Precise surface structure control of inorganic solid and metal oxide nanoparticles through surface-initiated radical polymerization

Motoyasu Kobayashi\textsuperscript{a}, Ryosuke Matsuno\textsuperscript{b}, Hideyuki Otsuka\textsuperscript{a,\textsuperscript{b}}, Atsushi Takahara\textsuperscript{a,\textsuperscript{b},*}

\textsuperscript{a}Institute for Materials Chemistry and Engineering, Graduate School of Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan
\textsuperscript{b}Graduate School of Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan

Received 12 June 2006; received in revised form 20 July 2006; accepted 26 July 2006
Available online 25 October 2006

Abstract

Surface-initiated radical polymerization was carried out in order to modify the surface of inorganic solid and metal oxide nanoparticles. Novel (inorganic nanoparticles/polymer) nanocomposites were prepared through a direct polymer grafting reaction from the surfaces of magnetite (Fe\textsubscript{3}O\textsubscript{4}) ($d = 10$ and $25$ nm) and titanium oxide (TiO\textsubscript{2}) ($d = 15$ nm) nanoparticles. The initiator for nitroxide-mediated radical polymerization with a phosphoric acid group was chemisorbed onto the nanoparticles and gave controlled polystyrene (PS) and poly(3-vinylpyridine) (P3VP) graft layers on their surfaces. The PS- and P3VP-modified nanoparticles were finely dispersed in organic solvents, whereas protonated P3VP-modified magnetite nanoparticles were dispersed in aqueous phase. The fine dispersion of nanoparticles in the polymer matrix was confirmed by microscopic observation. In order to realize tribological control, atom transfer radical polymerization of (2,2-dimethyl-1,3-dioxolan-4-yl)methyl methacrylate was also carried out from an immobilized initiator on a flat silicon wafer, resulting in a high-density polymer brush that was subsequently converted to a hydrophilic polymer brush consisting of 2,3-dihyroxypropyl methacrylate units. The poly(2,3-dihydroxypropyl methacrylate) brush-immobilized surface showed a low dynamic friction coefficient in water due to the highly stable hydrophilicity.

Keywords: Metal oxide; Nanoparticle; Hybrid material; Surface-initiated polymerization; Polymer brush

1. Introduction

The development of novel preparation methods via chemical science and technology is essential for innovation in polymeric hybrid materials research. For example, in the case of polymeric surface coating of functional inorganic materials, there are innumerable combinations between polymeric and inorganic materials. Therefore, the hybrid materials are potential candidates for molecular informatics, based on the employment of nanoparticles or well-defined surfaces as inorganic components. Needless to say, polymers and copolymers with a variety of molecular weights, compositions, structures, and end groups are all candidates for polymeric surface coating. Additionally, the conformation and density of polymeric coating are also important factors from the perspective of physicochemical properties.

When we focus on functional metal oxide nanoparticles, surface coating is indispensable to avoiding the aggregation of nanoparticles. Once a large number of nanoparticles aggregates in the polymer matrix, the aggregates are no longer “nanometer” size. On the other hand, if the dispersion state of the nanoparticles is controlled, mechanical, thermal, and optical properties of the hybrid materials would be improved. Surface coating of the flat inorganic surface is also important to decreasing the sliding friction and control of the wettability of micro-electromechanical systems (MEMS) devices. The reduced friction is known to improve the MEMS performance. The performance of microfluidic devices can be controlled through surface modification.

Since inorganic solid and metal oxide surfaces have higher surface energy compared with organic polymer...
surfaces, various surface-coating techniques have been utilized, including surface modification by surfactants. However, due to the lack of chemical, thermal, and mechanical stability, the development of stable-coating techniques is highly anticipated. In addition, uniform coating slightly thicker than the thickness of the surfactant is necessary to avoid coating defects. Surface coating with polymer brush [1] directly grafted from the surface appears to be a method that can overcome these disadvantages.

In past years, polymer brushes on a solid surface have been prepared by physisorption of end-functionalized polymers or of block copolymers with functional groups, which are strongly adsorbed at the surface and act as an anchor for the polymer chains [2]. This “grafting-to” technique, however, inherently affords a low grafting density because it is difficult for a large polymer chain to diffuse to a substrate surface, which is sterically hindered by surrounding bonded chains. In contrast, a “grafting-from” method combined with a living polymerization system enables us to prepare high-density polymer brushes due to the small molecules of the immobilized initiators and the high initiator efficiency. In particular, the recent development of living radical polymerization has resulted in the ability to precisely control the molecular weight and brush thickness through surface-initiated living polymerization. These conditions are more tolerant of impurities than anionic or cationic polymerization systems, and some methods are capable of aqueous solution polymerization. Representatively, the controlled radical polymerization technique can be accomplished by either nitroxide-mediated radical polymerization (NMRP) [3] or atom-transfer radical polymerization (ATRP) [4]. NMRP of styrene-based monomers is based on reversible capping of an active chain end radical with an alkoxyamine living radical group such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO). ATRP is based on the transfer of a halogen atom from the initiator to the monomer and successive transfer to the growing polymer chain catalyzed by a transition metal complex that mediates the propagation.

Undoubtedly, the most important part of this surface-grafting technique is the immobilization of initiators on the substrate surface. Considering the surface chemistry of substrate and the method of polymerization, the surface initiator should be carefully designed. Scheme 1 shows the design principle of initiators for surface-initiated polymerization from the surface of metal oxide nanoparticles and silicon substrate. The anchoring groups can be designed based on the state of the interaction with the substrate surface. It is well known that sulfides and thiols coordinate very strongly to metals such as gold, silver, copper, and platinum [5]. In the case of reactive silyl groups, the first event is hydrolysis resulting in the formation of silanol groups, followed by slow condensation to oligomers, which are then hydrogen-bonded to the surface hydroxy groups, leading to the formation of covalent bonding during annealing. The phosphoric acid group is well known to coordinate with metal oxide surfaces [6]. The interactions occurring in the immobilization described above are robust enough for practical applications. On the other hand, the initiator moieties are designed depending on the monomer used for polymerization. As mentioned above, polymerization of styrene derivatives are readily controlled by an NMRP system; therefore, a surface initiator having a TEMPO unit was prepared and employed. For the

Scheme 1. Design of initiator for surface-initiated radical polymerization on the surface of metal oxide nanoparticles and Si-wafer surfaces.
methacrylate and acrylate monomers, the suitable controlled polymerization method is ATRP system, which requires the use of alkyl halide as an initiator. Due to the excellent physicochemical properties and robustness of polymer brushes prepared by the grafting-from method, polymer brushes have been applied for various applications, including bionanotechnology [7]. The authors propose herein a method to modify the surface of inorganic solid and metal oxide nanoparticles through surface-initiated radical polymerization in order to prepare functional materials utilized for molecular informatics.

2. Experimental section

2.1. Materials

Styrene was obtained from WAKO Pure Chemical Industries, Ltd. and purified by distillation under reduced pressure over calcium hydride. Anisole was purified by refluxing over sodium for 6 h, followed by distillation from sodium under reduced pressure. CuBr (Wako, 98%) was purified by washing with acetic acid and was dried under vacuum. Sparteine (Nakalai Tesque, 99%) and ethyl 2-bromoisobutylate (TCI, 99%) were used as received. Magnetite particles (diameters of approximately 15 nm were given by the TAYCA Corporation. The synthesis and purification procedure for (2,2-dimethyl-1,3-dioxolan-4-yl)methyl methacrylate (DMM) has been described elsewhere [8].

2.2. Surface initiators

Nitroxide-mediated radical polymerization initiator (TP) containing a phosphoric acid moiety was synthesized according to a previous report [9]. TP was adsorbed to the nanoparticles in THF (TP/nanoparticle = 1/1, w/w) by suspension in ultrasonic bath for 24 h with cooling. The nanoparticles chemisorbed with TP were isolated by centrifugation of the suspension and were rinsed several times with ethanol. The surface initiator for ATRP, 6-centroxy-1-((2′-hydroxy-1′-phenylethyl)oxy)-2,2,6,6-tetramethylpiperidine (free initiator), and styrene were introduced into a glass tube, and were degassed by four freeze-pump-thaw cycles, and were sealed off under vacuum. Polymerization was carried out at 398 K for an arbitrary time. The reaction mixture was diluted with chloroform and was centrifuged to collect the dispersed nanoparticles. This cycle of the centrifugation and dispersion in chloroform was repeated several times to obtain poly(styrene (PS)-grafted nanoparticles). The PS generated from free initiator was isolated by precipitation in methanol and collected by filtration. A typical surface-initiated ATRP of DMM from flat silicon wafer was performed as follows [10]. The initiator-immobilized silicon wafer, CuBr, (−)-sparteine, ethyl 2-bromoisobutylate (free initiator), anisole, and DMM were quickly introduced into a glass tube under Ar atmosphere, and 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. The reaction mixture was poured into methanol to precipitate the free polymer, and the wafer was washed with toluene using a Soxhlet apparatus for 12 h.

2.4. Measurements

The number-average molecular weight (Mn) and molecular weight distribution (MWD) of free polymers were determined by SEC on a JASCO instrument equipped with a JASCO 830-R1 reflective index detection using THF as a eluent, which runs directly through three connected polystyrene gel columns (TSKgel SuperH6000, SuperH 4000, and SuperH 2500, flow rate 0.6 mL/min) at 313 K. Ultraviolet-visible absorption spectra were recorded on a Lambda 35 (Perkin Elmer Japan, Co., Ltd.). Thermogravimetric analysis (TGA) was performed by TG 8120 (Rigaku Corporation) using an alumina pan under a nitrogen atmosphere at a flow rate of 75 mL/min and a heating rate of 10 K/min from 293 to 923 K. Transmission electron microscopic (TEM) observations were made on an H-7500 (Hitachi) operated at 100 kV. The samples were prepared by dropping nanoparticle-dispersed solution onto a carbon-coated copper grid after sonication. The friction coefficients of the polymer brushes were recorded on a Tribostation Type32 (Shinto Scientific Co., Ltd.) by sliding a glass ball (d = 10 mm) onto the substrates over a width of 20 mm at a sliding velocity of 90 mm/min under loading of 0.49 N at 298 K.

3. Results and discussion

3.1. Preparation and physicochemical properties of high-density polymer brush on metal oxide nanoparticles

During past decades, surface-grown polymer brushes in general have been studied intensively with the intent of improving the physicochemical properties of solid planar surfaces as well as nanoparticle substrate. Surface modification by brush allows for the dispersion and stability of the nanoparticles in various solvents or polymer matrices while they maintain their physical characteristics. In
addition, the advantage of polymer brushes, especially in a surface-initiated approach, over other surface modification methods is their mechanical and chemical robustness, coupled with a high degree of synthetic flexibility towards the introduction of a variety of functional groups. Therefore, various types of polymer brushes have already been prepared by surface-initiated controlled radical polymerization from functionalized inorganic particles such as silica [11,12], gold [13,14], aluminum oxide [15], and titanium oxo clusters [16].

Magnetic nanoparticles have also attracted much attention due to their in vivo biomedical applications, including magnetic resonance imaging contrast enhancement [17] and drug-delivery systems [18]. MnFe₂O₄ and Fe₂O₃ core/PS shell nanoparticles have been synthesized by the ATRP technique through a surface initiator with carboxyl group [19,20], which is not stable in a hydrophilic environment due to non-covalent linkage. Neoh and his coworkers have reported that a surface initiator containing a highly reactive trichlorosilane unit was successfully immobilized on a Fe₃O₄ surface, allowing ATRP of methacrylate monomer to proceed [21]. Titanium oxide (TiO₂) exhibits various attractive properties such as a high refractive index, UV light absorption, and photocatalytic activity exploited for practical applications such as the photocleavage of water [22] and used in solar cells [23]. However, rutile-type TiO₂ has been used as a white pigment due to its high hiding power, and its solutions are not transparent since the particle size is generally more than a micrometer. Consequently, the preparation of transparent hybrid materials with well-dispersed TiO₂ particles and organic polymers has been done by sol–gel methods [24], treatment with silane coupling agents [25], and the liquid-phase deposition method using TiF₄ and organic surfactants [26]. Kickelbick et al. have prepared microemulsion-based Ti₃O₄(OH)₂ immobilized with triethoxysilane—substituted alkyl halide as a surface initiator for ATRP [27]. The hybrid TiO₂-PMMA core-shell type nanoparticle was obtained, but the surface coverage ratio of titanium oxide particle to surface initiator was lower than the ratios for iron, zinc, and zirconium oxide particles.

Organosilanes are known as good coupling reagents for making metal–carbon bonds; recently, however, organophosphorus compounds also appropriate be promising alternatives in the coupling of metal oxides other than those utilizing silica [28,29]. Actually, the stability of P–O–M bonds is demonstrated by numerous metal phosphate compounds [6,30,31] such as those including Zn, Al, Zr, Fe, and Ti. The authors wish to report here the surface modification of Fe₃O₄ and TiO₂ nanoparticles by phosphoric acid derivatives having a TEMPO-based initiator moiety to produce polystyrene brush via NMRP system. The dispersibility of the PS-grafted nanoparticles in various solvents and PS matrix was also investigated using UV absorption and TEM.

The graft density of adsorbed TP on Fe₃O₄ and TiO₂ nanoparticles were estimated by TGA to be 0.68 and 0.60–1.02 molecules/nm², respectively.¹ The formation of P–O–M bonds was detected by IR and XPS spectra, indicating the anchoring of TP on the surfaces of the metal oxide nanoparticles. Surface-initiated NMRP of styrene and 3VP from nanoparticles was carried out as shown in our previous report [32] (Scheme 2). Table 1 lists the Mₘ, s and MWDs of free polymers determined by SEC. The authors have previously found that the grafted polymer chains possess almost the same Mₘ and MWD as those of the free polymers based on SEC measurement of the grafted polymers cleaved from the Fe₃O₄ surface by acidic hydrolysis [32]. Accordingly, the Mₘ and MWD of polymer brushes on TiO₂ nanoparticle were evaluated by SEC measurements of the corresponding free polymers, suggesting that controlled NMRP successfully proceeds from surface-immobilized TP and the free initiator at the same rate of propagation. The graft densities of brushes were calculated from the weight loss of polymer-grafted nanoparticles by TGA, assuming that each nanoparticle is a whole sphere with given diameter. In all cases, the graft densities were relatively high compared with those prepared by the “grafting-to” method (approximately <0.01 chains/nm²). The initiator efficiency on a surface can also be estimated to be 10–30% from the grafting density of the surface initiator, the surface area of the nanoparticles, and the molecular weight of TP.

The obtained polymer-grafted nanoparticles were well-dispersed in organic solvent; PS-grafted nanoparticles were found to disperse in benzene, toluene, chloroform, THF, and ethyl acetate, while they precipitated in acetone and ethanol. P3VP-grafted-Fe₃O₄ particles were dispersed in chloroform, THF, ethanol, methanol, and weak acidic water (pH = 3), while they were insoluble in hexane, benzene, toluene, acetone, and ethyl acetate. In acidic water, protonated-P3VP-grafted magnetite would be formed. Fig. 1 shows the UV–vis absorption of chloroform solution dispersed with PS-grafted nanoparticles or non-modified nanoparticles by ultrasonic wave for 10 min. In the case of unmodified nanoparticles, as shown in Fig. 1(a) and (c), the absorbance decreased over time because the nanoparticles aggregated and precipitated to the bottom of the quartz cell. The observation of absorbance in the visible light wavelength region indicates formation of large

¹The graft density σ chains/nm² was calculated by TGA as follows. TGA of grafted nanoparticles gives us a weight loss z (0 < z < 1) due to the decomposition of grafting organic molecules or polymers. Supposing that the bare nanoparticles are sphere with radius of a nm and with density of ρ g/cm³, the weight of bare nanoparticle can be estimated

\[ (4\pi/3)\rho a^2 \{-\ln(1-z)/w\} = (1-z)\rho a^2 \]

where n and w are the number of nanoparticles and the weight of organic molecules or polymers in an alumina pan, respectively. The bulk density can be described by the number of grafting molecules (wN_A/M_w) and surface area of nanoparticle (4nπa² nm²) as a following equation:

\[ \sigma = (wN_A/M_w)/(4\pi a^2 n) = a^2\rho N_A \times 10^{-21}/\{3(1-z)M_w\} \]

where N_A is Avogadro’s number. The authors assumed the bulk density of Fe₃O₄ and TiO₂ nanoparticles to be 5.18 and 2.5–4.2 g/cm³, respectively,
aggregate, and the suspension was actually turbid. Finally, the absorbance disappeared from chloroform solution after centrifugation over a longer period of time. In contrast, PS-grafted Fe\(_3\)O\(_4\) and TiO\(_2\) nanoparticles dispersed in chloroform continue to exhibit UV absorbance even after centrifugation at 3500 rpm for 20 min, as shown in Fig. 1(b) and (d). In other good solvents such as THF, toluene, and ethyl acetate, PS-grafted TiO\(_2\) nanoparticles were stably dispersed. These results indicated that stable dispersion occurs due to the steric repulsion among polymer chains arising from osmotic pressure and the affinity of surface polymer chains against solvent. It seems that the dispersibility and stability were strongly influenced by the solubility of the polymers grafted on the nanoparticle surface.

The TEM images in Fig. 2 reveal that the non-grafted TiO\(_2\) nanoparticles formed aggregates several hundred nanometers in diameter. In contrast, PS-grafted TiO\(_2\) nanoparticles were finely dispersed as one or two particles. These findings clearly reveal that PS-grafted TiO\(_2\) nanoparticles allow for dispersion and stability in appropriate solvents. DLS measurement was also performed to
estimate the aggregation state of the nanoparticles and the size distributions in solution. The observed particle size of PS-grafted TiO$_2$ in chloroform dispersion at 0.01 mg/mL was 89 ± 10 nm, which is larger than the calculated diameter of a PS-grafted nanoparticle (ca. 45 nm)$^2$ in good solvents. These results indicate that the PS-grafted TiO$_2$ nanoparticles dispersed in solution, forming some tiny aggregates with one or two particles.

The phenomenon in which light is scattered by very small particles in its path results in a beam of visible light and is referred to as the Tyndall phenomenon, which suggests the fine dispersion of nanoparticles in solution. Fig. 3 shows the light-scattering behavior of a chloroform solution of PS-grafted TiO$_2$ particles. A green laser beam was irradiated through the solution. Light scattering from nanoparticles due to the Tyndall phenomenon was clearly observed.

In order to investigate the dispersion state of nanoparticles in polymer matrix, PS hybrid films were prepared on a glass dish by an air-dried chloroform solution of PS powder ($M_n = 230000$, prepared by free radical polymerization) and PS-grafted, as well as non-grafted nanoparticles. The obtained films were further dried under vacuum at 378 K for 24 h to completely remove the solvent. Fig. 4 shows the transmittance of PS films dispersed with various weight fractions of non-grafted TiO$_2$ particles (a), and PS-grafted TiO$_2$ (b). When non-grafted TiO$_2$ particles were added to the PS matrix, the hybrid film became clouded and the transparency was drastically decreased along with an increase in the weight ratio of non-grafted TiO$_2$. Additionally, specific ultraviolet light absorption due to TiO$_2$ was unclear, as shown in Fig. 4(a). In contrast, the

---

$^2$The height $h$ of the grafted layer in good solvents is given by the following equation: $h = (12/\pi)^{1/3}N_o^{1/3}(\omega/\eta)^{1/3}$ where $\omega$ is the excluded volume parameter, approximately (2 Å)$^3$; $N$ is the number of monomers; and $\eta = (a^3/3)^{-1}$, $a$ is the Kuhn statistical segment length with $a = 0.67$ nm for a PS monomer unit. This equation listed in: R. Jordan, A. Ulman, J.F. Kang, M.H. Rafailovich, J. Sokolov, J. Am. Chem. Soc. 121 (1999) 1016.
PS-grafted TiO<sub>2</sub>/PS hybrid film with 1.05 wt% of TiO<sub>2</sub> showed high transmittance of light in the visible region accompanying characteristic ultraviolet light absorption of TiO<sub>2</sub>, which was observed at 295 nm. In the case of the PS-hybrid film containing 1.98 wt% of TiO<sub>2</sub>, the UV-light absorption peak became broader and the difference in absorbance between the visible and ultraviolet regions was decreased. This change clearly shows the light scattering due to an increase in the number of aggregates and the aggregate size. Furthermore, the modulus of the PS-grafted TiO<sub>2</sub>/PS film at 298 K became approximately 1.15 times higher than that of PS film. The fine dispersion of nanoparticles also enhanced the wear resistance of the hybrid polymer thin films.

3.2. Preparation and physicochemical properties of high-density polymer brush on the Si-wafer surface

Water lubrication systems have attracted much attention due to their applications as medical implant devices [33] such as artificial joints for the human hip [34] as well as other environmentally friendly technologies. The surface grafting of polymers in general has been studied intensively to improve the lubrication properties of solid surfaces. Klein [35], Osada [36], and Sheth et al. [37] have already reported that the solid surface-bearing grafted hydrophilic polymers reduce the frictional forces between substrates in an aqueous medium, although the graft densities are very low. Furthermore, most previous research on the friction of grafted polymers has been carried out at very low normal force conditions, which are quite different from practical conditions. The authors have previously synthesized high-density PMMA brush on a flat silicon substrate [38] and have found that polymer brush affords a low-friction and wear-resistant surface under a high normal load [39]. Therefore, hydrophilic polymer brush can be expected to give a low friction surface under wet conditions. The authors focused on 2,3-dihydroxypropyl methacrylate (DHMA), of which polymer is a well-known as water-soluble polymer. As previously reported [10], a wettable surface was provided by surface-initiated ATRP of DMM followed by hydrolysis (Schemes 2 and 3). In this article, the authors carefully reviewed the preparation and wettability of the poly(DHMA) brush, and describe herein additional results regarding the macroscopic frictional properties of the brush.

A silicon wafer immobilized with ATRP initiator was prepared by a spin-cast process and was confirmed by IR and XPS spectra. Surface-initiated ATRP of DMM in the presence of sacrificial initiator proceeded to give the polymer brush and free polymer simultaneously. The results and reaction conditions are summarized in Table 2. The \(M_n\) of surface-grafted poly(DMM) on silicon wafer cannot yet be directly determined, but polymer brush should have the same \(M_n\) as the value of the corresponding free polymer, as mentioned above. The \(M_n\) of poly(DMM)s increased with increase in the additive molar ratio of the DMM. The MWDs of the obtained poly(DMM)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 that the surface roughness was 0.7–1.2 nm in a dry state over a 5 \(\times\) 5 \(\mu\)m<sup>2</sup> scanning area. The thickness of the polymer brush was determined by AFM scanning on the scratched surface of the polymer brush. As shown in Fig. 5, the thickness of the polymer brushes increased linearly with the molecular weight. The graft density was estimated to be ca. 0.36 \(\pm\) 0.09 chain/\(\text{nm}^2\) based on the relationship between \(M_n\) and the thickness.\(^3\)

\(^3\)The graft density was estimated to be ca. 0.36 \(\pm\) 0.09 chains/\(\text{nm}^2\) based on the relationship between \(M_n\) and the thickness, assuming that the bulk density of poly(DMM) was approximately the same as that of PMMA.
Considering this graft density, the tethered poly(DMM) brush would have a rather more extended conformation than the random coil structure.

Hydrolysis of poly(DMM) brushes was carried out by dipping the substrates into acidic solution consisting of MeOH/2N HCl (250/1, v/v) for 6 h at room temperature without stirring. The advancing contact angle ($\theta_A$) of the polymer brush did not change after the treatment with acidic MeOH, whereas the receding contact angle ($\theta_R$) decreased from 65° to 18°, as shown in Fig. 6 and Table 3. A 30μL water droplet on the poly(DMM) 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 attributed to the large contact angle hysteresis. Surface free energy calculated by static contact angles of methylene iodide using Owens and Wendt’s equation also increased from 38 to 47 mN/m by hydrolysis. These results indicate that the wettability against water was enhanced because hydrolysis of the acetal unit proceeded to afford hydroxyl groups, which form hydrogen bonds with water molecules.

**Scheme 2.** Nitroxide-mediated radical polymerization from the surface of metal oxide nanoparticles.

**Scheme 3.** Atom transfer radical polymerization of DMM from the surface of Si-wafer.

### Table 2

| Run | EB (mmol) | DMM (mmol) | Anisole (mL) | Time (h) | Conv. % | $M_n$ | $M_w/M_n$ | Thickness (nm) |
|-----|-----------|------------|--------------|----------|---------|--------|------------|----------------|
| 1   | 0.098     | 10.25      | 5.7          | 24       | 88      | 19000  | 18400      | 1.23           |
| 2   | 0.025     | 9.20       | 4.2          | 40       | 40      | 29800  | 28300      | 1.18           |
| 3   | 0.025     | 7.80       | 3.6          | 42       | 75      | 46300  | 41400      | 1.20           |
| 4   | 0.025     | 9.88       | 5.4          | 36       | 81      | 64200  | 52600      | 1.24           |
| 5   | 0.020     | 10.82      | 5.7          | 32       | 79      | 101000 | 68300      | 1.26           |

*Conditions: ethyl 2-bromoisobutylate (EB)/CuBr/(→)-sparteine = 1/1/2 (mol ratio) under Ar.*

**footnote continued**

According to the proportional relationship between the thickness $L_d$ (nm) and $M_n$, the graft density $\sigma$ was estimated by following equation,

$$\sigma = d N_A \times 10^{-21} / M_n,$$

where $d$ and $N_A$ are the assumed density of bulk PMMA at 293 K and Avogadro’s number, respectively.
However, due to the local orientation of the α-methyl group of DHMA at the air interface, a relatively large advancing angle was observed. Fig 7 shows IR spectra of polymer brush substrate before and after hydrolysis. The IR absorption at 3250 cm$^{-1}$ due to the hydroxy groups was increased, and that of the methyl groups at 2990 cm$^{-1}$ disappeared after the hydrolysis. In addition, the absorption peak position of the carbonyl groups shifted from 1732 to 1725 cm$^{-1}$ due to hydrogen bonding between the carbonyl groups and the hydroxy groups, implying that the poly(DMM) brush was successfully converted to poly(-DHMA).

The thickness of the polymer brush also changed as a result of hydrolysis; for example, the thickness of poly(DMM) ($M_n=59000$) decreased from 28 to 22 nm in the dry state. As the molecular weights of monomeric units of DMM and DHMA are 200 and 160, respectively, the $M_n$ of polymer brush should also decrease by hydrolysis. However, the proportional relationship between the thickness of poly(DHMA) brush and the $M_n$ calculated from the observed $M_n$ of the corresponding poly(DMM) multiplied by 0.8 (=$160/200$) was not changed. Assuming that the graft density and the chain length remain unchanged during hydrolysis, the structure of poly(DHMA) brush should be disordered or should shrink through the hydrogen-bonding interactions among the hydroxyl groups, leading to the formation of relatively thin polymer brush.

Dynamic friction tests were carried out by sliding a glass ball ($d=10$ 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 $3.51 \times 10^{-9}$ m$^2$ by Hertz’s theory, and the average pressure on the contact area was 0.49 N.

Table 3

| Droplet | Contact angle$^b$ | Poly (DMM) brush | Poly (DHMA) brush |
|---------|------------------|------------------|------------------|
| Water   | Static, $\theta$ | 75$^\circ$       | 63$^\circ$       |
| Water   | Advancing, $\theta_A$ | 78$^\circ$ | 76$^\circ$ |
| Water   | Receding, $\theta_R$ | 65$^\circ$ | 18$^\circ$ |
| Water   | Sliding, $\theta_S$ | 14$^\circ$ | 80$^\circ$ |
| Air     | Static, $\theta$ | 110$^\circ$ | 145$^\circ$ |
| Methylene iodide | Static, $\theta$ | 49$^\circ$ | 40$^\circ$ |
| n-Hexadecane | Static, $\theta$ | $<5^\circ$ | $<5^\circ$ |
| Surface free energy$^c$ | $\gamma_{SLV}$ (mN/m) | 38 | 47 |

$^a$Droplet volume was $30 \mu$L for water, $10–20 \mu$L for air bubble, and $3 \mu$L for methylene iodide and n-hexadecane, respectively.

$^b$Dynamic contact angles and sliding angle were measured using an inclinable plane.

$^c$Surface free energy was calculated from static contact angles of water and methylene iodide using Owens and Wendt’s equation.

Fig. 5. Relationship between molecular weight and thickness of poly(DMM) brush.

Fig. 6. Dynamic contact angle of poly(DMM) brush immersed in acidic solution consisting of MeOH/2N HCl (250/1, v/v); $\theta_A$ and $\theta_R$ are advancing and receding contact angle, respectively, using 30$\mu$L of a water droplet. See Table 3.

Fig. 7. Dynamic contact angle of poly(DMM) brush immersed in acidic solution consisting of MeOH/2N HCl (250/1, v/v); $\theta_A$ and $\theta_R$ are advancing and receding contact angle, respectively, using 30$\mu$L of a water droplet. See Table 3.
area was estimated to be 139 MPa. As shown in Fig. 8(a), the friction coefficients of poly(DHMA) brush with a sliding glass probe in air were found to be higher than those in water because hydrophilic poly(DHMA) does not prefer contact with air, it therefore interacts with the glass ball to increase adhesion. The fluid lubrication effect was also associated with lower friction coefficients in water and toluene compared with that in air. In particular, the interaction between poly(DHMA) and the glass probe in aqueous media would be moderated, resulting in a low-friction surface because water is a good solvent for poly(DHMA). In a poor solvent such as toluene, however, poly(DHMA) brush would interact with a glass probe rather than toluene, thus giving a higher friction coefficient. Fig. 8(b) presents the friction coefficient of sliding by a glass ball immobilized with poly(DHMA) brush. Reductions in the friction coefficients were observed for all conditions. Both polymer brushes grafted on a flat silicon substrate and a glass ball worked as a lubricant, preventing direct contact between the wafer and the probe even under dry conditions. In water, the authors supposed that fluid lubrication of water effectively took place in the interface between brush and brush to reduce the friction efficient, whereas a strong adhesive interaction between both hydrophilic brushes in toluene increased the friction forces. It is noteworthy that the friction coefficient of polymer brush depends on the solvent quality.

4. Conclusions

In conclusion, the authors have successfully prepared polymer brush on a Si-wafer and metal oxide nanoparticles through controlled radical polymerization from an immobilized initiator. In the case of the Si-wafer surface, the first results of a water lubrication system consisting of well-defined high-density hydrophilic polymer brush were realized under a loading of practical loading condition. In the case of PS-grafted TiO₂ nanoparticles, stable dispersion in good solvents for polymer chain was accomplished due to steric repulsion among the grafted chains derived from an osmotic pressure effect and affinity for solvents. The PS-grafted TiO₂ particles were also finely dispersed in polymer matrix. In the present study, either NMRP- or ATRP-initiating units were appropriately employed in the initiators by considering the monomers for coating and the phosphoric acid group or the triethoxysilyl group were also designed as an anchoring group depending on the target inorganic surfaces. The authors believe that the results obtained above will provide useful guidelines for the future design of polymer brushes or polymer/inorganic hybrid materials being applicable for molecular informatics.

(footnote continued)

\[ E = \frac{1}{C_0} - \frac{1}{C_N} \]

\[ a = (3/4 \times 2/E \times P \times R_A)^{3/2} \]

where \( R_A \) is curvature radius \( (5.00 \times 10^{-3} \text{ m}) \) of glass ball.
Fig. 8. Friction coefficient of poly(DHMA) brushes sliding by bare glass ball (a) and brush-immobilized glass ball (b) in air, water, and toluene.

Acknowledgments

The authors would like to thank TAYCA Corporation for providing TiO$_2$ nanoparticles. R.M. acknowledges the financial support of a Grant-in-Aid for JSPS Fellows. This work was partially supported by a Grant-in-Aid for the 21st Century COE Program “Functional Innovation of Molecular Informatics” from the Ministry of Education, Culture, Science, Sports and Technology of Japan.

References

[1] R.C. Advincula, W.J. Brittain, K.C. Caster, J. Ruhe, Polymer Brushes: Synthesis, Characterization, Applications, Wiley VCH, Weinheim, 2004.
[2] A. Halperin, M. Tirrell, T.P. Lodge, Adv. Polym. Sci. 100 (1992) 31.
[3] C.J. Hawker, J. Am. Chem. Soc. 116 (2004) 11185.
[4] K. Matyjaszewski, J. Xia, Chem. Rev. 101 (2001) 2921.
[5] A. Ulman, Chem. Rev. 96 (1996) 1533.
[6] A. Clearfield, Prog. Inorg. Chem. 47 (1998) 371.
[7] W. Senarantne, L. Andruzzi, C.K. Ober, Biomacromolecules 6 (2005) 2427.
[8] H. Mori, A. Hirao, S. Nakahama, Macromolecules 27 (1994) 35.
[9] R. Matsuno, K. Yamamoto, H. Otsuka, A. Takahara, Chem. Mater. 15 (2003) 3.
[10] M. Kobayashi, A. Takahara, Chem. Lett. 34 (2005) 1582.
[11] O. Prucker, J. Ruhe, Macromolecules 31 (1998) 592.
[12] T. von Werne, T.E. Patten, J. Am. Chem. Soc. 121 (1999) 7409.
[13] S. Nuß, H. Böttcher, H. Wurm, M.L. Hallensleben, Chem. Int. Ed. 40 (2001) 4016.
[14] K. Ohno, K. Koh, Y. Tsujii, T. Fukuda, Macromolecules 35 (2002) 8989.
[15] B. Gu, A. Sen, Macromolecules 35 (2002) 8913.
[16] G. Kickelbick, D. Holzinger, C. Brick, G. Trimmel, E. Moons, Chem. Mater. 14 (2002) 4382.
[17] W. Jung Chu, P. Jacobs, Magn. Reson. Imag. 13 (1995) 661.
[18] A.S. Lubbe, C. Bergemann, H. Riess, F. Schriefer, P. Reichardt, K. Possinger, M. Matthias, B. Dorken, F. Herrmann, R. Gurtler, P. Hohenberger, N. Haas, R. Sohr, B. Sander, A.J. Lemke, D. Ohlendorf, W. Huhn, D. Huhn, Cancer Res. 56 (1996) 4686.
[19] C.R. Vestal, Z.J. Zhang, J. Am. Chem. Soc. 126 (2002) 14312.
[20] Y. Wang, X.W. Teng, J.S. Wang, H. Yang, Nano Lett. 3 (2003) 789.
[21] F. Hu, K.G. Neoh, L. Cen, E. Kang, Biomacromolecules 7 (2006) 809.
[22] A. Fujishima, K. Honda, Nature 238 (1972) 37.
[23] B. O’Regan, M. Grätzel, Nature 353 (1991) 737.
[24] M. Volel, M. Armand, Chem. Mater. 17 (2005) 2028.
[25] M. Yang, Y. Dan, Colloid Polym. Sci. 284 (2005) 243.
[26] N. Steunou, S. Forster, P. Florian, C. Sanchez, M. Antonietti, J. Mater. Chem. 12 (2002) 3426.
[27] D. Holzinger, G. Kickelbick, J. Mater. Chem. 14 (2004) 2017.
[28] G. Guerrero, P.H. Mutin, A. Vioux, Chem. Mater. 13 (2001) 4367.
[29] P.H. Mutin, G. Guerrero, A. Vioux, J. Mater. Chem. 15 (2005) 3761.
[30] J.G. Van Alsten, Langmuir 15 (1999) 7605.
[31] C. Yee, G. Kataby, A. Ulman, T. Prozorov, H. White, A. King, M. Raffelovich, J. Sokolov, A. Gedanken, Langmuir 15 (1999) 7111.
[32] R. Matsuno, K. Yamamoto, H. Otsuka, A. Takahara, Macromolecules 37 (2004) 2203.
[33] T. Matsuda, Adv. Polym. Sci. 197 (2006) 67.
[34] T. Moro, Y. Takatori, K. Ishihara, T. Konnno, Y. Takigawa, T. Matsushita, U. Chung, K. Nakamura, H. Kawaguchi, Nature Mat. 3 (2004) 829.

[35] N. Kamph, J.F. Gohy, R. Jerome, J. Klein, J. Polym. Sci. B: Polym. Phys. 43 (2005) 193.

[36] Y. Ohsedo, R. Takashina, J.P. Gong, Y. Osada, Langmuir 20 (2004) 6549.

[37] S.R. Sheth, N. Efremove, D.E. Leckband, J. Phys. Chem. B 104 (2000) 7652.

[38] K. Tanaka, K. Kojio, R. Kimura, A. Takahara, T. Kajiyama, Polym. J. 35 (2003) 44.

[39] H. Sakata, M. Kobayashi, H. Otsuka, A. Takahara., Polym. J. 37 (2005) 767.