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Synthesis and Frictional Properties of Poly(2,3-dihydroxypropyl methacrylate) Brush Prepared by Surface Initiated Polymerization on Silicon Wafer

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Surface initiated atom transfer radical polymerization of (2,2-dimethyl-1,3-dioxolan-4-yl) methyl methacrylate (**1**) using copper/sparteine complexes was carried out from immobilized initiator on silicon wafer to result in an assembly of polymer chains tethered by one end to a surface. Contact angle measurement, XPS, and FTIR studies revealed that isopropylidenyl groups of the hydrophobic poly(**1**) brush were converted to the hydroxyl groups by treatment with hydrochloric acid, producing the amphiphilic poly(2,3-dihyroxypropyl methacrylate) (**2**) brush, successively. Frictional properties of the poly(**1**) and (**2**) brushes were characterized by sliding the stainless ball probe on their surface in air and water. Frictional coefficient of poly(**2**) brush was significantly lowered in water compared with that of poly(**1**) brush, while poly(**2**) brush showed larger frictional coefficient than poly(**1**) brush surface in air.

Key words: polymer brush, frictional coefficient, 2,3-dihydroxypropyl methacrylate, atom transfer radical polymerization, hydrophilic polymer

1. INTRODUCTION

Since the controlled / "living" polymerization technique applied to the surface-initiated polymerization, high density and well-defined polymer brushes have been synthesized and characterized.[1, 2] Especially, atom transfer radical polymerization (ATRP) has been widely employed for the formation of polymer brushes, because ATRP is compatible with a various functionalized monomers, and the living / controlled character of the ATRP process yields polymers with a low polydispersity. A lot of researchers are investigating the surface properties of tailored polymer brushes, such as wettability, biocompatibility and friction. The sliding friction of polymer brushes are important in the design of low frictional or wear resistable surfaces, and in understanding frictional processes in biological systems.

Recently, Klein et al, found the reduction of frictional forces between solid surfaces bearing polymer brushes,[3] and they also reported that brushes of charged polymer (polyelectrolyte) could act as efficient lubricants between mica surfaces in an aqueous medium.[4] Similarly, Osada and his coworkers reported that the well-defied polyelectrolyte brushes, prepared by controlled radical polymerization using TEMPO, reduce the surface friction of hydrogels in water.[5] They also found that the friction depended on brush length; i.e., the gel with longer polymer brush showed a higher friction.

In this study, hydrophilic polymer brush consisting of poly(2,3-dihydroxypropyl methacrylate) (**2**) was synthesized using ATRP of (2,2-dimethyl-1,3-dioxolan-4-yl)methyl methacrylate (**1**) followed by hydrolysis. As poly(**2**) is well known as one of the water-soluble polymers,[6] wettable surface will be provided by poly(**2**) brush which attracts a great deal of interest in the frictional behaviors in aqueous media.

2. EXPERIMENTAL

2-1. Materials

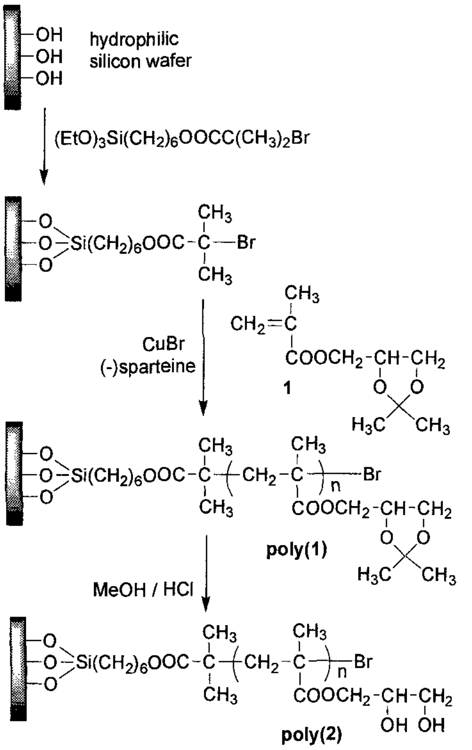
Anisole was purified by refluxed over the sodium for 6 h followed by distillation from sodium under reduced pressure. CuBr (Wako, 98%) was purified by washing with acetic acid and dried under vacuum. Sparteine (Nakalai tesque, 99%) and ethyl 2-bromo isobutyric acid ethyl ester (TCI, 99%) was used as received. 6'-Triethoxysilylhexyl-2-bromo isobutylate [7] was synthesized by hydrosilylation of 5'-hexenyl 2-bromo-isobutylate[8] using triethoxysilane. Water for contact angle measurements and frictional tests was purified with the NanoPure Water system (Millipore, Inc.). Synthesis and purification procedure of (2,2-dimethyl-1,3-dioxolan-4-yl)methyl methacrylate (**1**) was described elsewhere.[9]

2-2. Initiator-Immobilized Silicon Substrate

Silicon wafers (Si(111)), cut into 1 × 4 cm pieces, were cleaned by washing with piranha solution (H_2SO_4/H_2O_2 = 7/3, v/v) at 100 °C for 1 h and by irradiation of vacuum ultraviolet-ray (VUV, $\lambda = 172$ nm) for 10 min under 15 mmHg. Toluene solution of 6'-triethoxysilylhexyl-2-bromoisobutylate (5 wt%) was spin coated on silicon wafer (2000 rpm, 20 sec). The wafers were annealed at 110 °C for 9 h, cleaned by toluene using Soxhlet extraction for 3 h, rinsed with absolute ethanol, and dried under vacuum at 100 °C for 1 h.

2-3. Grafting Procedures

The silicon wafers, 4 mg (0.028 mmol) of CuBr and stirring bar were placed into a baked glass tube, which was degassed and purge with Ar gas three times. The anisole solution of (–)-sparteine (0.050 mmol) and **1** (15.0 mmol) were introduced into the glass tube, then degassed by repeating the freezing and pumping up.



Scheme 1

After introduce of Ar gas again, anisole solution of ethyl 2-bromoisobutyric acid ethyl ester (0.025 mmol) was injected to the reaction solution. The glass reactor was degassed again by freezing and pumping up, and then sealed off under the vacuum condition. Total volume of anisole was about 5 mL. The polymerization reaction was carried out at 65 °C for 24 h, and was quenched by addition of methanol at 0 °C under the ambient pressure in air. The conversion of **1** was determined by GC with a certain amount of internal standard. The reaction mixture was poured into methanol to precipitate the polymer, and the wafer was washed with toluene using Soxhlet apparatus for 12 h, followed by dried at 100 °C for 3 h *in vacuo*.

2-4. Sample Characterization

XPS measurements were carried out on a PHI ESCA 5800 (Phisical Electronics Co. Ltd.) at 10^{-5} Pa using monochromatic Al-Kα X-ray source. IR spectra of the polymer brush grown on silicon substrates were measured in the transparent mode using a Spectrum One KY type (Perkin-Elmer) system coupled with a Mercury Chromium Tell detector. Contact angle against water were recorded with a drop shape analysis system DSA10 Mk2 (KRÜSS Inc.) equipped with video camera. Size exclusion chromatogram (SEC) of the free soluble poly(**1**) was measured by a JASCO LC system connected two polystyrene gel columns of TSK-gel Super AW-4000 and refractive index detector (JASCO RI-740) using DMF containing 0.01M of LiBr as an eluent. Molecular weights were determined by polystyrene standards. Atomic force microscopic (AFM) measurements were operated by a SPI4000 (SII NanoTechnology Inc.) using a Si_3N_4 tip on a cantilever with a spring constant of 0.09 N m^{-1} at an ambient pressure. Frictional coefficient of polymer brush were recorded on Tribostation Type32 (Shinto Scientific Co. Ltd.) by sliding a stainless or a glass ball (ϕ10 mm) on the substrates in width of 25 mm at the rate of the 90 mm/min under the loading of 0.49 N. The morphologies of the wear trace of the thin films were observed with an S-4300SE field-emission SEM (Hitachi Co., Ltd.) equipped with X-ray microanalysis system (Genesis 7000, EDAX Co., Ltd.) in order to examine the elements on wear surface.

3. RESULTS AND DISCUSSION

3-1. Synthesis of Hydrophilic Polymer Brushes

Thin layer film of radical initiator was prepared by spin coating with a toluene solution of 6'-triethoxysilylhexyl-2-bromoisobutylate on flat silicon substrate, followed by annealing and washing. Water contact angle of the substrate increased to 81.8° from <5° (typical value for silicon wafer just after irradiation of VUV) by spin coating. Film thickness is estimated to be 1.2 ± 0.15 nm by AFM of micropatterned substrate which was prepared using a photolithography method by means of area-selective decomposition of organic layer by VUV-ray. Surface roughness of the substrate was 0.42 nm (5×5 μm^2). XPS spectra of initiator-immobilized silicon wafer showed the carbon signal (C_{1s}) at 286 eV associated with the organic portion of the attachable initiator along with the bromide (Br_{3d}) signal at 71 eV. The signals attributed to C=O and C-O bonds was also observed by narrow scan mode. These results confirm the formation of densely covered thin layer of initiator on silicon wafer.

Table I. Molecular weights and thickness of polymer brushes

run	polymer	M_n [a]	M_w/M_n [a]	thickness [b] / nm	roughness [c] / nm	contact angle [d] / deg	remarks
1	poly(**1**)	18400	1.23	9		75	
2	poly(**1**)	52600	1.24	25	0.67	75	
2-OH	poly(**2**)			15	0.39	35	after hydrolysis of run 2
3	poly(**1**)	53600	1.28	24		78	
3-OH	poly(**2**)			14		39	after hydrolysis of run 3
4	poly(**1**)	12700	1.51	12	0.74	77	
4-OH	poly(**2**)			8	0.75	24	after hydrolysis of run 4
5	poly(**1**)	55400	1.50	27	3.02	80	
5-OH	poly(**2**)			22	2.46	29	after hydrolysis of run 5
6	poly(**1**)	98800	2.67	54	8.29	80	
6-OH	poly(**2**)			33	5.34	27	after hydrolysis of run 6

[a] Determined by SEC using polystyrene standards in DMF containing 0.01M of LiBr. [b] AFM in dry state. [c] 5 x 5 μm^2.
[d] Water.

Surface-initiated radical polymerizations of **1** were carried out in the presence of ethyl 2-bromoisobutyric acid ethyl ester as a free initiator coupled with CuBr/(–)-sparteine (Table I). The number-average molecular weight (M_n) of a poly(**1**) brush on a silicon wafer was determined by measuring the molecular weight of a free polymer because reports described that these molecular weights have similar value.[8] Thickness of the polymer brushes increased with molecular weights. The AFM observation revealed that a homogeneous polymer layer was formed on the substrate. Since the film thickness did not change by washing with toluene using Soxhlet apparatus repeatedly, the polymer chains were not physically adsorbed but chemically anchored on the substrate. The graft density was estimated to be ca. 0.4±0.09 chain/nm^2 from the relationship between M_n and thickness in Table 1, assuming that the bulk density of poly(1) was approximately same as that of PMMA. The water contact angle of poly(**1**) brush with large molecular weight (M_n > 50,000) was 80°, which was very close value (83°) of spin-coated poly(**1**) film. The poly(**1**) brush with shorter length (M_n < 20,000) presented lower contact angle of 75°.

Hydrolysis of poly(**1**) brushes were employed by dipping the substrates into the acidic solution consisting of MeOH/2N HCl (100/1, v/v) (or 1,4-dioxane/1N HCl = 10/1, v/v) for 12 h at room temperature without stirring. The water contact angle of the polymer brush decreased from 80° to 30° after the treatment with MeOH/HCl solution (Fig.1), whereas the no such a large change was observed by soaking in a mixed solution of MeOH and acetic acid (10/1, v/v) for 16 h. Sharp decline of contact angle was observed in the case of run 4, probably due to the smaller molecular weight (M_n = 12700) than that of run 6 (M_n = 98800). Fig.2 shows IR spectra of poly(**1**) brush before and after the hydrolysis. Although the absorption of carbonyl group did not change, the absorption at 3250 cm^{-1} due to the hydroxyl groups are increased after hydrolysis reaction. These results imply that the hydrolysis of poly(**1**) brush proceeded successfully.

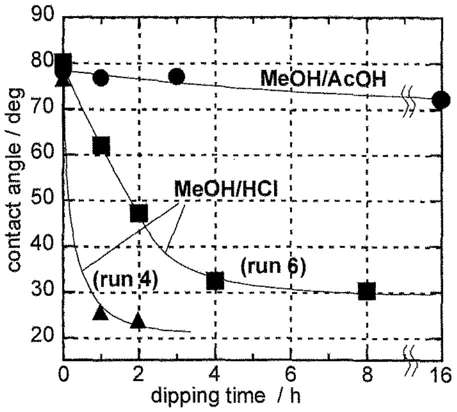


Fig.1. Water contact angle of poly(1) brush treated with acidic solution consisting of MeOH/2N HCl (20/1, v/v) and MeOH/AcOH (20/1, v/v)

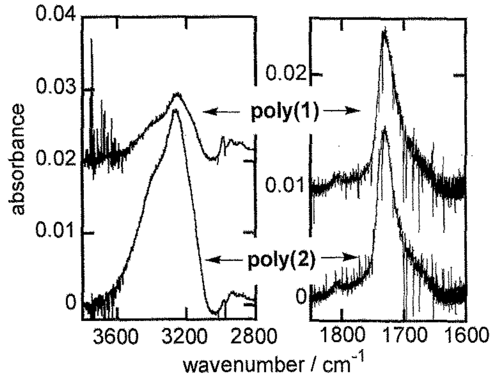


Fig. 2. IR spectra of poly(1) brush and poly(2)

Thickness of polymer brush also changed by hydrolysis; in the case of run 6, for example, the thickness of poly(**1**) (run 6) decreased from 62 to 35 nm (Table I). As the molecular weights of **1** and **2** are 200 and 160, respectively, the molecular weight of poly(**1**) should also decrease by hydrolysis. If we consider a polymer chain as a cylinder, a cross-sectional area should also decrease after the transformation of acetal to hydroxyl groups. Therefore, assuming that the graft density and the chain length are unchangeable during hydrolysis, poly(**2**) brush is supposed to tilt the main chain, or to shrink through hydrogen bonding interaction between each hydroxyl groups, leading to small thickness of polymer brush. The thickness of polymer brushes is known to be depending on their graft density and interchain interactions. For example, the thickness of poly (*N*-isopropylacrylamide) brush is sensitive to temperature because hydrogen bonding interaction between polymer chains extremely changes around at lower critical solution temperature.[10] The thickness of poly (2-methacryloyloxyethyl phosphorylcholine) brushes tends to be smaller than that of hydrophobic ones, such as PMMA brush, if they have same molecular weights,[11] probably due to the strong interactions of polar functional groups. These interaction effects could be applied to polar poly(**2**) brush, in order to explain the reason for the shrinkage thickness. On the other hand, it is also possible that the cleavage of Si-O bonds between tethered polymer and surface of silicon wafer took place when the substrate was treated with acidic solution. Unfortunately, it is difficult to elucidate the mechanism of large reduction of thickness of polymer brush.

3-2. Friction Behavior of Polymer Brush

The samples used for frictional tests were runs 2 and 5 in Table I as poly(**1**) brush, runs 2-OH and 5-OH as poly(**2**) brush. Fig. 3 shows dynamic friction coefficients of brush films investigated by friction tester under the dry and wet state. Either a stainless or a glass ball was used as a sliding probe under a load of 0.49 N at a rate of 90 mm/min. The hydrophilic poly(**2**) brush surface showed higher frictional coefficient in air than hydrophobic poly(**1**) brush one. This suggests that the poly(**2**) brush performed as an adhesive, probably because hydrophilic surface of poly(**2**) was unwilling to contact with air, and was willing to interact strongly with the glass probe. When the frictional test was carried out in water, both frictional coefficients of poly(**1**) and poly(**2**) brushes were reduced due to the effect of fluid lubrication. It is noteworthy that frictional coefficient of poly(**2**) brush was lower than that of poly(**1**) under aqueous condition. As water is a good solvent for poly(**2**), the interaction

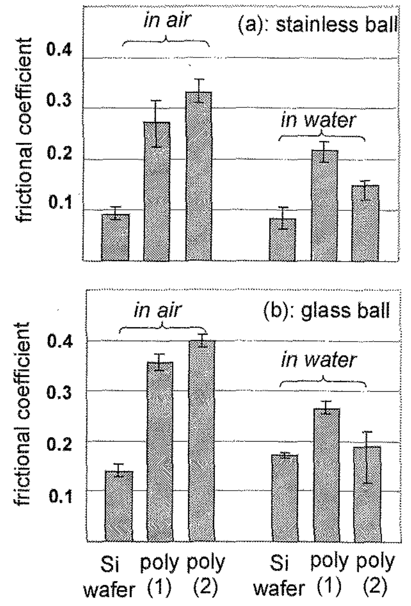


Fig. 3. Friction coefficient of polymer brushes by sliding a stainless-ball (a) and a glass-ball (b) in air and in water.

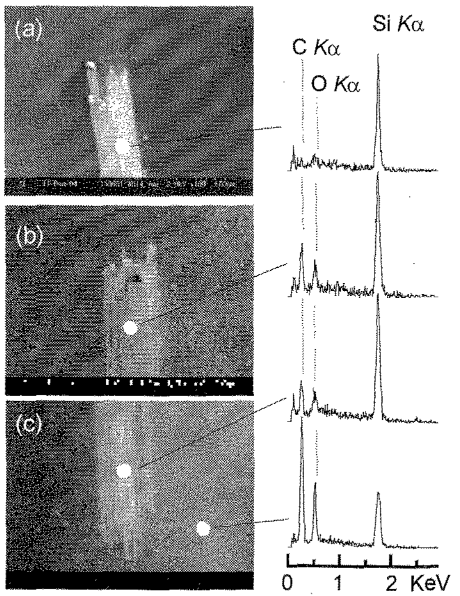


Fig. 4. SEM images and SEM-EDX spectra of spin-cast film of poly(1) (a) and poly(1) brush (b) after frictional test in air, and poly(2) brush film after frictional test in water (b) by sliding a glass-ball.

between the poly(**2**) and the probe would be moderated to result in low frictional surface. Sliding of glass ball provide higher frictional coefficient than that of stainless ball, as shown in Fig.3 (a) and (b).

After the frictional test using glass ball as a probe by reciprocating twice with linear motion between 25 mm distance under the normal load of 0.49 N to give a pressure of 223 MPa, the surface morphology of brush film and cast film were analyzed by means of SEM and energy dispersive X-ray (EDX) spectra. As shown in Fig.4(a), the glass ball scratched the surface of the spin-coating film of poly(**1**) under the dry condition. The peaks due to neither carbon $K\alpha$ nor oxygen $K\alpha$ were observed in EDX spectrum from the wear track of the spin-cast film. The observed peak at 1.8 keV attributed to silicon $K\alpha$ must be originated from silicon substrate. The same spectrum was observed in the spin-cast film of poly(**1**) after the sliding of glass ball in water. These results indicate that the sliding probe readily peeled the cast film completely. In addition, frictional coefficient of spin-cast film of poly(**1**) in air and water were 0.39 and 0.32, respectively, these magnitudes are larger than value of poly(**1**) brushes. On the other hand, EDX spectrum at the point of wear track on poly(**1**) brush showed the peaks due to the carbon and oxygen from poly(**1**) components. {Fig.4(b)} The residue of poly(**2**) brush was also observed on the wear track surface after the friction under aqueous condition, as shown in Fig.4(c). These results imply the potential for wear resistance of the polymer brush film.

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[7] MW = 413.4; bp = 122 - 123 °C / 0.1mmHg; ^{1}H NMR ($CDCl_3$) 0.61 (2H, $SiCH_2$), 1.23 (3H, $SiOCH_2CH_3$), 1.37 (6H, CH_2), 1.68 (2H, $COOCH_2CH_2$), 1.92 (6H, αCH_3), 3.82 (4H, $SiOCH_2$), 4.17 ($COOCH_2$). ^{13}C NMR ($CDCl_3$) 10.4 ($SiCH_2$), 18.4 ($SiOCH_2CH_3$), 22.7 ($SiCH_2CH_2$), 25.5 ($SiCH_2CH_2CH_2$), 28.3 (OCH_2CH_2), 30.9 (αCH_3), 32.7 ($OCH_2CH_2CH_2$), 50.3 ($SiOCH_3$), 56.0 (CBr), 58.4 ($SiOCH_2$), 66.2 (OCH_2), 171.7 (C=O).

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