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"Substitutable" Polymer Brushes: Reactive Poly(methacrylate) Brushes with Exchangeable Alkoxyamine Units in the Side Chain

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A reactive polymer brush containing alkoxyamine units in the side chains, when heated with an alkoxyamine-terminated fluorinated nongrafted polymer, gave a grafted copolymer brush by a radical crossover reaction of alkoxyamine units. The fluorinated grafted copolymer brush could be converted back to the parent polymer brush upon treatment with an excess of low-molecular alkoxyamine. The reversible change in the surface properties of the brush was confirmed by X-ray photoelectron spectroscopy and contact angle measurements.

High-density polymer brushes have been prepared over the last decade, since controlled polymerization techniques[1–3] have been applied to surface-initiated polymerization.[4–6] Further, well-defined polymer brushes[7] can provide various types of surface properties and functions such as adhesion,[8,9] chromatography,[10] wettability,[11–13] frictional control,[14,15] and biocompatibility.[16,17]

Herein, a novel surface modification system that employs polymer brushes with exchangeable dynamic covalent bonds in the side chain is described. Recently, structural reorganization systems of polymers via radical crossover reaction have progressed. These systems are based on the principle of reversibility of C–ON bonds in alkoxyamine derivatives as dynamic covalent bonds.[18] Our group has reported that the reorganization of polymers by using alkoxyamine units is useful in reversibly synthesizing graft polymers,[19] crosslinked polymers,[20,21] cyclic polymers,[22] linear polymers with desired molecular weights and compositions,[23–25] and star polymers.[26–30]

As mentioned above, the key technique for the present system is the radical crossover reaction of alkoxyamine units, as represented in Figure 1. The exchange reaction between polymer brushes and nongrafted polymers, both having alkoxyamine units, is considered to be a novel reversible polymer reaction system and the constitution of the product depends on equilibrium control. This potential of reversibility can aid the development of "smart" surface modification methods that can substitute many times and can be applied to various polymers because of reversible covalent bonds.

Polymer brush **1** containing alkoxyamine units in the side chain was designed as shown in Scheme 1. Surface initiator with a trimethoxysilyl group was prepared and immobilized as previously reported.[31] By using the surface modifier, smooth and uniform surface initiator monolayer was obtained by chemical vapor adsorption.[32–34] The monomer with alkoxyamine units was prepared and purified as reported previously.[27] Polymer brush **1** was prepared by random copolymerization of methyl methacrylate (MMA) and methacrylic ester **2** with an alkoxyamine moiety ([MMA]/[**2**] = 10/1) using surface-initiated atom transfer radical polymerization (ATRP).[1] At the same time, a free initiator, ethyl 2-bromoisobutyrate, was added to generate the corresponding free polymer **4**.[35] The molecular weight and polydispersity index (PDI) of **4** were estimated by gel permeation chromatography (GPC) measurements using polystyrene standards to be $M_{\mathrm{n,GPC}} = 22700$ and $M_{\mathrm{w}}/M_{\mathrm{n}} = 1.22$, respectively. Previous studies on polymer brushes prepared by the ATRP method have revealed that M_{n} of a polymer brush is almost the same as that of the corresponding free polymer prepared simultaneously from a free initiator.[6,36] M_{n} of polymer brush **1** cannot be directly determined yet, however polymer brush should have the same M_{n} as the value of the corresponding free polymer **4** which was determined by GPC. Since the PDI of

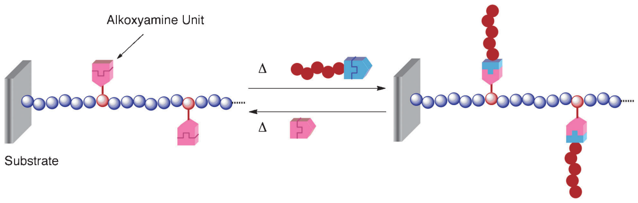
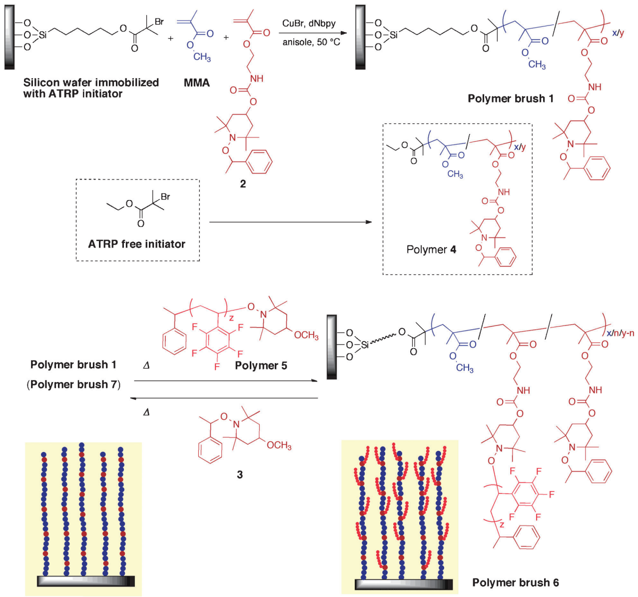


Figure 1. Schematic representation of grafting and degrafting reaction of a "substitutable" polymer brush via radical crossover reaction of alkoxyamine units.



Scheme 1. Synthesis and reaction of "substitutable" polymer brushes with alkoxyamine units in the side chain.

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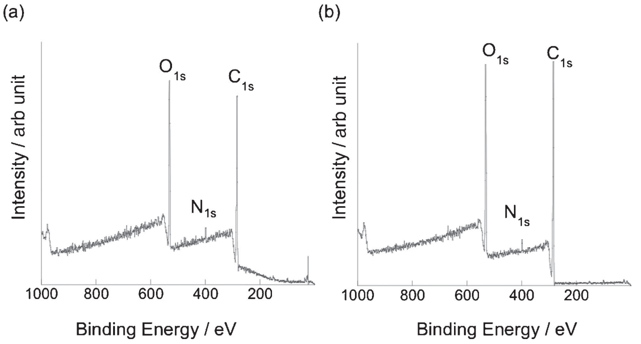

Figure 2. Wide-scan XPS spectra of (a) polymer brush **1** and (b) spin-coated free polymer **4** on Si substrate.

4 was relatively narrow, the surface-initiated ATRP seemed to proceed in a living fashion. The graft density (σ) of this alkoxyamine-containing polymer brush was estimated to be 0.36 chains/nm^2 by the following equation,

$$\sigma = d \times L_{\mathrm{d}} \times N_{\mathrm{A}} \times 10^{-21}/M_{\mathrm{n}} \qquad (1)$$

where d and N_{A} are the assumed graft density of bulk PMMA at 293 K and Avogadro's number, respectively. This graft density 0.36 is lower than that of the reported PMMA brush (0.56 chains/nm^2)[31] prepared by the same method, probably due to the steric effect of alkoxyamine-containing monomer **2**.

The structure of **4** was fully characterized by ^{1}H NMR and IR spectroscopy. The composition of polymer **4** was estimated to be MMA/**2** = 10/1, which is consistent with feed ratio. To confirm the composition of polymer brush **1**, X-ray photoelectron spectroscopic (XPS) measurement was carried out. Figure 2 shows wide-scan XPS spectra of **1** containing alkoxyamine units and of the corresponding spin-coated free polymer **4**. These spectra are similar to each other; this similarity can be attributed to the fact that the ratio of nitrogen atoms derived from alkoxyamine units in both the polymer brush and the free polymer is almost the same. From this, it can be concluded that surface-initiated living radical polymerization that afforded a random copolymer of MMA and **2** was successful.

For investigating the reactivity of the alkoxyamine-containing polymer brush **1**, it was treated with an excess of alkoxyamine-terminated poly(2,3,4,5,6-pentafluorostyrene) (**5**; $M_{\mathrm{n,GPC}} = 3700$ and $M_{\mathrm{w}}/M_{\mathrm{n}} = 1.21$), which was prepared by conventional nitroxide-mediated radical polymerization.[37,38] Polymer brush **1** was placed in an anisole solution of polymer **5** and heated at 100 °C under degassed conditions for 24 h. Then, the substrate was rinsed with dichloromethane using a Soxhlet extractor for 6 h. Figure 3a shows the wide-scan XPS spectrum of **1** after treatment with **5**. After the reaction, a strong peak for $\mathrm{F_{1s}}$ at 685 eV was clearly observed, indicating that the polymer brush contains fluorine atoms in its structure. This is undoubtedly owing to the introduction of poly(pentafluorostyrene) into the side chains of **1**. These findings confirmed that the radical crossover reaction of polymer brush **1** with excess polymer **5** successfully proceeded to afford grafted polymer brush **6**.

Furthermore, the reversibility of the developed reaction system was also investigated, because polymer brush **6** has dynamic covalent bonds at the branching points. For this investigation, a mixture of **6** and an excess (50 times the amount of poly(pentafluorostyrene)) of free alkoxyamine **3** was added to anisole and heated at 100 °C under vacuum conditions for 24 h. Physically adsorbed polymer could be removed from the substrate by washing with dichloromethane using a Soxhlet extractor for 6 h. Figure 3b shows the wide-scan XPS spectrum of the obtained (degrafted) polymer brush after the treatment of grafted polymer brush **6** with free alkoxyamine **3**. The XPS spectra confirmed the presence of C, N, and O elements but not of the F element. These results indicate that the grafted poly(pentafluorostyrene) side chains were completely removed by treatment with **3** and that **6** was converted to the degrafted polymer brush **7**, which is expected to have the same structure as **1**.

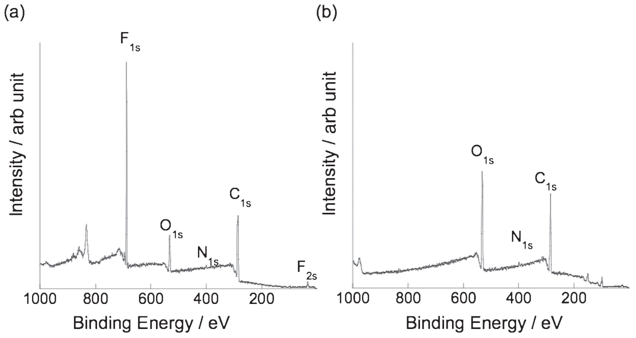

Figure 3. Wide-scan XPS spectra of (a) grafted polymer brush **6** and (b) degrafted polymer brush **7**.

Table 1. Static contact angles and surface free energies of polymer brushes and spin-coated film of free poly(pentafluorostyrene)

Contact angle/ surface free energy	Polymer brush **1**	Polymer brush **6**	Polymer brush **7**	Free polymer **5**$^{\mathrm{b}}$
$\theta_{\mathrm{H_2O}}/°$ $^{\mathrm{a}}$	85.0	94.0	83.6	97.7
$\theta_{\mathrm{CH_2I_2}}/°$ $^{\mathrm{a}}$	44.3	56.8	43.8	65.9
$\gamma_{\mathrm{SV}}/\mathrm{mJ\,m^{-2}}$	37.9	30.6	38.3	25.4

$^{\mathrm{a}}$The liquid volume for each measurement was 2 µL, and contact angles were those obtained by averaging over five measurements. $^{\mathrm{b}}$Spin-coated film of free polymer **5**.

In order to gain further insight into the exchange reactions, we carried out contact angle measurements of the polymer brushes **1**, **6**, and **7**. In Table 1, the static contact angles (θ) of these polymer brushes and of the spin-coated film of free polymer **5** are listed. The static contact angle of polymer brush **1** after its grafting reaction with poly(pentafluorostyrene) (polymer brush **6**) increased from 85.0 to 94.0° for water and from 44.3 to 56.8° for diiodomethane; these angles were approaching the corresponding values for the spin-coated film of free poly(pentafluorostyrene) (**5**) (97.7° for water and 65.9° for diiodomethane). These results agreed well with the expected structures of the polymer brushes from XPS measurements. In contrast, the θ values decreased from 94.0 to 83.6° for water and from 56.8 to 43.8° for diiodomethane, respectively, after polymer brush **6** was converted to polymer brush **7**. The surface free energies[39] of the polymer brushes changed reversibly by the introduction of the poly(pentafluorostyrene) side chains into the brushes. The XPS and contact angle measurements indicate that alkoxyamine-terminated poly(pentafluorostyrene) was reversibly attached to and detached from the alkoxyamine-containing reactive polymer brush.

In summary, the authors have demonstrated that alkoxyamine-containing polymer brushes can function as "substitutable" polymer brushes because of a radical crossover reaction among the complementarily reactive alkoxyamine units attached to the side chain of the polymer brush and chain end of the free polymer. Since a radical reaction is tolerant of various functional groups, the system developed in this study can be applied to the preparation of surfaces with desired hydrophilicity/hydrophobicity, biocompatibility, tribological properties, adsorption properties, adhesion properties, and so on. Inorganic nanostructures such as nanoparticles, nanorods, and nanofibers are also candidates for modification with substitutable polymer brushes.

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