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Fabrication of Patterned High-Density Polymer Graft Surfaces. 1. Amplification of Phase-Separated Morphology of Organosilane Blend Monolayer by Surface-Initiated Atom Transfer Radical Polymerization

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ABSTRACT: Patterned films of a low-polydispersity polymer densely end-grafted on a silicon substrate were fabricated for the first time by the combined use of the Langmuir−Blodgett (LB) and the surface-initiated atom transfer radical polymerization (ATRP) techniques: a blend monolayer of 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (CTS: ATRP initiator) and *n*-octadecyltrimethoxysilane (OTS: non-initiator) was immobilized on a silicon wafer by the LB technique, and then the ATRP of methyl methacrylate was carried out on the modified wafer in the presence of the Cu/ligand complexes. Atomic force microscopic studies revealed that the CTS/OTS blend was immiscible and phase-separated into two monolayer phases: most OTS molecules aggregate with each other, forming a condensed-type monolayer domain with CTS molecules excluded from there almost perfectly, and the remaining OTS molecules are incorporated in the matrix region. This 2-dimensionally phase-separated structure was successfully amplified by the controlled growth of a high-density graft layer only on the matrix phase of CTS as a main component. The amplification by the ATRP technique was characterized by a sharp boundary between the grafted and ungrafted domains; as a measure of the spatial resolution, the boundary sharpness Δw was evaluated to be ca. 100 nm. The domain size in the phase-separated structure was independent of the mole fraction of CTS, while it could be changed by changing the pH of the subphase water: namely, the higher was the pH, the larger was the domain size. It was deduced that a change in pH of the subphase water gave rise to a change in the hydrolysis rate of the methoxysilyl groups into silanol groups and hence a change in the rate of condensation of the silanol groups into domains.

Introduction

In recent years, surface modifications by polymers have been increasingly important for various applications ranging from biotechnology to advanced microelctronics. Graft polymerization starting with the initiating sites fixed on a surface is one of the most effective and versatile methods for this purpose, since surface properties can be widely changed by graft-polymerizing a variety of functional monomers.[1−7] Recently, some living polymerization techniques were successfully applied to surface-initiated graft polymerization to prepare a dense polymer brush.[8−16] We were the first to succeed in applying atom transfer radical polymerization (ATRP)[17] to the graft polymerization on a solid surface and yielding a graft layer of low-polydispersity polymer with the highest graft density reported to date.[9] Furthermore, we revealed that in such a graft layer polymer chains were highly extended in a good solvent, nearly to their full lengths, and that the properties of this high-density polymer brush were quite different and unpredictable from those of the “moderately dense” polymer brushes previously studied.[9c,d] In addition to such parameters as graft density and the chain length and length distribution of graft polymer, the morphology of the grafted surface is also an important factor determining such surface properties as chemical reactivity, wettability, permeability, lubricity, biocompatibility, and electrical properties. For example, it was reported that the surface coated with a poly(2-hydroxyethyl methacrylate-*b*-styrene-*b*-2-hydroxyethyl methacrylate) triblock copolymer exhibits an excellent blood compatibility, possibly because of the unique surface morphology resulting from the microphase separation of the block copolymer.[18−23]

In this paper, we attempt to control the surface morphology of a high-density graft layer by using the two-dimensional phase separation of an organosilane blend. The blend of organosilanes with different alkyl or fluoroalkyl chains was reported to form a phase-separated monolayer, which could be transferred on a substrate with silanol groups and immobilized by Si−O−Si covalent bonds.[24] 2-(4-Chlorosulfonylphenyl)ethyltrimethoxysilane (CTS) with an ATRP initiating group[17c,25,26] was blended with *n*-octadecyltrimethoxysilane (OTS) having a long alkyl chain. In this blend, OTS was expected to aggregate with each other to form a characteristic surface morphology.[24] After immobilizing the blend monolayer on a silicon substrate, the graft polymerization of methyl methacrylate (MMA) was carried out by the surface-initiated ATRP technique. The blend monolayer was prepared at different pHs of subphase water. Both CTS and OTS have a methoxysilyl group, which can be hydrolyzed to a silanol group. The hydrolysis rate of the methoxysilyl group is much smaller than that of the chlorosilyl group, and it is controllable by changing the pH of the subphase water.[27,28] For this reason, we expected that the growth rate of the domain structure and hence the domain size would be controllable by changing the pH of the subphase water. Another point of scientific importance is to clarify the spatial resolution of pattern amplification by the controlled growth of a high-density, low-polydispersity graft layer. For this purpose, the phase-separated pattern formed by the blend of low-mass compounds on a fluid surface is suitable as a model

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system, because the boundary should be sharp enough compared with the molecular scale of graft polymers.

Experimental Section

Materials. CTS was obtained as a dichloromethane solution from Gelest, Inc., Tullytown, PA, and its concentration was determined by a ^{1}H NMR measurement. OTS from Tokyo Chemical Industry Co., Ltd., Tokyo, Japan, was used without further purification. MMA was obtained from Nacalai Tesque Inc., Kyoto, Japan, and distilled under reduced pressure over CaH_2 before use. 4,4′-Di-*n*-heptyl-2,2′-bipyridine (dHbipy) was synthesized according to the method of Matyjaszweski et al.[29] Copper bromide (CuBr, 99.0%) and *p*-toluenesulfonyl chloride (TsCl) were purchased from Nacalai Tesque Inc., Kyoto, Japan, and used without further purification. Chloroform (Spectrograde, Dojindo Laboratories, Kumamoto, Japan) was used as received. Unless otherwise specified, all other reagents were purchased from commercial sources and used as received.

Preparation of Monolayer. The organosilane compound was spread from a solution of chloroform on the clean water surface in a Teflon-coated rectangular Langmuir trough (200 × 500 × 3 mm^3). Blend monolayers were prepared by spreading a mixture solution of CTS and OTS. The total concentration of solutes was about 0.20 wt %. The acidity of the subphase water was adjusted to a desired pH by adding aqueous HCl solution to the water purified by means of a Mitamura Riken model PLS-DFR automatic still. By circulating thermostated water, the temperature of the subphase was kept at 25 °C. After spreading the solution, 30 min was allowed for the solvent to evaporate off. The surface pressure (π)−occupied area (A) isotherms were recorded at a constant compression speed of 15 cm^2/min; π was measured by the Wilhelmy method hanging a quartz plate or a filter-paper blade (Advantec no. 131, Toyo Roshi Kaisha, Ltd., Tokyo, Japan).

The surface monolayer, compressed up to 8 mN/m at a constant compression speed of 15 cm^2/min, was annealed at that pressure for 30 min and transferred by the lifting-up method onto a polished silicon wafer with an oxidized surface. Just before use, the silicon substrate was cleaned by ultrasonication in acetone for 5 min and sputtered with air under a reduced pressure to make the surface hydrophilic. After the deposition of monolayers, the substrates were annealed for 20 min at 110 °C.

Graft Polymerization. The graft polymerization of MMA was carried out for various periods of time at 90 °C by dipping the modified wafer in a degassed diphenyl ether solution of CuBr (10 mM), dHbipy (20 mM), MMA (4.7 M), and TsCl (4.8 mM). TsCl was added as a free initiator to control the polymerization as well as to produce the reference free polymers whose number- and weight-average molecular weights (M_n and M_w) and polydispersity index (M_w/M_n) are known to well approximate those of the graft polymers.[9,30] After the polymerization, the grafted wafer was washed with toluene in a Soxhlet apparatus for 10 h to remove ungrafted (free) polymers and impurities.

Measurements. Atomic force microscopic (AFM) observations were performed at room temperature with a contact-mode atomic force microscope (Seiko Instruments Inc., Chiba, Japan, SFA300 controlled by SPI3600) using a V-shaped Si_3N_4 cantilever (Park Scientific Instruments, Sunnyvale, CA, spring constant 0.064 N/m). Topographic images were taken in the air under the constant-force mode with an applied force of 0.2 nN at a scanning speed of 25 μm/s unless otherwise noted. Several images were taken at different locations on a sample to determine the height difference and the surface coverage.

The thickness of the graft layer on the silicon wafer was determined by an analyzer−rotating ellipsometer (DVA ellipsometer, Mizojiri Optical Co., Ltd., Tokyo, Japan) equipped with a He−Ne laser (632.8 nm). The polarizer angle and the incident angle were fixed at 30° and 70°, respectively, and the refractive index of the graft layer was assumed to be 1.49, the value for a poly(methyl methacrylate) (PMMA) bulk film, for the evaluation of the thickness.

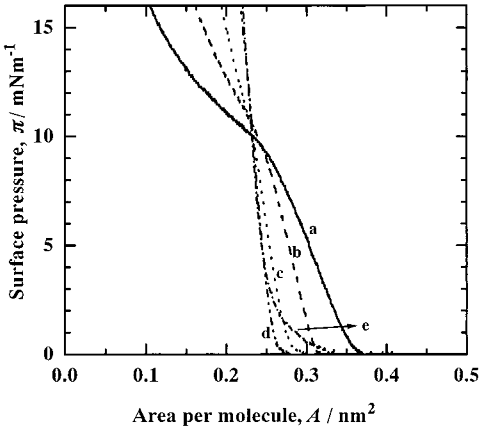


Figure 1. Surface pressure (π)−occupied area (A) isotherms of OTS/CTS blends at pH = 1.6; f_{CTS} = (a) 1, (b) 0.68, (c) 0.40, (d) 0.20, and (e) 0.

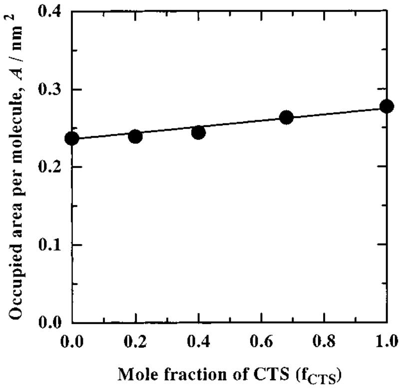
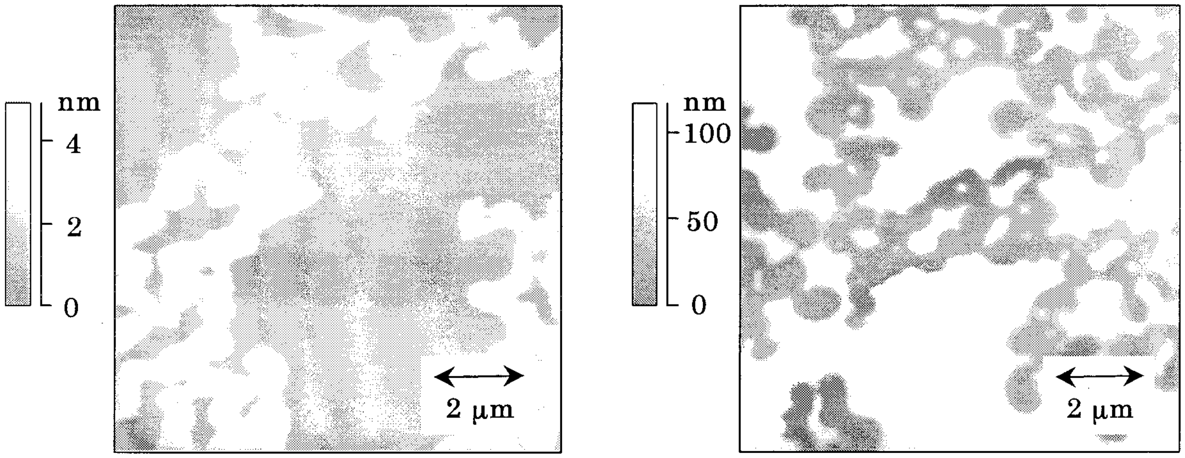


Figure 2. Plot of the average occupied area per molecule at π = 8 mN/m and pH = 1.6 as a function of f_{CTS} in CTS/OTS blend monolayers.

Gel permeation chromatographic (GPC) measurements were made on a Tosoh GPC-8010 high-speed liquid chromatograph (Tosoh Corp., Tokyo, Japan). Tetrahydrofuran (THF) was used as an eluent, and the temperature was maintained at 40 °C. The column system was calibrated by standard PMMA samples.

Results and Discussion

Phase Separation in Blend Monolayer. We first focus on monolayers of CTS, OTS, and their blends spread on the water with pH = 1.6. For a pure-OTS monolayer, the methoxysilyl group was reported to be readily hydrolyzed, giving a condensed packing by compression. Figure 1 shows the π−A isotherms for these monolayers at 25 °C, where A is the average occupied area per molecule. As previously reported,[31] the OTS monolayer gave a steep increase in π with decreasing A and a collapse pressure higher than 30 mN/m, suggesting the formation of a stable condensed-type monolayer. On the other hand, the CTS monolayer gave a shoulder in the isotherm at π = 10 mN/m, indicating a partial collapse of the monolayer. The observed lower stability of the CTS monolayer than the OTS one may be understandable by comparison of their chemical structures. A similar shoulder was observed for the blend of CTS and OTS. Figure 2 gives the plot of the value of A at π = 8 mN/m, at which CTS, OTS, and their blend are expected to form a stable compressed monolayer, as a function of the mole fraction of CTS (f_{CTS}). This figure shows that the following additivity rule approximately holds:



(a) (b)

Figure 3. Topographic AFM images of the blend monolayer-fixed substrate (f_{CTS} = 0.40) (a) before and (b) after the graft polymerization for 10 h.

$$A = A_{CTS}\, f_{CTS} + A_{OTS}\, (1 - f_{CTS}) \qquad (1)$$

where A_{CTS} and A_{OTS} are the occupied areas per molecule in the pure monolayers of CTS and OTS, respectively. This relationship was proposed for an immiscible as well as an ideally miscible blend.[32,33] The CTS/OTS blend system corresponds to the former one (see below).

The monolayer was transferred onto a cleaned silicon wafer at $\pi = 8$ mN/m. The transfer ratio, which is defined as the difference in the water surface area before and after deposition divided by the substrate surface area, was approximately unity in all cases, indicating a successful transfer of the monolayer film. Figure 3a shows the AFM image of the deposited blend monolayer at $f_{CTS} = 0.40$. This figure clearly shows a phase-separated structure of the monolayer, in which circular domains with a diameter of ca. 1 μm are connected with each other. Such a clear phase separation can be ascribed to the OTS molecules easily aggregating with each other on the water surface and forming a condensed-type monolayer with the alkyl chains in an all-trans conformation.[34,35] The height difference of the circular domains from the matrix domain is ca. 1.9 ± 0.4 nm, which is comparable to the difference of the molecular lengths of CTS and OTS in their possible all-trans conformations shown in Figure 4. However, the fractional area, a_{matrix}, of the matrix region with the lower height (corresponding to the CTS domain) was larger than the value calculated by the following equation based on the assumption of the complete phase separation into the two pure-component monolayer phases.

$$a_{matrix} = A_{CTS}\, f_{CTS}/(A_{CTS}\, f_{CTS} + A_{OTS}\, (1 - f_{CTS})) \qquad (2)$$

This means that some OTS molecules were left behind in the CTS domain. The details will be discussed later.

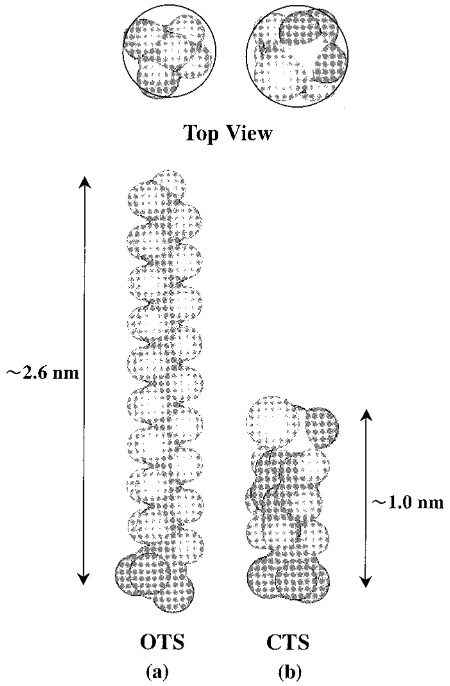


Figure 4. Space-filling models of (a) OTS and (b) CTS in a possible all-trans conformation.

Amplification of Phase-Separated Structure by ATRP. The graft polymerization of MMA was carried out for various periods of time on the silicon wafer on which the blend monolayer (pH = 1.6) with $f_{CTS} = 0.40$ was immobilized. After the polymerization, the free polymer produced in solution was characterized by GPC as a measure of the graft polymer; the M_n of the free polymer increased proportionally to the monomer conversion, and the polydispersity remained relatively low (see Figure 5). This suggests that the graft as well as free polymerization processes were successfully controlled with a negligible contribution of chain transfer and termination reactions. The AFM imaging of the graft surface gave nearly the same domain morphology independent of polymerization time. Figure 3b shows a typical AFM image. Clearly, the morphologies before and after graft polymerization are almost the same excepting that the contrast of the two domains has been reversed, as it should be. The height difference Δh of the two domains increased with increasing polymerization time and hence increasing chain length of the graft polymer (Figure 6). In Figure 7, the Δh value was plotted against the M_n value of the free polymer. (Note that the M_n value of the free polymer should well approximate that of the graft polymer.[9,30]) For comparison, the graft polymerization of MMA was carried out on a pure-CTS-immobilized substrate under the same conditions; the graft-layer thickness was measured by ellipsometry and shown by the open circles in Figure 7

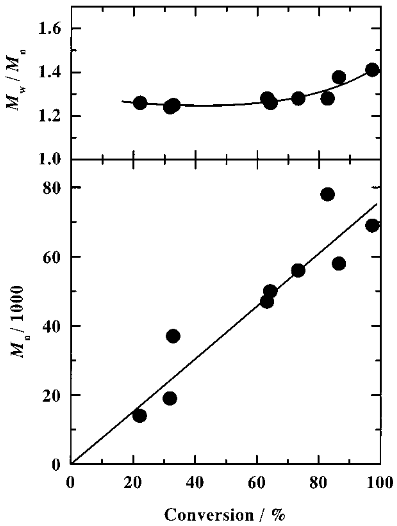


Figure 5. Plots of M_n and M_w/M_n of the free polymer vs monomer conversion.

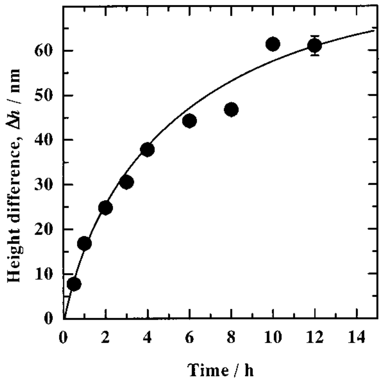


Figure 6. Plot of the height difference Δh vs polymerization time.

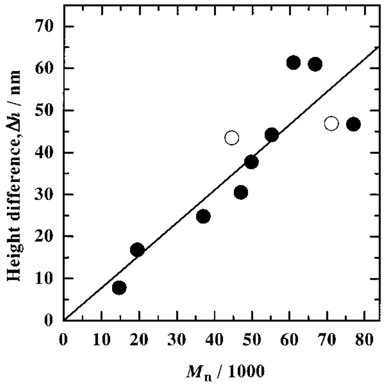


Figure 7. Plot of Δh vs M_n of the free polymer (the filled circles): the open circles represent the thickness of the graft layer produced on a 100% CTS-immobilized substrate.

as an upper limit of Δh (to be exact, Δh + the thickness (2.6 nm) of the OTS monolayer). The open circles approximately fall on the line formed by the Δh data (filled circles). This means that PMMA chains were grafted only on the matrix region with the same graft density as on the pure-CTS-immobilized substrate. The proportional relationship between Δh ($\approx$ graft layer thickness) and M_n, observed in Figure 7, suggests that the graft density remains constant throughout the course of polymerization. From the slope of the indicated line, the graft density in the grafted region of the surface was estimated to be ca. 0.45 chains/nm^2. This value is nearly the same as the one previously obtained for the pure monolayer of CTS.[9]

To investigate the dependence of the phase structure on blend composition (f_{CTS}), blend monolayers with different compositions (f_{CTS} = 0.20, 0.40, and 0.68) spread on the water with pH = 1.6 were immobilized on the silicon wafer and then subjected to the ATRP graft polymerization of MMA for 10 h. In all cases, a free polymer with nearly the same M_n (~80 000) and M_w/M_n (~1.2) was produced, and this suggests that a low-polydispersity polymer with nearly the same chain length was grafted. Figure 8a–c shows the AFM images of the grafted layers (pH = 1.6): the average size of circular domains was almost independent of f_{CTS}, but the number of domains per unit area increased with decreasing f_{CTS}. In Figure 9, the values of Δh and a_{matrix} were plotted against f_{CTS}. The figure reveals that Δh is independent of f_{CTS} and nearly equal to the value read from Figure 7 (dotted line). This means that the PMMA was densely grafted only on the matrix region, indicating that most OTS molecules aggregate with each other, forming a condensed-type monolayer domain with CTS molecules excluded from there almost perfectly. On the other hand, a_{matrix} increases with increasing f_{CTS} and is slightly larger than the value (solid line in the figure) given by eq 2. This suggests that some OTS molecules are left behind in the matrix region. From the value of a_{matrix}, the mole fraction of OTS in the matrix region was estimated to range from 0.2 at f_{CTS} = 0.68 to 0.4 at f_{CTS} = 0.2. As mentioned above, however, this much of incorporation of OTS did not cause any decrease in graft density and hence graft-layer thickness. This is because there is a limiting value of the CTS surface density beyond which the graft density stays constant for a steric reason.[9d] In all studied cases, the surface density of CTS is much higher than this limiting value, and this explains the constancy of graft density despite the incorporation of the considerable amounts of OTS in the matrix. On the other hand, if the OTS domain contains even a few mole percent of CTS, the polymerization should produce a thick graft layer that can be easily detected. As mentioned above, the observed Δh value suggests the absence of graft polymer in the OTS domain, indicating the absence of CTS in the OTS domain.

We can expect that densely grafting a low-polydispersity polymer on an initiating surface with a two-phase morphology would bring about a sharp boundary between the grafted and ungrafted domains. From the cross-sectional AFM images (an example is shown in Figure 10), the boundary sharpness Δw was evaluated to be ca. 100 nm, independent of f_{CTS}. Here, Δw is defined as the boundary width between the two points where the tangential line at the midpoint of Δh intersects the upper and lower levels of the two domains (see Figure 10). Although the high-resolution AFM image could not be obtained for the blend monolayer, we may expect that the boundary between the two phases composed of low-mass molecules should be sharp enough compared with the molecular scale of graft polymers. The Δw value may be overestimated, since the used AFM cantilever has a pyramidal tip with a radius of curvature of ca. 50 nm, which is comparable to the step height (Δh = 70 nm).[36] We, therefore, conclude that the controlled graft polymerization can amplify a pattern with a spatial resolution at least comparable to the

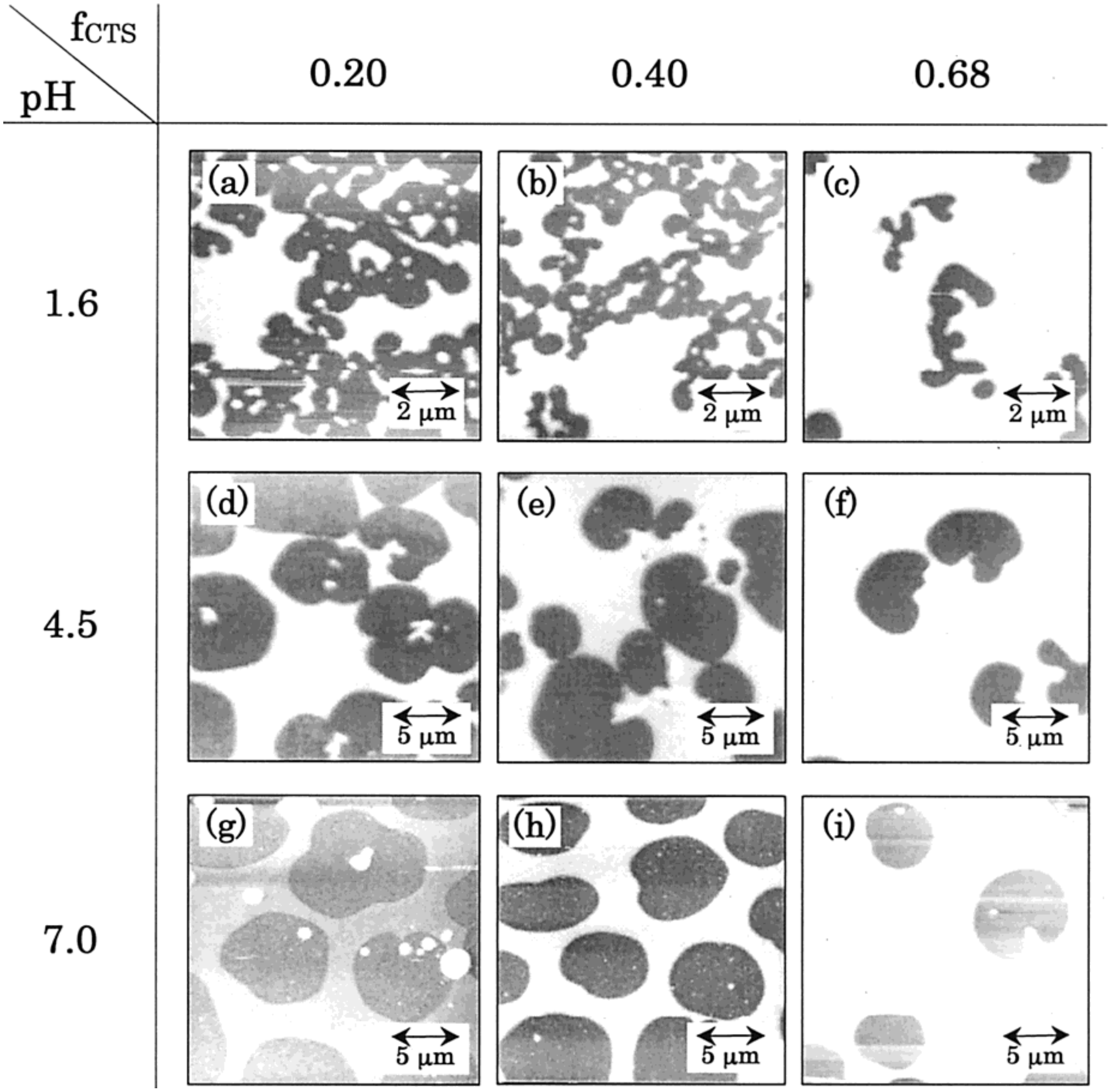


Figure 8. Topographic AFM images of grafted surfaces after 10 h of graft polymerization for various values of f_{CTS} and pH. Each image was shown in an arbitrary height scale.

graft-layer thickness. This resolution may be attributed to the high-density and low-polydispersity grafting achieved here.

Morphology Control of High-Density Graft Surface. The morphology of the high-density graft layer prepared in this study is a direct magnification of the 2-dimensional phase-separated structure of the CTS/OTS blend monolayer. To control the morphology, we have attempted to change the acidity of the subphase water, on which the blend monolayer was prepared. In the CTS/OTS blend monolayer, the methoxysilyl groups would be first hydrolyzed to silanol groups, which can be condensed with each other, forming a network structure. The acidity of the subphase water must affect the rate of hydrolysis and hence the rate of condensation. The domain size in the phase-separated structure is probably determined by the relative rate of phase separation to that of network formation. Therefore, a change in pH of the subphase water was expected to give rise to a change in the domain size.

The blend monolayers spread on the subphase water of different pH values (pH = 1.6, 4.5, and 7.0) were successfully deposited at $\pi = 8$ mN/m and immobilized on the silicon substrate. The graft polymerization of MMA on these substrates for 10 h gave patterned graft surfaces. Figure 8 shows typical AFM images of the obtained graft surfaces. The domain size was almost independent of the blend composition, but it was much smaller at pH = 1.6 than at the other pH conditions. Linden et al. studied the relaxation of surface pressure of a OTS monolayer on the water with different pHs: when the surface area was kept constant, the surface pressure of 8 mN/m at the initial stage decreased down to 0.5−1 mN/m in 2 min at pH = 2, in 50 min at pH = 4.1, and in more than 600 min at pH = 7.0.[31] These data suggest that the hydrolysis rate of the methoxysilyl group decreases with increasing pH. In our experiment, before compressing the monolayer spread on the water surface, 30 min was allowed for the solvent to evaporate off. During this time, the methoxysilyl groups were almost completely hydrolyzed at pH = 1.6, and they were readily condensed, thus fixing the domain structure in an early stage. On the other hand, at pH = 4.5 or 7.0, the hydrolysis was not completed during the 30 min time before the compression, and hence the domain of OTS could grow to be as large as 5−10 μm in

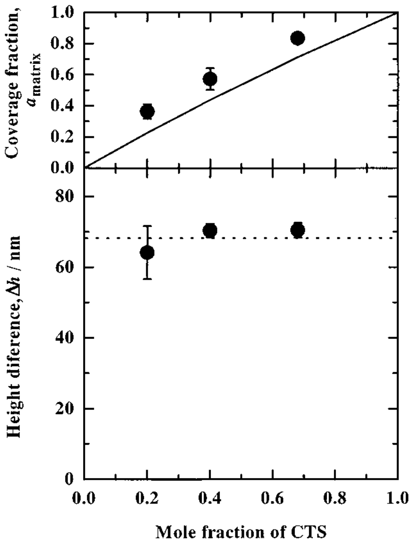


Figure 9. Plots of height difference, Δh, and surface coverage, a_{matrix}, of grafted region as a function of f_{CTS}. The blend monolayer was transferred at pH = 1.6, and the graft polymerization was carried out for 10 h.

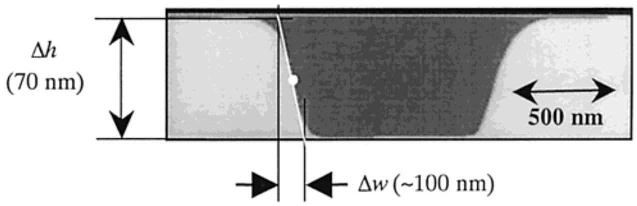


Figure 10. Cross-sectional profile across the boundary between the two domains of the graft layer ($f_{CTS} = 0.68$, pH = 1.6.).

diameter. Thus, the domain size is controllable by changing the rate of hydrolysis and subsequent condensation.

Conclusions

We have succeeded in immobilizing a 2-dimensionally phase-separated monolayer of the CTS/OTS blend on a silicon wafer by the LB technique and amplifying the two-phase morphology into a high-density graft layer of exactly the same morphology by using the surface-initiated ATRP technique. AFM observations showed that most OTS molecules were easily aggregated with each other on the water surface, forming a condensed-type monolayer domain with CTS molecules excluded from there almost perfectly, and that the remaining OTS ones are incorporated in the matrix region. The OTS fraction in the matrix region was low enough to end-graft, by the ATRP technique, a low-polydispersity polymer with a graft density as high as 0.45 chains/nm^2. The amplification by the ATRP technique was characterized by a sharp boundary between the grafted and ungrafted domains; as a measure of the spatial resolution, the boundary sharpness Δw was evaluated to be ca. 100 nm. The domain size in the phase-separated structure was independent of f_{CTS}, while it could be effectively changed by changing the pH of the subphase water.

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