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Surface Modification

Surface Modification by Electrostatic Self-Assembly Followed by Covalent Fixation**

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Modification of solid surfaces is quite common for materials in which surface and bulk property requirements diverge or a responsive surface is desired. Surface-modifying agents (SMAs) are applied using various approaches, including adsorption,[1] grafting,[2] or surface segregation.[3] Here, we describe a novel concept for applying SMAs that is highly efficient and leads to permanent surface modification. It is based on electrostatic self-assembly of ionically charged SMAs to oppositely charged surfaces, followed by thermal conversion of the resulting ionic bonds to covalent bonds (Figure 1). The ionic functional groups that make this possible are cyclic onium cations (e.g., ammonium or sulfonium): thermally induced ring opening by anions, generated simply by pH control, eliminates the ionic bond. The approach is demonstrated here by modification of cellulose, glass, and nylon with ionically functionalized silicone, alkane, and fluorochemical SMAs.

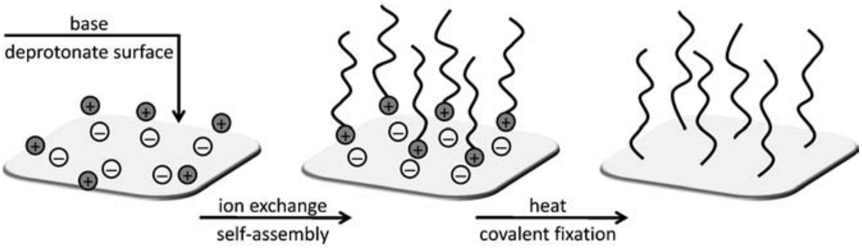

Figure 1. Surface modification by electrostatic self-assembly followed by covalent fixation: implementation in which reactive ionic groups (i.e., moderately strained cyclic oniums) are incorporated into surface-modifying agents (SMAs) and applied to surfaces made anionic by deprotonation using base (e.g., those containing -OH or -COOH groups). Alternatively, surfaces could be modified with reactive ionic groups and anionic SMAs applied. Potential advantages of this surface modification approach include high-yield deposition, homogeneity and permanency.

Covalent bonding of SMAs to surfaces requires the presence of appropriate functional groups at the surface in sufficient concentration. A large variety of functional groups have been inserted and employed for this purpose, with those that allow click reactions currently enjoying much popularity because they occur cleanly in high yields and various solvents.[4] However, for most click reactions, including the prototypical copper-catalyzed reaction between alkynes and azides, the driving force for the functionalized SMA to leave solution and adsorb onto an appropriately functionalized surface may not be particularly strong. This is especially important for commercial operations in which anything that remains in the processing bath must be recycled or treated as effluent. High exhaustion from a processing bath can be ensured by applying ionically charged SMAs onto surfaces with complementary electrostatic charges. The result is a more environmentally friendly process that is demanded by general public sentiment and increasingly stringent legislation of ecotoxicological considerations.

For SMAs that are polymeric, surface adsorption to give brushes occurs in two stages. The initial stage is diffusion-limited and subsides when the kinetics decrease at an apparent saturation level due to the reduction of available sites and screening by the adsorbed layer. The second, slower stage is referred to as the penetration-limited regime because penetration of chains through the maturing brush is the rate-limiting step.[5] It has been shown that increasing the end-group sticking energy of a polymeric SMA results in higher surface coverage as long as the coverage is monitored into the second stage.[6] Adding ionic functional groups to polymeric SMAs increases sticking energy and helps overcome the entropic penalty to adsorption. Moreover, because of the non-permanency of the ionic bond between SMA and substrate, exchange and rearrangement on the surface remains possible to facilitate production of level (i.e., homogeneous) conformal coatings.

Here, we describe a novel approach to surface modification that employs reactive ionic functional groups in SMAs that are applied to surfaces through electrostatic assembly and subsequently heated to convert the ionic bonds to covalent bonds (Figure 1). Electrostatic assembly followed by covalent fixation at elevated temperatures has been pioneered by Tezuka et al. for the purposes of making

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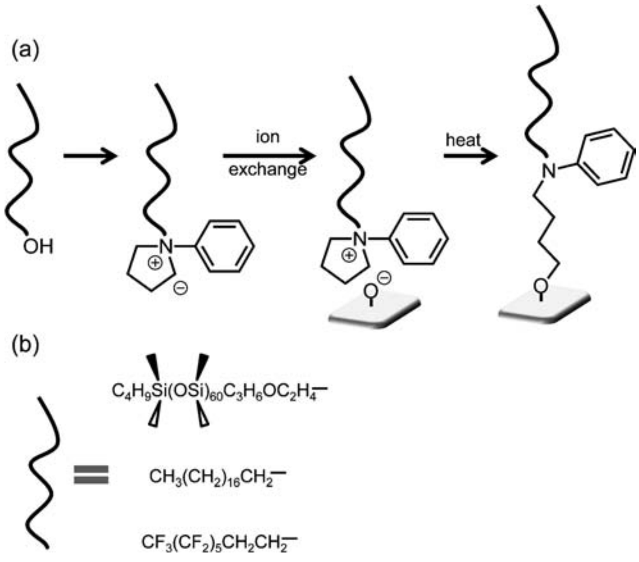
precisely designed macromolecules with complex architectures and topologies,[7] including some that have been prepared only through this synthetic route. The special features of this chemistry that allow one to synthesize a manacle or theta-shaped polymer, for example, are the same that make it useful for surface modification. Namely, electrostatic interactions allow for high-fidelity control of assembly; thermally induced transformation of ionic bonds to covalent bonds allows for controlled conversion to a permanent structure.

The functional groups that make this possible are moderately strained cyclic ammonium or sulfonium groups, collectively known as cyclic onium cations. Reaction of cyclic onium salts with nucleophiles can proceed through elimination or substitution, endocyclic or exocyclic, routes.[8] The desired route is exocyclic substitution as it leads to coupling of the reactants by ring opening of the cyclic onium. By judicious choice of heteroatom substituent and processing conditions, the desired route can be maximized.[9] The thermal conversion from ionic bond to covalent bond takes place from 25 °C to over 100 °C, depending primarily on the choice of cyclic onium.[10] The final product contains no charged species, and the covalent bond connecting SMA to the surface is an ether linkage, which is relatively stable to hydrolysis and other bond-breaking reactions.

Incorporation of the reactive ionic cyclic onium groups into surface-modifying agents is a straightforward, two-step procedure that begins with commercially available, commodity organic chemicals. A synthetic route is depicted in Scheme 1 for incorporating one type of cyclic onium cation. For starting materials that contain primary hydroxy groups, reaction with triflic anhydride quantitatively incorporates a trifluoromethanesulfonyl (i.e., triflate) leaving group that can be substituted with *N*-phenylpyrrolidine (NPP) to provide a reactive ionic NPP-functionalized SMA. This sequence was successfully carried out on stearyl alcohol to produce a reactive ionic wax, on monocarbinol-terminated poly(dimethylsiloxane) to produce a reactive ionic silicone, and on 1*H*,1*H*,2*H*,2*H*-perfluoro-1-octanol to produce a reactive ionic fluorochemical SMA. The reactive ionic group in each of these SMAs is the cyclic *N*-phenylpyrrolidinium cation. Details of the synthetic procedures and material characterization are provided in the Supporting Information.



Scheme 1. a) Synthetic scheme for incorporating one type of reactive ionic group, an *N*-phenylpyrrolidinium (NPP) cation, into surface-modifying agents (SMAs) and application of the resulting NPP-functionalized SMA to a surface. b) Tail structures giving rise to reactive ionic silicone, alkyl, or fluorochemical SMAs.

Conversion of starting materials to reactive ionic SMAs occurred in nearly quantitative yields and was confirmed by nuclear magnetic resonance (NMR) spectroscopy. The ^{1}H NMR spectra of the starting material, triflate intermediate and reactive ionic SMA are shown in Figure 2 for the silicone SMA. All peaks in the spectra are assigned, thus indicating pure materials. The primary hydroxy group in the starting material (2.2 ppm) does not appear in the spectrum for the triflate or final product. The protons attached to the carbon next to the hydroxy group, α protons labeled *g* in Figure 2, are shifted downfield in the triflate and final product with respect to the starting material, indicating changes in the chemical environment of these protons. The aliphatic (*d*, *e*, *f*) and aromatic (*a*, *b*, *c*) peaks of the *N*-phenylpyrrolidinium cation appear in the spectrum for the NPP-functionalized silicone. Clustering of the aromatic protons at 7.6 ppm is diagnostic for the formation of the cyclic ammonium salt; these protons appear at 7.3 and 6.6 ppm in the unreacted NPP. Confirmation that these peaks belong to NPP groups attached to the silicone was provided by diffusion-ordered NMR spectroscopy (DOSY), in which peaks due to the silicone backbone and NPP exhibit the same diffusion coefficient; DOSY of a physical mixture of the unreacted NPP and PDMS starting materials shows two distinct diffusion coefficients since the PDMS is much larger ($M_n = 5.5\,\text{kg}\,\text{mol}^{-1}$) than the NPP

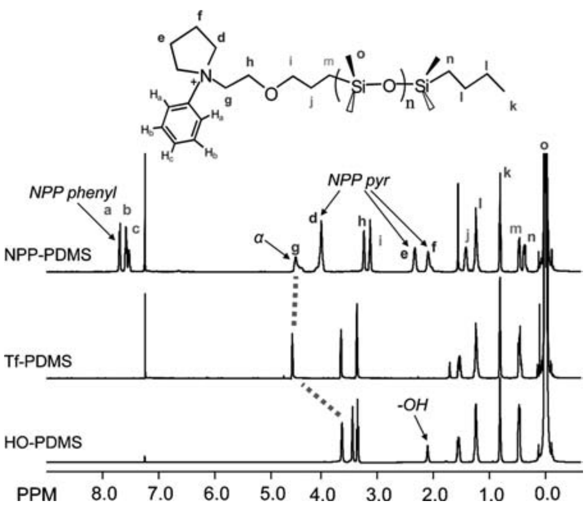


Figure 2. ^{1}H NMR spectra of a monocarbinol-terminated poly(dimethyl siloxane) (HO-PDMS), its triflate (Tf-PDMS) and *N*-phenylpyrrolidinium-functionalized product (NPP-PDMS), a reactive ionic silicone. Note the disappearance of the hydroxy resonance, shift of the α proton resonances, and appearance of peaks due to aromatic and aliphatic protons of NPP.

(147 g mol^{-1}). Gel permeation chromatography revealed the molecular weight and polydispersity ($M_w/M_n = 1.2$) of the starting material were not altered significantly during the triflation and substitution reactions. Changes noted in the NMR spectra for the silicone were also observed for the alkane and fluorochemical SMAs. Matrix-assisted laser desorption mass spectrometry and infrared spectroscopy provided further evidence of the structure.

To demonstrate the versatility of this new concept in surface modification, reactive ionic SMAs were applied to a naturally produced biomaterial, a ceramic, and a synthetic polymer. The reactive ionic silicone was applied to cellulose, the reactive ionic wax was applied to glass, and the reactive ionic fluorochemical was applied to nylon. In each case, the substrate was first prepared by deprotonating surface hydroxy and carboxy groups using a base. The reactive ionic SMA was then applied to the surface by adsorption from solution. The substrate was then washed or heated. Surfaces were analyzed spectroscopically using attenuated total reflectance infrared (ATR-IR) spectroscopy and macroscopically using contact angle measurements or micrographs of water droplets. The results are summarized in Figure 3 and Table 1. For the reactive ionic silicone application (Figure 3 a), adsorption onto a cellophane surface was confirmed by the appearance of ATR-IR peaks at 1257 and 790 cm^{-1} which are characteristic of silicones. After washing the treated cellophane with tetrahydrofuran (THF), these peaks disappeared indicating the NPP-PDMS was not bonded to the substrate. However, if the substrate is heated at 80 °C for 10 min and then washed repeatedly, the silicone peaks remain. The cellulosic surface has been permanently modified with a silicone.

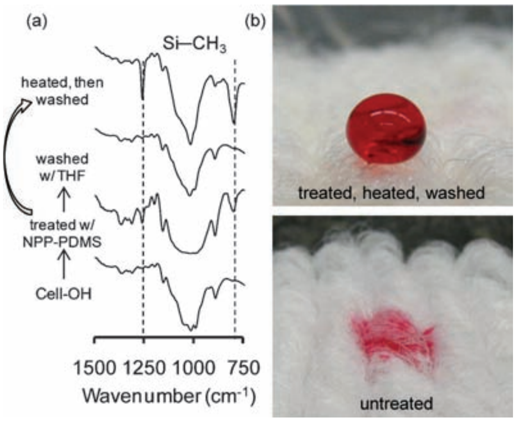


Figure 3. a) Attenuated-total-reflectance (ATR) infrared spectra of cellophane, cellophane treated with NPP-PDMS showing that this reactive ionic silicone does adsorb to the surface, cellophane treated with NPP-functionalized PDMS and then Soxhlet-extracted with tetrahydrofuran (THF) showing that it is not permanent, and cellophane treated with NPP-functionalized PDMS and then heated at 80 °C for 10 min and then Soxhlet-extracted with THF showing that the surface modification is permanent. Vertical dashed lines at 1257 and 790 cm^{-1} mark Si–CH$_3$ vibrations characteristic of silicones. b) Micrographs of a piece of nylon carpet after a drop of water (containing red dye for visualization) was placed on the surface: untreated, and treated with NPP-functionalized fluorochemical followed by heating and washing showing permanent surface modification by this reactive ionic fluorochemical.

Table 1: Reactive ionic wax applied to glass.

Glass slide	H_2O contact angle
treated, heated, washed	63 ± 6°
treated, washed	22 ± 3°
untreated	19 ± 5°

The contact angle of a water droplet (1 μL) on a glass slide is 19 ± 5° (Table 1). After exposing the glass slide to base, treating with the reactive ionic wax and washing, the contact angle was unchanged at 22 ± 3°. If the glass slide is heated at 80 °C before washing, the water contact angle is 63 ± 6°, indicating the surface is more hydrophobic due to the presence of the alkane. The triflate intermediate could also be used to modify the surface of glass, but the temporal stability of triflates in solution is poor and surface reaction depends on random collisions of the SMA with the surface as opposed to the more directed adsorption made possible with the NPP-functionalized SMAs due to complementary ionic charges.

The reactive ionic fluorochemical was applied to a piece of cationic-dyeable nylon carpet (Figure 3 b). Deprotonation of carboxy groups by base was followed by treatment with the reactive ionic fluorochemical, heating and washing. A drop of water placed on the surface of this nylon carpet remains on the surface indefinitely with a contact angle greater than 130°. The drop could be rolled around the surface by tilting the carpet. Without treatment with the reactive ionic fluorochemical, a water drop disappears into the substrate in less than a second.

In addition to the examples presented here, we also expect that reactive ionic chemistry will have applications in layer-by-layer assembly protocols and modifying surfaces of a variety of functional nanostructured materials.[11] We have recently shown that it is also very effective to employ for dyeing of films and fibers.[12] Reactive dyeing is practiced world-wide using anionic dyes that are applied primarily to anionically charged cellulosic fibers. To push exhaustion of such dyes from solution, large quantities of electrolyte (up to 100 g L^{-1}) must be added to the process bath, which makes for a tremendous economic and environmental load. By incorporating a positively charged reactive ionic group into a typical azo chromophore used in dyes, we showed that we could produce a reactive dye that could be exhausted from the processing bath at 98 % without addition of any electrolyte. The new reactive ionic dye was successfully applied to cellophane and nylon 6,6 films, and to cotton and nylon fabrics.

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