Synthesis of Responsive Polymer Brushes via Macromolecular Anchoring Layer

Igor Luzinov[1], Viktor Klep[1], Sergiy Minko[2], K. Swaminathan Iyer[1], John Draper[1], and Bogdan Zdyrko[1]

[1]*School of Materials Science and Engineering, Clemson University, 263Sirrine Hall, Clemson, SC 29634*

[2]*Department of Chemistry, Clarkson University, Potsdam, NY, 13699*

INTRODUCTION

Switchable surfaces can be described as surfaces that have the ability to respond in a controllable fashion to specific environmental stimuli. A prospective means to build an adaptive polymer layer is fabrication of a mixed polymer brush by combination in one grafted layer polymers of different nature. Then, each component of the nanostructured heterogeneous layer will play its specific role and support versatile behavior of the surface. Moreover, the combination of two or more polymers in the brush may act not as a simple addition of different functions, but it may affect a specific morphology of the film driven by a subtle interplay between increased numbers of interactions.

The properties of mixed brushes were theoretically analysed.[1-3] It was shown that the heterogeneous brush morphology is affected by the interplay between lateral and perpendicular to the substrate phase segregation governed by solvent quality. These brushes, composed of two (or more) distinct spices of homopolymers, may change wettability and adhesion in response to variation of environment. Both "grafting to" and "grafting from" methods were successfully applied to synthesize the mixed polymer brushes.[4-8]

In the present communication, we describe synthesis of the mixed polymer brushes via macromolecular anchoring layer. Namely, the brushes were grafted to the surface through ultrathin reactive poly(glycidyl methacrylate) (PGAM) film. The heterogeneous grafted layers were synthesized by "grafting to" approach, "grafting from" approach, and their combination. The morphology and surface chemical composition of the responsive brushes were investigated using scanning probe microscopy and contact angle measurements.

EXPERIMENTAL

Anchoring layer: Highly polished single-crystal silicon wafers of <100> orientation (Semiconductor Processing Co) were used as a substrate. The wafers were first cleaned in an ultrasonic bath for 30 minutes, placed in a hot piranha solution (3:1 concentrated sulfuric acid/ 30% hydrogen peroxide) for one hour, and then rinsed several times with high purity water. Glycidyl methacrylate (Aldrich) was polymerized radically to give PGMA. To prepare the macromolecular anchoring layer PGMA was dissolved in Methyl Ethyl Ketone (MEK) and thin films (1-5 nm) were deposited on the surface by dip coating and dried overnight.

Grafting from: Copper (I) bromide (CuBr), Copper (II) bromide ($CuBr_2$), 4,4'-dinonyl-2,2'-dipyridyl (di-No-di-Py), bromoacetic acid (BAA), and tert- butylbromacetate (BBA) were obtained from Aldrich and used as received without further purification. All monomers were purified by treatment with inhibitor removing sorbent and vacuum distillation. The PGMA films were treated by BAA vapor in argon atmosphere at different temperatures (30~90 ^{0}C) to synthesize polymerization initiator attached to a substrate. Unbound BAA was removed by multiple washing with ethanol including washing in an ultrasonic bath. Silicon wafers modified with PGMA/BAA macroinitiator were placed into a reaction vessel containing monomer, CuBr, di-No-di-Py, and BBA or $CuBr_2$. The mixture was degassed by purging with argon and five freeze-pump-thaw cycles. After polymerization, unbound polymer was removed by multiple washing with a good solvent including washing in an ultrasonic bath.

Grafting to: Carboxy-terminated and amino-terminated polymers of different molecular weights were used for the synthesis of the responsive polymer brushes. In a typical procedure, thin film (40-100 nm) of end-functionalized polymer was deposited onto the wafers modified by the PGMA. The specimens were placed in a vacuum oven at a temperature above glass transition or melting temperature of the polymer being grafted to enable the end groups to react with the epoxy-modified substrate. Unbound polymer was removed by multiple washing with a good solvent including washing in an ultrasonic bath.

Characterization: The brush samples were characterized by ellipsometry and scanning probe microscopy (SPM). Ellipsometry was performed with a COMPEL automatic ellipsometer (InOm Tech, Inc.). Scanning Probe Microscopy (SPM) in tapping mode was performed on a Dimension 3100 (Digital Instruments, Inc.) microscope.

RESULTS AND DISCUSSION

There are two major techniques available for preparation of the grafted layers, namely attachment of end-fuctionalized polymers ("grafting to" method),[9,10] and polymerization initiated from solid surfaces ("grafting from" method).[11-15] Each method has advantages and limitations. When exceptionally high grafting density is needed, the "grafting from" approach is the only method for brush formation. The polymer brushes grown from the surface by the technique, indeed, possess extremely high density of the attached chains. In the "grafting to" approach, end-functionalized polymers react with a suitable substrate surface under appropriate conditions to form a tethered polymer brush. The advantage of the method is that well-defined end-functionalized polymers with a narrow molecular weight distribution can be used for the grafting and, as a result, well-defined brushes can be readily synthesized. On the other hand, the technique has a constraint in terms of the maximum grafting that can be obtained, namely that the grafting is self-limiting. Hence, the typical polymer brush obtained in this way has relatively low grafting density. It is necessary to highlight that the most of the developed grafting ("to" and "from") methods require attachment either end-functionalized polymers or low molecular weight substances (e.g. initiators) to the substrate for the brush synthesis.

There are two common approaches for the attachment of polymerization initiators or end-fictionalized polymers for the brush fabrication. The first one relies on the reactions between end-functionalized initiator/polymer and native functional groups originally present on the substrate surface.[9,16,17] A different approach involves the formation of a monolayer consisting of functional groups active towards terminally functionalized (e.g. epoxide, amine, anhydride or hydroxide) initiator/polymer.[10,18] Silane and thiol chemistries have proved to be suitable for the grafting in this case. Usually the coupling methods are relatively complex and specific for certain substrate/(macro)molecule combinations. An alternative method for the attachment involves primary polymer (mono)layer with activity towards both surface and functionalized (macro)molecule.[19,20] The polymer is used for the initial surface modification as well as generation of the highly reactive primary layer. When deposited on a substrate, the primary layer first reacts with the surface through formation of covalent bonds. The reactive units located in the "loops" and "tails" sections of the attached macromolecules are not connected to the surface.[21] These free groups offer a synthetic potential for the further chemical modification reactions and serve as reactive sites for the subsequent attachment of the initiators. If the polymer used for building the primary layer contains functional groups highly active in various chemical reactions, the primary layer approach become virtually universal towards both surface and end-functionalized initiating species being used for the brush formation.

We used PGMA to form a reactive anchoring polymer layer. A polymer with epoxy functionality was chosen, since the reactions of epoxy groups are quite universal and can covalently anchor PGMA to the substrate surface.[19] The glycidyl methacrylate units located in the "loops" and "tails" sections of the attached PGMA chain were not connected to the substrate. These free groups could serve as reactive sites for the subsequent attachment of (macro)molecules with complementary functional groups. Indeed, we successfully used the PGMA platform for synthesis of polymer brushes by both grafting to and grafting from methods.[22] Grafting density, molecular weight, and thickness of the attached layers were readily varied.

When the mixed polymer brushes are considered, variety of parameters influence the mixed brush structure and morphology such as solubility of the grafted polymers in a solvent, substrate preference

of the polymers, grafting density, molecular weight, thickness, and composition. Namely, those parameters dictate overall switching/responsive performance of the brush.[23] Thus, availability of the reasonably universal surface modification methods that offer opportunity to alter the parameters of the brush in a wide range is important. Activation of the surface with a PGMA primary layer, in fact, offers the opportunity to carry out the grafting employing the different approaches using, however, the same initial surface modification step. In our recent study, we verified that the macromolecular anchoring layer approach allowed fabrication of the mixed polymer brushes by grafting to and grafting from methods and their combination. Figures 1 and 2 display morphology of the several mixed brushes synthesized. The brushes demonstrated pronounced tendencies to lateral and layered phase segregation. Rinsing the synthesized brushes in selective solvents and observing the change in water contact angle as a function of the grafted layer composition and solvent treatment showed the switching nature of the surface.

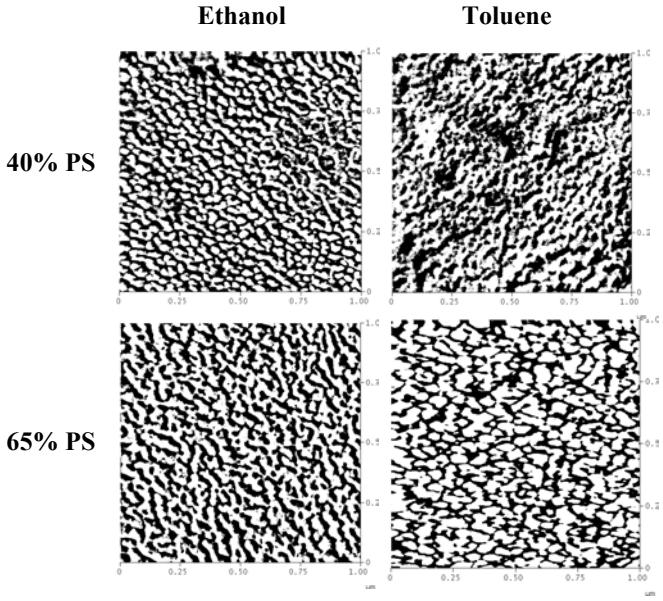

Figure 1. SPM phase images of polystyrene/poly(2-vinyl pyridine) mixed brush after treatment with different solvents. The brush fabricated by the grafting to technique. Image dimension 1x1 μm. Vertical scale 3 degree.

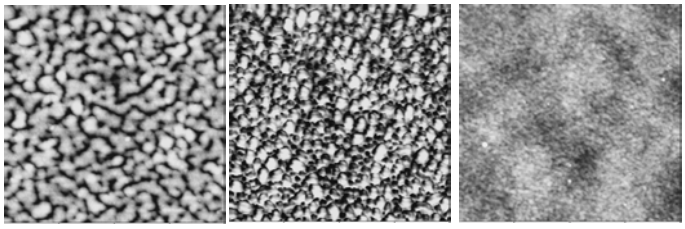

Figure 2. SPM topography images of mixed polystyrene/polyacrylic acid brushes treated with different solvent. From left to right: benzene-THF- ethanol. The brush fabricated by the grafting to/grafting from combination. 72% polystyrene content. Image dimension 1x1 μm. Vertical scale 10 nm.

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