SYNTHESIS OF GRADIENT COPOLYMER BRUSHES VIA SURFACE INITIATED ATOM TRANSFER RADICAL COPOLYMERIZATION[*]

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Introduction

Immobilizing polymer brushes on surfaces provides a versatile way to alter surface properties.[1] Generally, two different methods, "grafting to"[2] and "grafting from",[3] are used to form tethered polymer brushes on surfaces. By polymerization from a self-assembled monolayer of initiator molecules on a surface, "grafting from" can often render high-density polymer brushes on that surface. Recently, free radical,[4,5] cationic,[6] anionic,[7] and ring opening metathesis polymerization[8] were all demonstrated to form polymer brushes on surfaces. Among all types of polymerization methods, atom transfer radical polymerization (ATRP) attracts significant interest for its wide range of polymerizable monomers and the comparatively simple preparation of alkyl halide initiator-functionalized surfaces.[9]

To form "smart" surfaces, amphiphilic block copolymers are often used to modify a substrate. Selective solvent treatment exposes the miscible chain segments at the surface.[10] As a result, the surface properties can be tuned from one polymer segment to the other. This switching can also change the surface morphology, leading to a nano-structured topology on the surface.[10]

Unlike block copolymers, which possess an abrupt change of composition, the composition of gradient copolymers gradually changes from one end of the polymer chain to the other. Therefore, gradient copolymers have distinct properties.[9] In this work, we report the synthesis of gradient copolymer brushes with surface initiated ATRP of methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA).

Experimental

Certain commercial equipment, instruments or materials are identified in this article to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment are the best available for the purpose.

Materials and Characterization. Deionized H_2O was obtained through a Barnstead EASYpure system. Copper bromide (CuBr, Aldrich) was purified by subsequent washing with glacial acetic acid, absolute ethanol and acetone. For MMA (Aldrich), the inhibitor was removed by passing through a column (DHR-4, Scientific Polymer Products, Inc.). The initiator, 11-(2-bromo-2-methyl)propionyloxyundecenyltrichlorosilane, was synthesized according to the literature procedure.[5] HEMA (Polysciences), bipyridine (Aldrich, 99%) and methanol were used as received. Polymer brush thickness was measured using a J. A. Woollam Co. Inc. VASE. Surface contact angle was measured using a Krüss G2 contact angle instrument.

Synthesis of initiator modified silicon surface. A silicon wafer (1 cm × 3 cm) was rinsed with acetone, treated with UV-Ozone for 30 min, and quickly immersed into an initiator toluene solution overnight. Following rinsing with toluene and acetone, the initiator modified substrate was dried under a flow of nitrogen.

Synthesis of MMA-grad-HEMA brushes on surface. To synthesize gradient copolymer brushes on the surface, we first prepared two solutions. One solution (A) had MMA as the monomer and the other (B) had HEMA. For both solutions, bipyridine (250 mg) and CuBr (114 mg) were added to a flask fitted with a rubber septum. Each flask then underwent three cycles of evacuation and backfilling with argon, followed by addition of degassed H_2O (1.6 mL), methanol (6.4 mL), and monomer (8 mL), the reaction mixtures were stirred at room temperature for 1 h.
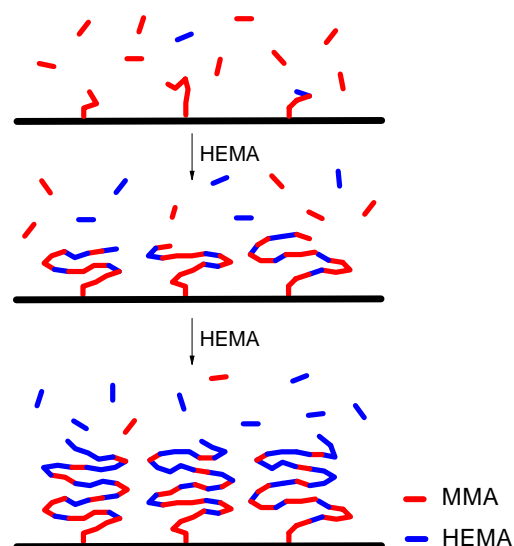
Scheme 1

An initiator modified silicon wafer was placed in a vial capped with a septum. After the vial was degassed, 5 mL of solution A was quickly injected into the vial. At the same time, solution B was slowly pumped into the vial at a rate of 100μL/min with constant stirring. At fixed intervals, the introduction of HEMA was ceased. The wafer was immediately taken out and thoroughly rinsed with DMF and methanol, followed by characterization of film thickness and surface water contact angle measurements.

Results and Discussion

As shown in Scheme 1, initially, the only monomer accessible to the surface tethered initiator is MMA. As the HEMA solution enters the reaction vial, the concentration of HEMA increases while the concentration of MMA decreases (Figure 1). As a result, the polymer will be MMA-rich at the early stage of polymerization and will become increasingly HEMA-rich as polymerization progresses.
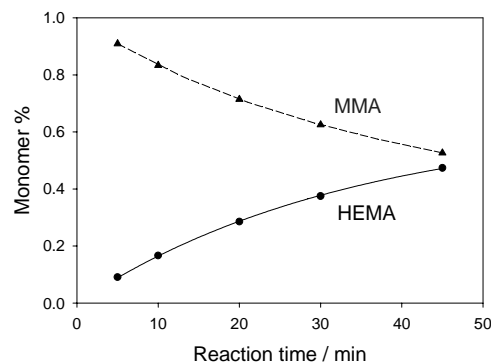

Figure 1. Calculated evolution of monomer composition in the polymerization mixture, initial MMA solution volume is 5mL, the addition rate of HEMA solution is 100μL/min ▲ MMA, ● HEMA

To form a gradient copolymer, it is essential that the polymerization be living. Unlike solution ATRP, due to the extremely small amount of initiator on the surface relative to the solution concentration of monomer and catalyst, surface initiated ATRP often has less or even no controllability. By taking the silicon wafer out of the polymerization mixture at different polymerization intervals, we were able to analyze how the polymer brushes grow as a function of time. As shown in Figure 2, despite the change in monomer composition throughout the course of the polymerization, a linear increase of polymer brush thickness was observed. This result suggests that the

polymerization is controlled and the majority of surface-tethered propagating chain-ends remain active under our experimental conditions.
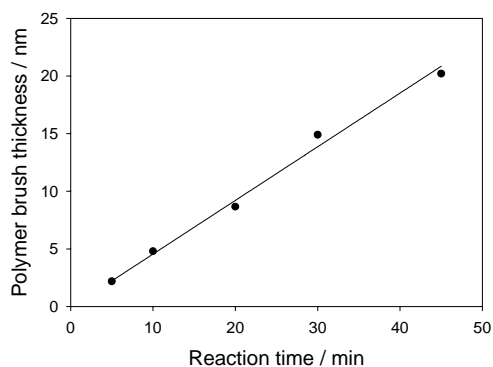

Figure 2. Thickness of gradient copolymer brushes during the course of polymerization. Two standard deviations in this data is ± 1nm

The formation of gradient copolymer brushes was also evidenced by contact angle measurements. The surface contact angles are 70 for MMA and 48 for HEMA modified surfaces. For MMA and HEMA copolymers, we expected the surface would become more hydrophilic and that surface contact angle would decrease with decreasing MMA composition. Figure 3 shows the result of contact angle measurements of samples taken out at different polymerization times. As anticipated, larger contact angles were observed for samples at early polymerization times. For example, after 5min of reaction, the monomer mixture contains only 8 mol% HEMA. The contact angle for this sample is 65, which is close to that of MMA. After 45 min, the HEMA concentration has reached 44 mol% and the contact angle of this sample is 48, identical with pure poly-HEMA brushes previously synthesized. Thus, the change in contact angle clearly reveals that the surfaces are more hydrophilic and have higher HEMA composition for samples with longer polymerization times.
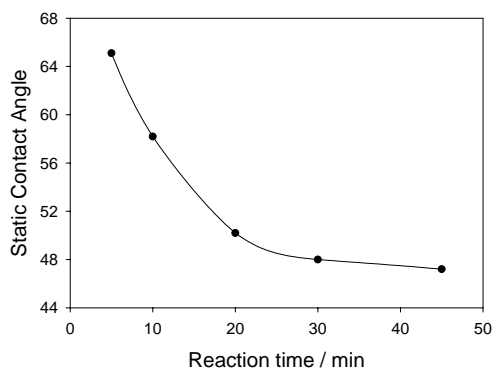

Figure 3. Contact angle of gradient copolymer brushes as a function of action time as it relates to HEMA content under the experimental conditions. Two standard deviations in this data is ± 2

Conclusions

In summary, by gradually adding HEMA monomer into the polymerization mixture, we successfully synthesized tethered poly-MMA-*grad*-HEMA brushes with surface initiated atom transfer radical polymerization. The gradual increase of HEMA composition on the surface with extended polymerization time is supported by our contact angle measurement results. A linear growth behavior, as determined by ellipsometry, up to 25 nm thickness was observed for the polymerizations.

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