Mixed Polymer Layers by "Grafting to"/"Grafting from " Combination

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INTRODUCTION

Living/controlled Atom Transfer Radical Polymerization (ATRP) is novel and one of the most advanced technique for synthesis of well defined polymers.[1] If initiator of ATRP is attached to substrate surface, polymer chains covalently bonded to the solid substrate can be obtained.[2-4] Such end-grafted macromolecules are forming polymer brushes at high grafting densities. The brushes are important for modification of material's surface properties that continue to be of remarkable interest in various aspects of material science and engineering.[5]

When typical homopolymer brushes are synthesized, only one polymer material is grafted to the surface to target some specific property such as wettability, colloidal stability, adhesion, friction, biocompatibility, conductivity or adsorptivity. However, further advance in polymer films imposes requirements for the surface and interfacial modifications that frequently are in conflict: a given material, depending on the conditions under which it is utilized, has to have adhesion to different surfaces, has to be hydrophobic or hydrophilic, conductive or nonconductive, deliver or adsorb some species, etc. An effective means to build an adaptive polymer layer is fabrication of a hybrid (mixed) polymer brush by combination in one grafted layer polymers of different nature. In the present communication, we describe synthesis of mixed polymer brushes prepared by "grafting to"/"grafting from" (ATRP) combination.

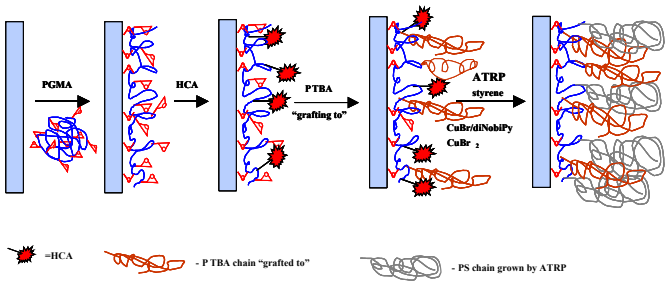
EXPERIMENTAL

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. Monomers (obtained from Aldrich) were purified by treatment with inhibitor removing sorbent and vacuum distillation. Glycidylmethacrylate was polymerized radically to give poly(glycidyl methacrylate) (PGMA), M_n=84,000, PDI=3.4. Copper(I) bromide (CuBr), copper(II) bromide ($CuBr_2$), 4,4'-dinonyl-2,2'-dipyphyridyl (di-No-di-Py), and 2-bromoisobutyric acid (BiBA) were obtained from Aldrich and used as received. PGMA ultrathin films (1-10 nm) were deposited on the surface by deep coating or absorption from solution. Resulting PGMA layers were treated with vapor of BiBA in argon at 110 ^{0}C and then washed with ethanol. The synthesized macroinitiator was dip coated with film of carboxy terminated poly(tert-butylacrylate) (PTBA) possessing M_w = 40000 g/mole (Polymer Source Inc., Canada). PTBA was melt grafted to the PGMA layer for 12 hrs at 130^{0}C. Ungrafted PTBA was removed by multiple rinsing with THF, including sonication. Thickness of the PTBA layer was within 12-20 nm. ATRP of styrene initiated from the surface was carried out at 110 ^{0}C. Ungrafted PS was removed by multiple washing with toluene including washing in an ultrasonic bath. PTBA hydrolysis to polyacrylic acid was performed in benzene solution of p-toluenesulfonic acid. The brushes were characterized with COMPEL Automatic Ellipsometer (InOm Tech, Inc.) and Scanning Probe Microscope 3100 (Digital Instruments, Inc.).

RESULTS AND DISCUSSION

The silicon wafers covered with the adsorbed PGMA layers were vigorously rinsed by series of highly polar solvents including DMSO and THF. It was found that the layer could not be removed from the substrate after the vigorous solvent treatment. The result suggested that the epoxy groups of the polymer chemically anchored the PGMA to the surface.[6]

Attachment of the BiBA molecules to the surface covered with the PGMA film was conducted from gaseous phase (**Scheme 1**). It was observed that, measured by ellipsometry, thickness of the PGMA layer increased in 1.3-1.6 times after the BiBA treatment. It indicated attachment of significant amount of the substance. The reaction between the epoxy groups and carboxyl functionalities of the halogen acid led to 2-bromoisobutyric esters derivatives of the PGMA. Next, the synthesis of the PTBA brush was carried out by the "grafting to" method. The PTBA melt grafting buried the ATRP initiator under the polymer brush of significant thickness – 12-20 nm (**Scheme 1**). To complete the fabrication of the mixed brush, ATRP of styrene initiated by the PGMA/BiBA macroinitiator was carried out.



Scheme1. Preparation of the mixed polymer brushes. HCA - halogen carboxy acid.

Figure 1 presents kinetics of ATRP polymerization through PTBA polymer brush in comparison with free, non-screened, macroinitiator surface. Two regimes of polymerization can be distinguished. Initially polymerization in both cases goes in the controlled manner. Screening of the initiator by PTBA polymer brush significantly decreases the reaction rate, but it does not prevent the polymerization completely. At some point, self-initiating of styrene leads to consumption of the terminating agent ($CuBr_2$) and the polymerization proceeds in the uncontrolled manner. The thickness of polymer film rises drastically. It is accompanied by formation of high molecular weight polymer in bulk (M_w>200000 g/mole; PDI>2). Formation of such polymer contradicts "living" mechanism of the process and can be explained by chain free radical polymerization.

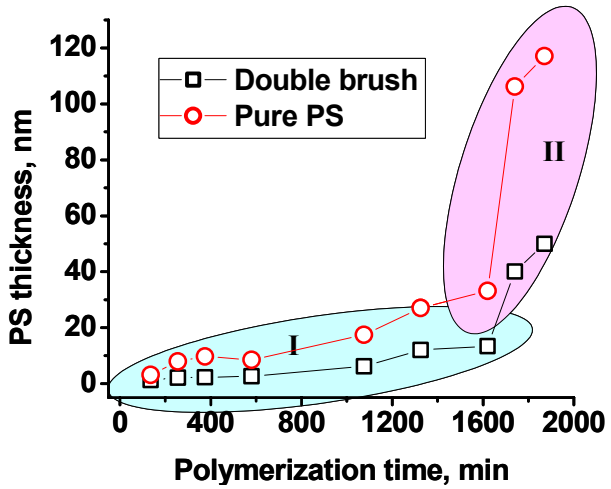


Figure 2. Kinetics of ATRP styrene grafting from free and screened with PTBA brush macroinitiator.

As a result of the developed process, the mixed polymer brushes with PTBA brush thickness 12-20 nm and PS layer 1-100 nm were obtained. Hydrolysis of PTBA to polyacrylic acid (PAA) was utilized to synthesize polymer layers possessing hydrophobic/hydrophilic properties. The brushes changed their surface morphology, when they were exposed to solvent with different polarity (**Figure 3**).

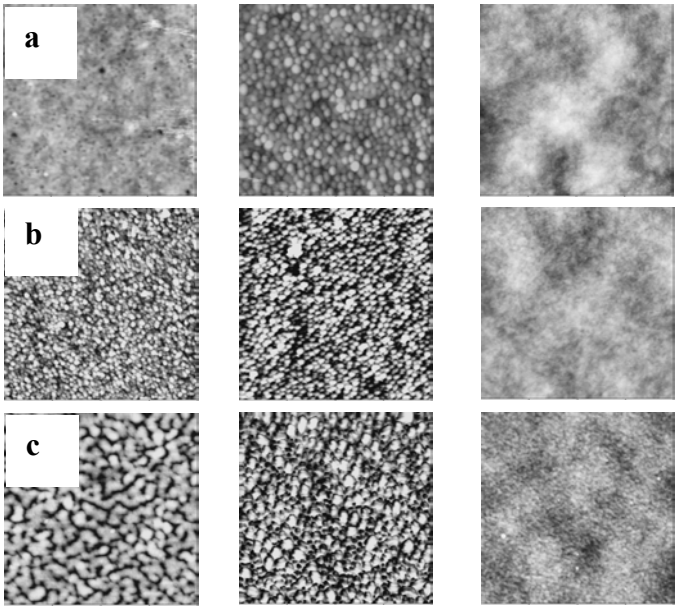


Figure 3. SPM topography images (1x1 μm) of mixed PS/PAA brushes treated with different solvent. Row: a)benzene; b)THF; c)EtOH. Thickness of PS/PAA (columns from left to right): 2.6/15; 15/15 and 40/15 nm

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