Effect of the Atoms in Outermost Layers upon Friction Behavior of Organized Molecular Films of Comb-polymers Containing Fluorocarbon Chains

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Several newly synthesized comb-polymers with fluorocarbon side-chains have been found to form stable monolayers on the water surface, which could be deposited on solid substrates as the Z-films. Friction behavior of the Z-films measured by atomic force microscopy has been clearly affected by the atom (–F/–H) of ends of the fluorocarbon chains exposed in the outermost layers of the polymer as well as those of the corresponding monomer Z-films

Fluorinated amphiphiles are expected to be useful for tribological studies in the molecular-level. Recently, using atomic force microscopy (AFM)[1] chemical phase-separated Langmuir–Blodgett (LB) films[2,3] and the fluorinated self-assembled monolayers (SAMs)[4,5] have been measured for their frictional properties. Previously, for acrylic and methacrylic acid esters with long fluorocarbons formation of these monomer monolayers at the air/water interface and the structures of their organized molecular films were investigated,[6] in addition to the study of the polymerizations with γ-ray irradiation in the bulk-states.[7] LB films of polymers containing fluorocarbon side-chains should have excellent surface properties as oil resistance, low friction and so on.[8,9] In the present work, using the comb-polymers containing fluorocarbons as the side-chains which were obtained by γ-ray polymerization in the bulk-states of the corresponding fluorinated amphiphiles with the vinyl group, the monolayer on the water surface and the transferred films on solid substrates have been characterized by the surface pressure – area isotherm measurements, and scanning electron and atomic force microscopies, respectively. Furthermore, friction behavior for deposited molecular films of those comb-polymers as well as those of the corresponding monomer has been compared by friction force microscopy (FFM).

For fluorinated amphiphilic comb-polymers, poly(2-perfluoroalkylethyl acrylate) $[F(CF_2)_n(CH_2)_2O–COCHCH_2]_m$ (n = 6, 8, 10) [abbrev. as poly-FF_nEA], poly(2-perfluoroalkylethyl methacrylate) $[F(CF_2)_n(CH_2)_2O–COC(CH_3)CH_2]_m$ (n = 6, 8, 10) [poly-FF_nEMA], poly(1H,1H,(n+1)H-partialfluoroalkyl acrylate) $[H(CF_2)_nCH_2O–COCHCH_2]_m$ (n = 6, 8, 10) [poly-F_nA], and poly-(1H,1H,(n+1)H-partialfluoroalkyl methacrylate) $[H(CF_2)_nCH_2O–COC(CH_3)CH_2]_m$ (n = 6, 8, 10) [poly-F_nMA], were used in this work. These comb-polymers were obtained by post-polymerization after [60]Co γ-ray irradiation to the corresponding monomers at –196 °C, dissolving in a little acetone or tetrahydrofuran, and these purifying by precipitation through pouring into tetrachloromethane.[7] The tacticity of these polymers was obtained to be syndiotactic (Diad : 58%) by ^{1}H-NMR analysis according to the reference.[10]

The monolayers of the fluorinated amphiphilic monomers were conventionally spread from the chloroform solutions onto the distilled water. On the other hand, the monolayers of the fluorinated comb-polymers were spread from the solutions dissolved in trifluoroacetic acid as a good solvent, according to the Trurnit's suggestion that a complete spreading is to allow the spreading solution to flow down a small hydrophilic glass rod projecting from the surface of the subphase in the trough.[11] The surface pressure – area (π – A) isotherms for the monolayers were measured by a Lauda film balance at different temperatures. These monolayers were transferred onto solid substrates at 5 °C by a surface-lowering method[12] at various surface pressures to obtain the non-alternating Z-type films, in which the hydrophobic moieties were oriented toward the air and the outermost surfaces could be controlled to consist of the atoms (fluorine or hydrogen) at the end of the fluorocarbon side-chains. Surface structures of the deposited films were observed by an atomic force microscope (Seiko Instruments SPA300 with SPI-3800 probe station) and simultaneously the frictional force was also measured as a function of the applied load for each tip-film system.[13,14]

Figure 1 shows the π – A isotherms for monolayers of poly-FF_nEA (n = 6, 8 and 10) on the water surface. Among these fluorinated comb-polymers, it has been found that poly-FF_nEA's form considerably stablized and condensed monolayers in the temperature range of 5–40 °C as compared to the corresponding monomer monolayers.[6] The values of the limiting area extrapolated to π = 0 from the steep region of the curve for poly-FF_nEA were about 22, 27 and 30 Å^2/repeating unit at 5 °C and also about 28, 31 and 31 Å^2/repeating unit at 40 °C for n = 6, 8 and 10, respectively. These values except for the poly-FF_6EA at 5 °C are well corresponding to the cross-sectional area reported previously for other perfluorinated amphiphiles, which is considered to be large enough to accomodate the helical segments.[15,16]
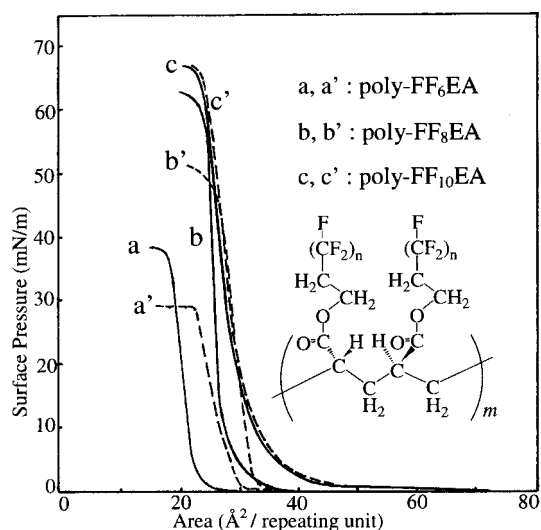

Figure 1. Surface pressure – area isotherms for poly – FF_nEA on the distilled water at 5 °C (solid lines) and 40 °C (dashed lines)

On the other hand, poly-F_8A and poly-$F_{10}A$ gave stable condensed monolayers with small limiting areas of 24 and 20 Å^2/repeating unit at 5 °C and 23 and 21 Å^2/repeating unit at 40 °C, respectively, suggesting that the monolayers of these comb-polymers could not completely spread onto the water surface and some crystalline domains were retained on the water surface. The poly-F_6A monolayer was stable only below about 23 mN/m even at 5 °C, having the limiting areas of 29 and 34 Å^2/repeating unit at 5 and 40 °C, respectively. For the poly-$F_{10}MA$ monolayer on the distilled water at 5 and 40 °C, the condensed monolayer was apparently formed at 5 °C with the limiting area of 17 Å^2/repeating unit, which seemed too small to be occupied by the fluorocarbon side-chains in the films. The monomer $F_{10}MA$ could form a condensed monolayer with the limiting area of about 25 Å^2/repeating unit and collapsed around 25 mN/m and at 5 °C, though its area reduced remarkably by increase of the temperature of the aqueous subphase and its monolayer collapsed about 10 mN/m at 15 °C.

When these monolayers were transferred onto the solid substrate by the surface-lowering method, the ends of the fluorocarbon chains of the outermost layers of the obtained Z-type films should be exposed to air. Friction properties of these Z-type films could be measured using atomic force microscopy (spring constant of 0.09 N/m) by measuring frictional forces as a function of the applied load for each system.[13,14] For the Z-type films of poly-$FF_{10}EA$, poly-$FF_{10}EMA$, poly-$F_{10}A$, and poly-$F_{10}MA$ deposited at 15 mN/m and 5 °C, the results of the frictional measurements are shown in Figure 2 as a plot of friction versus applied load, together with those for the corresponding monomer film. The difference of voltage in the vertical axis was detected as a measure of friction force. The inclination and the intercept on the vertical axis could be considered a friction and an attractive force between the tip and the film, respectively. A considerable difference in the friction forces between the group of poly-$FF_{10}EA$ and poly-FF_{10}-EMA and
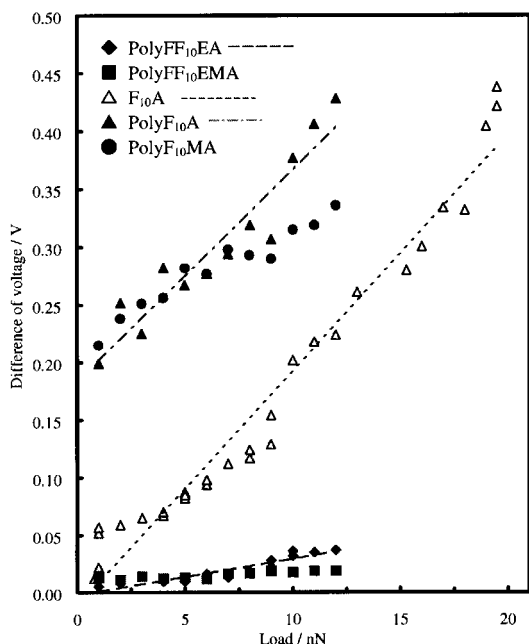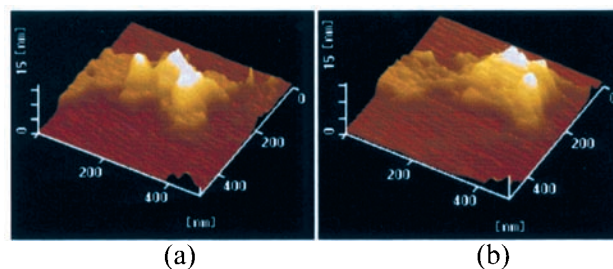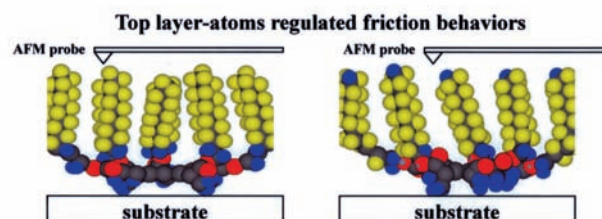

(a)   (b)
Figure 3. AFM images before (a) and after (b) the loading of 10 nN for the Z-type film of poly-$F_{10}A$, deposited at 15 mN/m and 5 °C.

Top layer-atoms regulated friction behaviors

that of poly-$F_{10}A$ and poly-$F_{10}MA$ has been found for applied load up to ~12 nN, which can be ascribed to the friction properties of only the outermost surface of the Z-type films. The former group and the corresponding monomer films have the fluorine atoms in the outermost layer, indicating a low friction, while the latter and the corresponding monomer films have the hydrogens, showing a relatively large friction, and also having any interaction with the tip even at zero load. Furthermore, it was found that the effect of the outermost atoms on the friction properties was expected to be enhanced by the polymerization. In the former films with a low friction the AFM images were unchanged after the friction measurements at loading up ~10 nN, however, some deformation of the latter films at higher applied loads has been obseved in the AFM image, as shown in Figure 3 for the poly-$F_{10}A$ film after loading up ~10 nN.

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Figure 2. Plot of friction force versus applied load for the Z-type films of fluorinated amphiphiles and their polymers on mica