Synthesis and Frictional Properties of Poly(2,3-dihydroxypropyl methacrylate) Brush Prepared by Surface-initiated Atom Transfer Radical Polymerization

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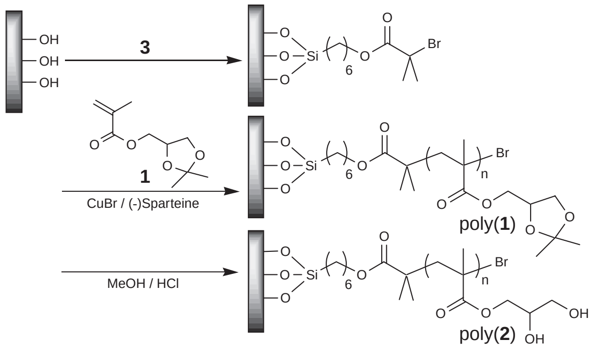
Surface-initiated atom transfer radical polymerization (ATRP) of (2,2-dimethyl-1,3-dioxolan-4-yl)methyl methacrylate (**1**) was carried out from an immobilized initiator on a silicon wafer to result in a high-density polymer brush, which was converted to the hydrophilic polymer brush consisting of 2,3-dihyroxypropyl methacrylate (**2**) units, successively. The poly(**2**) brush showed low dynamic friction coefficient in water.

The water lubrication systems have attracted much attention due to its applications to medical implant devices[1] such as artificial joints for the human hip[2] as well as environmentally friendly technologies. The surface grafting of polymers in general has been studied intensively to improve the lubrication properties of solid surfaces. Klein,[3] Osada,[4] and Sheth et al.[5] already have reported that the solid surface bearing grafted hydrophilic polymers reduced the frictional forces between the substrates in an aqueous medium, however, graft densities were very low. Furthermore, the most of the previous research on the friction of the grafted polymer was done in a very low normal force condition, which is quite apart from the practical conditions. During past decades, marvelous progress in ATRP allows us to boost the efficiency of initiation from a solid surface to generate high-density and well-defined polymers,[6–9] which form an assembly of tethered polymer chains with a relatively extended conformation, a so-called "polymer brush."[10] The lubrication of a polymer brush is so attractive that the authors have previously synthesized high-density PMMA brush on a flat silicon substrate[11] and have found that polymer brush affords a low-friction and wear-resistant surface under a high normal load.[12] In the present study, the authors demonstrated the macroscopic frictional properties of high-density hydrophilic poly(**2**)[13] brush prepared by ATRP of **1** followed by hydrolysis.

The synthetic procedure of polymer brush was shown in Scheme 1. The silicon wafer immobilized with the radical initiator was prepared by spin-coating of a toluene solution of 6-(triethoxysilyl)hexyl 2-bromoisobutylate (**3**) on a hydrophilic silicon substrate[12] followed by annealing at 383 K for 9 h and cleaning by toluene using Soxhlet extraction for 3 h. A typical surface-initiated ATRP of **1** was performed as follows; the initiator-immobilized silicon wafer and 3.6 mg (0.025 mmol) of CuBr, the anisole solution of (−)-sparteine (0.050 mmol), ethyl 2-bromoisobutylate (**4**) (0.025 mmol), and **1** (15.0 mmol) was introduced into a glass tube under Ar atmosphere, the reaction mixture was then degassed by repeating the freeze-and-thaw process. The polymerization reaction was carried out at 338 K for 24 h under Ar to generate poly(**1**) brush from the substrate and free poly(**1**) from **4** at the same time. The reaction mixture was poured into methanol to precipitate the polymer, and the wafer was washed with toluene using a Soxhlet apparatus for 12 h. The number-average molecular weight (M_n) of surface-grafted poly(**1**) on silicon wafer cannot be yet directly determined, however, polymer brush should have the same M_n as the value of the corresponding free polymer,[14] which was determined by the size exclusion chromatography using polystyrene standards. The poly(**1**)s in the range of M_n were obtained by changing the ratio of the **1** to **4**. The molecular weight distributions of the obtained poly(**1**)s were relatively narrow ($M_w/M_n = 1.1$–1.3). The AFM observation revealed that a homogeneous polymer layer was formed on the substrate, and the surface roughness were 0.7–1.2 nm in a dry state in $5 \times 5\,\mu m^2$ scanning area. The thickness of the polymer brush was determined by AFM scanning on the scratched surface of the polymer brush. As shown in the filled symbols plots in Figure 1, the thickness of the polymer brushes linearly increased with the molecular weight. The graft density was estimated to be ca. 0.36 ± 0.09 chain/nm^2 based on the relationship between M_n and the thickness. Considering this graft density, the tethered poly(**1**) brush would have a rather more extended conformation than the random coil structure.

Hydrolysis of poly(**1**) brushes was employed by dipping the substrates into the acidic solution consisting of MeOH/2M HCl (250/1, v/v) for 6 h at room temperature without stirring. The



Scheme 1.

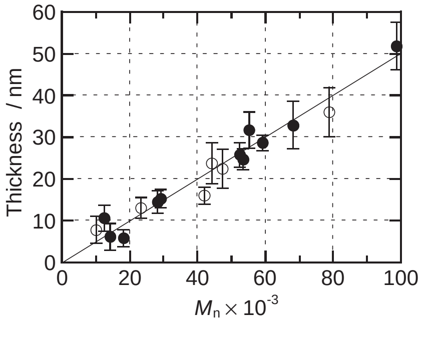


Figure 1. Relationship of molecular weight and thickness of poly(**1**) (filled symbols) and poly(**2**) (open symbols) brushes.

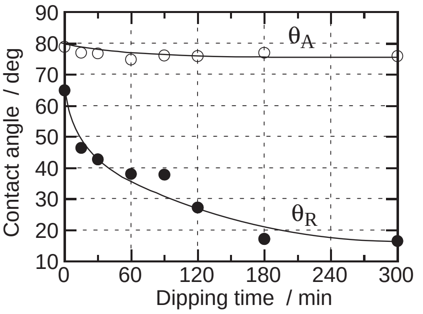


Figure 2. Advancing (θ_A) and receding (θ_R) contact angles of poly(**1**) brush immersed in acidic solution.

advancing contact angle (θ_A) of the polymer brush did not change after the treatment with acidic MeOH, whereas the receding contact angle (θ_R) decreased from 65 to 18°, as shown in Figure 2. A 30-μL water droplet on the poly(**1**) brush surface began to slide when the sample plate was tilted to 14°; in contrast, the sliding angle increased to 80° after the hydrolysis. The observed large sliding angle can be ascribed to the large contact angle hysteresis. These results indicate that the wettability against water was enhanced because hydrolysis of the acetal unit proceeded to afford hydroxy groups, which form hydrogen bonds with water molecules. The IR absorption at $3250\,\mathrm{cm}^{-1}$ due to the hydroxy groups was increased, and that of the methyl groups at $2990\,\mathrm{cm}^{-1}$ disappeared after the hydrolysis reaction, implying that the poly(**1**) brush was successfully converted to poly(**2**).

The thickness of the polymer brush also changed as a result of hydrolysis; for example, the thickness of poly(**1**) ($M_n = 59000$) decreased from 28 to 22 nm in the dry state. As the molecular weights of **1** and **2** are 200 and 160, respectively, the M_n of polymer brush should also decrease by hydrolysis. However, the open symbol plots in Figure 1 show proportional relationship between the thickness of poly(**2**) brush and the M_n estimated from the observed M_n of the corresponding poly(**1**) multiplied by 0.8 (=160/200). Assuming that the graft density and the chain length are unchangeable during hydrolysis, the structure of poly(**2**) brush should be disordered, or should shrink through the hydrogen-bonding interactions among the hydroxy groups, leading to a relatively thin polymer brush.

Dynamic friction tests were carried out by sliding a glass ball ($\phi = 10$ mm) on the substrates at a rate of 90 mm/min under loading of 0.49 N at 298 K. The theoretical contact area between a glass ball probe and a silicon wafer under these conditions can be calculated to be $3.51 \times 10^{-9}\,\mathrm{m}^2$ by Hertz's theory, and the average pressure on the contact area was estimated to be 137 MPa. As shown in Figure 3a, the friction coefficients of poly(**2**) brush with a sliding glass probe in air was found to be higher than that of poly(**1**) because hydrophilic poly(**2**) does not prefer to contact with air, thus interacting with the glass ball to increase adhesion. In the case of friction in water (Figure 3b), the friction coefficients of both poly(**1**) and poly(**2**) brush were reduced due to the fluid lubrication effect of water. However, it is noteworthy that the friction coefficient of poly(**2**) brush was lower than that of poly(**1**) under aqueous conditions. As water is a good solvent for poly(**2**), the interaction between poly(**2**) and the glass probe would be moderated, resulting in a low-friction surface. The molecular weight dependence on the friction coefficient was also observed in Figure 3. We suppose that the polymer brush with larger molecular weight has stronger adhesive properties, resulting in an increase in the friction coefficient.

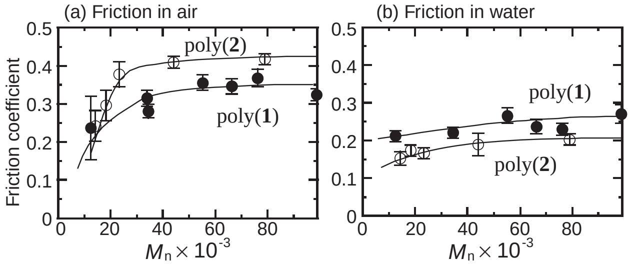


Figure 3. Molecular weight dependence of friction coefficient of poly(**1**) (filled symbols) and poly(**2**) (open symbols) brushes by sliding a glass prove in air (a) and in water (b).

In conclusion, the authors have showed the first results of the water lubrication system consisting of well-defined high-density hydrophilic polymer brush under loading of practical pressure.

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