2nd-heating, scanning rate; 10 °Cmin⁻¹).

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 π -A isotherms, these phase-separated fluorinated comb copolymers formed extremely stable condensed monolayers at the air/water interface and it was possible to transfer these monolayers on solid substrates.¹⁷ Figure 3 shows the in-plane X-ray diffraction profiles of several transferred films (20 layers) of FF₁₀EMA : OMA. These profiles indicate the packing mode in the organized molecular films of these copolymer system analogous to the bulk state. It is found that FF₁₀EMA : OMA = 1:1 and 1:2 copolymer LB films exhibited only one short spacing which mean formation of hydrogenated hexagonal sub-cell. That is to say, in the organized molecular films, fluorinated region is corresponding to the expand phase, and hydrogenated region is condensed phase with highly order molecular orientation. Early on this work, the molecular orientation and surface morphology of

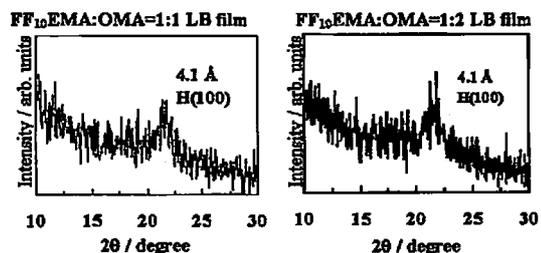


Fig. 3 In-plane XRD profiles of multilayers of FF₁₀EMA : OMA copolymers (20 layers).

monolayer and LB multilayers for corresponding acrylate comb polymer studied on in-plane XRD, AFM, and so on.¹⁷ In the acrylate system (co-polymerization of octadecyl acrylate (OA) and 2-(perfluorodecyl)ethyl acrylate (FF₁₀EA) system), both oriented side-chain crystals in the copolymer film was formed, and miniaturized domains at 10-30 nm scales were confirmed by AFM. From the results of this previous work, we concluded the relationships between molecular orientation and formation of size-controlled domain in the 'sea'-'island' type phase-separated surface morphology. Hence, in the present work, we also examine the morphology of the monolayers related to the molecular arrangement, after that.

Surface morphology of monolayers on solid for fluorinated comb copolymers.

Figure 4 shows AFM images of Z-type monolayers for FF₁₀EMA : OMA = 1:1 copolymer on mica at room temperature. In the case of FF₁₀EMA : OMA = 1:1 copolymer monolayer, circular domains made from the hydrogenated side-chain crystal at about 200-250 nm diameter and fluorinated 'sea' region were confirmed.

Figure 5 shows the AFM images of monolayers for comb copolymers with several compositions at the 1 × 1 μm² scales. With the increasing of hydrogenated side-chain ratio, the film surface is gradually covered by hydrogenated island, and fluorinated sea region decrease. As the overview of formation of surface morphology on previous reported corresponding 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. On the other hand, in the case of methacrylic system, it was confirmed obvious different tendency to the acrylic monolayer. The hydrogenated domain sizes of these methacrylic monolayers are corresponded to the sub-micrometer scale. It is supposed that this difference closely relate the orientation regularity of fluorinated side-chain crystal.



Fig. 5 AFM images of comb copolymers with several ratios of Z-type monolayer on mica substrate.

4. CONCLUSION

The fine structure in the solid state and phase transition behavior of fluorinated methacrylate comb copolymers has been

estimated by WAXD, DSC, and temperature controlled WAXD. 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. 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 measurements. From the results of AFM observation, it was found that there were hydrogenated domains at sub-micron diameter scales in these phase-separated surface structure of monolayers on solids, whereas corresponding acrylate copolymer monolayers form the surface patterning structure at 10-30 nm order scales. The reason of these results is suggested hindrance of packing for fluorinated side-chain by arrangement of low mobility methacrylate main-chain.

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