

# Synthesis and Characterization of Tapered Copolymer Brushes via Surface-Initiated Atom Transfer Radical Copolymerization

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Tapered copolymer brushes of methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) were synthesized via surface-initiated atom transfer radical polymerization (ATRP) by gradual addition of HEMA to a reaction mixture that originally only had MMA as monomer. The copolymer brush grew linearly with polymerization time. The tapered copolymer brushes responded to selective solvent treatments. For the same tapered copolymer brush, pretreating the surface with methylene chloride made the surface more hydrophobic; pretreating the surface with methanol increased the surface hydrophilicity. This change in surface properties was reversible and considered to be caused by the solvent induced rearrangement of the polymer brushes, which is supported by atomic force microscopy images of the surface. Our work demonstrates that the properties of the tapered copolymer brush could be finely tuned by careful control of the composition profile.

## Introduction

Tethering surfaces with polymer brushes provides a versatile method for tailoring surface properties such as wettability,<sup>1</sup> friction,<sup>2</sup> and protein/cell adhesion.<sup>3</sup> Polymerization from initiator moieties anchored on surfaces, surface-initiated polymerization, can provide high-density polymer brushes on surfaces. Different polymerization strategies, such as free radical,<sup>4,5</sup> cationic,<sup>6</sup> anionic,<sup>7</sup> and ring opening metathesis polymerization,<sup>8</sup> have been applied to form polymer brushes on surfaces. Among all types of polymerization methods, atom transfer radical polymerization (ATRP) attracts significant interest for its living/controlled character, tolerance of functional groups, and mild experimental conditions.<sup>9,10</sup>

Recently, a variety of applications of copolymer brushes were demonstrated. For example, statistical copolymer

brushes of styrene and methyl methacrylate were utilized to control domain orientation in thin block copolymer films on surfaces.<sup>11</sup> In addition, block copolymer brushes were exploited to synthesize responsive surfaces. Selective solvent treatment preferentially expressed polymer segments favored by the solvent at the surface. Therefore, the surface properties could be switched from one component of the copolymer to the other upon different solvent treatments.<sup>12,13</sup> This switching also changed the surface morphology, leading to the formation of a nano-structured surface.<sup>14–18</sup>

The properties of a copolymer are influenced by the distribution of comonomers in the chain. Tapered/gradient copolymers are the class of copolymers that have gradual composition variations from one end of the polymer chain to the other.<sup>19</sup> This architecture imparts tapered copolymers with unique behavior in thermal transitions, phase separation, and aggregation in solution.<sup>20–23</sup> Tapered copolymers were also used to stabilize polymer blends during melt processing.<sup>24–26</sup>

In this work, we report the synthesis and characterization of surface-immobilized tapered copolymer brushes of methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) (poly-MMA-*tap*-HEMA) via surface-

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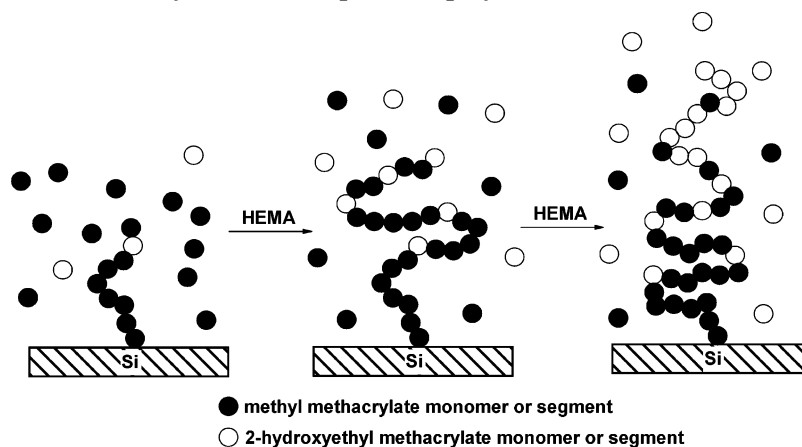
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Scheme 1. Synthesis of Tapered Copolymer Brushes on a Surface



initiated ATRP. To synthesize the tapered copolymer brushes, the monomer composition inside the reaction flask was adjusted by gradual addition of HEMA to a polymerization solution that only contained MMA as monomer. The kinetics of polymer brush growth was monitored by ellipsometric measurement of film thickness. The resulting polymer brushes were tested for their solvent response behavior, which was characterized by surface static water contact angle ( $\theta_w$ ) measurement and atomic force microscopy (AFM).

### Experimental Section<sup>27</sup>

**Materials and Characterization.** Deionized H<sub>2</sub>O ( $\rho \geq 18.2$  M $\Omega$ -cm) was obtained from a Barnstead EASYpure system. The initiator, 11-(2-bromo-2-methyl)propionyloxyundecyltrichlorosilane, was synthesized according to the literature procedure.<sup>5</sup> 2-Hydroxyethyl methacrylate (HEMA, ophthalmic grade) was ordered from Polysciences. All other chemicals were purchased from Aldrich and used as received unless otherwise specified. Inhibitor was removed from methyl methacrylate (MMA) through a DHR-4 column (Scientific Polymer Products Inc.). A BS-8000 programmable syringe pump (Braintree Scientific, Inc.) was used to control the injection rate of the reaction mixture.

**Synthesis of Initiator Modified Silicon Surface.** A fresh cut silicon wafer (1 cm  $\times$  3 cm) was first rinsed with acetone, dried, and treated with ultraviolet-ozone for 30 min. The wafer was quickly immersed into an initiator toluene solution (0.5 mmol/L) and kept overnight. After thorough rinsing with toluene and acetone, the initiator-modified substrate was dried under a flow of nitrogen.

**Synthesis of poly-MMA-*tap*-HEMA Brushes on Surface.** To synthesize tapered copolymer brushes on the surface, two solutions were prepared. One solution (A) had MMA as the monomer, and the other (B) had HEMA. For both solutions, 2,2'-bipyridine (250 mg) and CuBr (114 mg) were added to a flask, which was sealed with a rubber septum. Each flask then underwent three cycles of evacuation and backfilling with argon,

followed by addition of degassed H<sub>2</sub>O (1.6 mL), methanol (6.4 mL), and monomer (8 mL). The reaction mixtures were stirred at room temperature for 1 h to ensure complete dissolution of the catalyst. A separate flask containing the initiator-modified silicon wafer was capped with a septum. After the flask was degassed, 5 mL of solution A was quickly injected into the flask. At the same time, solution B was pumped into the vial at a rate of 100  $\mu$ L/min using a syringe pump with constant stirring of the mixture. After a certain period of reaction time, the introduction of HEMA was ceased and the wafer was removed from the reaction vial, thoroughly rinsed with DMF and ethanol, and dried under a flow of nitrogen.

**Solvent Treatment of the Surface.** The polymer brushes were subject to the solvent treatment of methanol or methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>). Mixtures of these two solvents were prepared to assist the rearrangement of the polymer chains during the solvent treatment. For example, after methanol treatment, the slide was sequentially immersed in a solution containing 20 vol %, 50 vol %, and 80 vol % CH<sub>2</sub>Cl<sub>2</sub> before it was immersed in CH<sub>2</sub>Cl<sub>2</sub>. For each solvent treatment, the substrate was immersed in the solvent for 60 min and then taken out of the solution and dried under a flow of nitrogen.

**Characterization Methods.** Polymer brush thickness was measured using a J. A. Woollam Co. Inc. VASE ellipsometer. Surface water contact angle ( $\theta_w$ ) measurement was carried out with a Krüss G2 contact angle goniometer. The standard uncertainties for the ellipsometry and  $\theta_w$  measurement are 0.2 nm and 2°, respectively. Tapping mode atomic force microscopy (AFM) images were collected on a Dimension 3100 system (Veeco Instruments).

### Results and Discussion

**Synthesis and Characterization of Homo- and Copolymer Brushes.** Aqueous ATRP, as demonstrated by Baker et al.<sup>28</sup> and Huck et al.,<sup>29</sup> provides a facile route to synthesize thick polymer brushes from initiator-modified surfaces. In this work, the same conditions utilized by Huck et al. for MMA polymerization were adopted and expanded to synthesize tapered copolymer brushes. MMA and HEMA were selected as monomers. To form tapered copolymer brushes, it is necessary that the relative incorporation of the monomers into polymer chains gradually change throughout the polymerization process. For this purpose, one monomer (HEMA) solution was gradually added to a polymerization solution of the other (MMA) at a controlled rate (Scheme 1). In our approach, the polymer only grows from the extremely small amount of initiator sites tethered on surfaces, so the amount of monomer consumed is negligible during the polymerization. Therefore, the relative concentration of monomers

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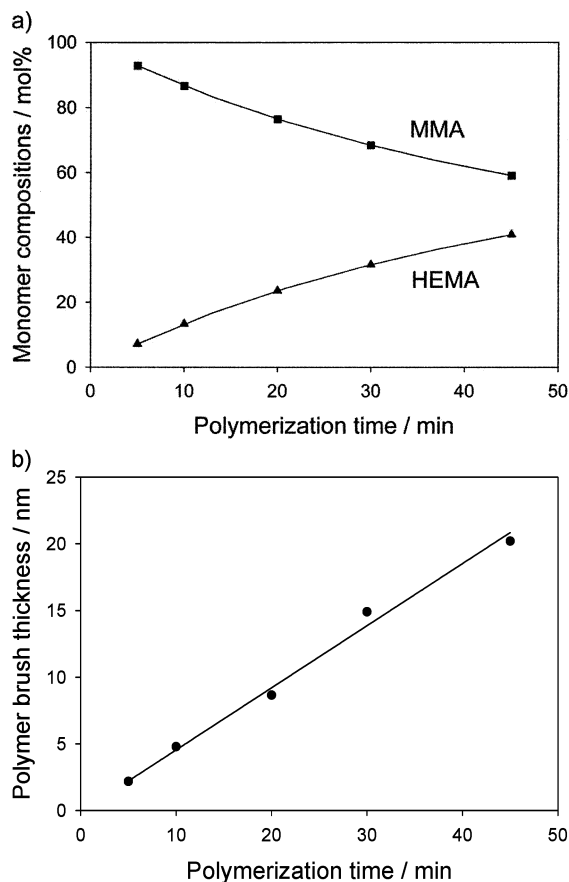
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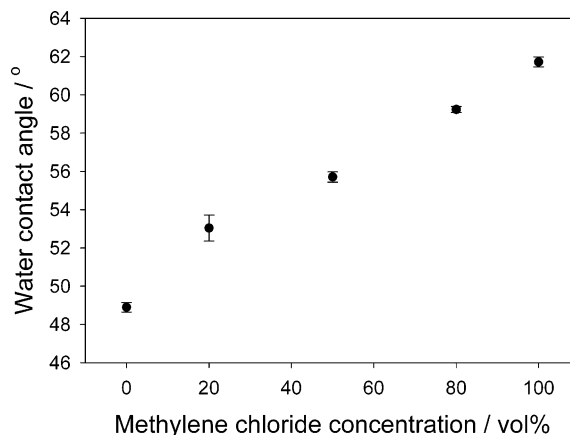


**Figure 1.** Synthesis of tapered copolymer brushes from surface. (a) Calculated monomer molar percentage through the course of polymerization. ■: methyl methacrylate, ▲: 2-hydroxyethyl methacrylate. (b) Growth of tapered copolymer brushes on surface.

in solution at any given polymerization time can be determined from the feed ratio of the monomers.

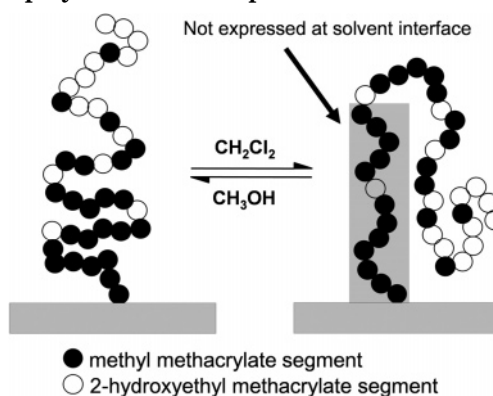
Figure 1 shows the changes of monomer molar percentages in solution as a function of polymerization time. Initially, the only monomer exposed to the surface-tethered initiators was MMA. As the HEMA solution was gradually introduced into the reaction mixture, the concentration of HEMA increased, whereas the concentration of MMA decreased (Figure 1a). Hence, the concentration of individual monomer can be adjusted without disturbing other polymerization conditions. To form a tapered copolymer, it is essential that the polymerization is living/controlled.<sup>9</sup> Removal of the silicon substrate from the polymerization mixture after different periods of polymerization time allowed determination of how the copolymer brushes grew during the polymerization process. As shown in Figure 1b, despite the gradual change in monomer composition, a nearly linear increase in polymer brush thickness with polymerization time was observed. This result indicated that the polymerization was controlled and most of the surface-tethered propagating chain-ends remain active throughout the course of polymerization.

At any given reaction time, the composition of the polymer brushes should reflect the monomer composition history through the polymerization process and the reactivity ratios of the monomer pair. In the current case, the instantaneous polymer composition should be enriched in HEMA relative to the monomer feed ratio because the reactivity ratios indicate favorable HEMA addition over MMA.<sup>30</sup> This would determine that chain segments formed at late stages of polymerization would be higher in HEMA content than the feed ratio would suggest.



**Figure 2.** Static water contact angle measurement of the tapered copolymer brush that is synthesized after 30 min polymerization. The surface is treated with methanol, methylene chloride or their mixture. Error bars represent standard uncertainty of six repeated measurements.

### Scheme 2. Proposed Rearrangement of Tapered Copolymer Brushes upon Solvent Treatment



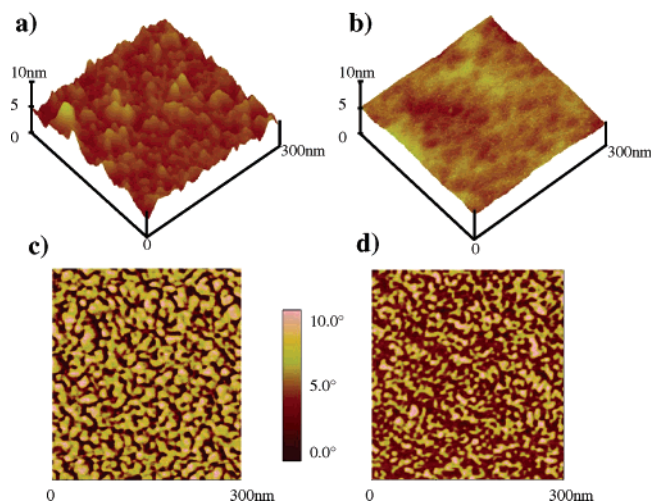
**Solvent Response of Tapered Copolymer Brushes.** Similar to block copolymer brushes, due to the composition variation along the polymer chains, tapered copolymer brushes should respond to selective solvent treatment. Two solvents, CH<sub>2</sub>Cl<sub>2</sub> and methanol, were chosen to treat the tapered copolymer brushes. While HEMA swells preferentially in methanol, MMA swells preferentially in CH<sub>2</sub>Cl<sub>2</sub>.

Static  $\theta_w$  measurement was used to assess the surface composition changes of the polymer brushes due to solvent response. For homopolymer brushes synthesized with the same procedure, the static  $\theta_w$  measured are 70° for PMMA and 46° for PHEMA. Treating the copolymer brushes with a mixed solvent of CH<sub>2</sub>Cl<sub>2</sub> and methanol clearly revealed that the surface  $\theta_w$  went up with increasing CH<sub>2</sub>Cl<sub>2</sub> concentration (Figure 2). The change of surface wetting properties was reversible, as reproducible  $\theta_w$  values were observed through several cycles of solvent treatment. We attributed the change of surface wetting properties to the rearrangement of polymer brushes (Scheme 2). When the surface is treated with CH<sub>2</sub>Cl<sub>2</sub>, the MMA-rich segments of the polymer chains would swell and segregate to the solvent interface while HEMA-rich segments would collapse and bury themselves into the polymer film to reduce interaction with the solvent.

**AFM Measurement of Surface after Solvent Treatments.** Tapping mode AFM measurements of the sample after 30 min polymerization support the postulation of

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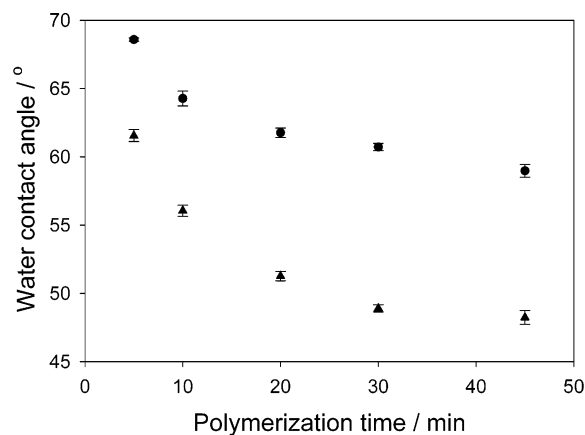




**Figure 3.** Atomic force images of tapered copolymer brushes with 30 min polymerization time after selective solvent treatment. (a) Three-dimensional view of topographic image after methanol treatment. (b) Three-dimensional view of topographic image after methylene chloride treatment. (c) Phase image of the sample after methanol treatment. (d) Phase image of the sample after methylene chloride treatment. The RMS roughness for image (a) and (b) are 1.1 and 0.23 nm, respectively.

segment rearrangement in tapered copolymer brushes during solvent treatment. As shown in Figure 3, after methanol treatment, a rough surface was observed (Figure 3a); after  $\text{CH}_2\text{Cl}_2$  treatment, the surface became smoother (Figure 3b). Moreover, phase imaging of the sample suggests a surface composition change after solvent treatments. After methanol treatment, the phase image was dominated by bright regions (Figure 3c); after  $\text{CH}_2\text{Cl}_2$  treatment, the phase image was almost evenly occupied by the dark and bright regions (Figure 3d). After methanol treatment, higher regions in the topography image were correlated with the bright area in the phase image. In contrast, after  $\text{CH}_2\text{Cl}_2$  treatment, high regions in the topography image appeared dark in the phase image. We hypothesize that brighter regions in phase image represent areas richer in the more polar HEMA while darker regions in phase image represent areas richer in MMA. Therefore, after methanol treatment, most of the surface was rich in HEMA composition. After  $\text{CH}_2\text{Cl}_2$  treatment, the MMA rich segments moved to the surface, increasing the surface  $\theta_w$ .

**Solvent Response Behavior Comparison among Tapered Copolymer Brushes.** With increased polymerization time, the surfaces of the tapered copolymer brushes are expected to become more hydrophilic and the  $\theta_w$  would decrease as the copolymer becomes HEMA-rich. Figure 4 shows the  $\theta_w$  measurement results of samples removed from the reaction mixtures after different periods of polymerization time.  $\theta_w$  of each substrate was measured after both methanol and  $\text{CH}_2\text{Cl}_2$  treatments. In all cases, the  $\theta_w$  fell between that of PMMA and PHEMA homopolymer brushes. For each tapered copolymer brush, higher  $\theta_w$  was recorded after  $\text{CH}_2\text{Cl}_2$  treatment than after methanol treatment. As anticipated, higher contact angles were observed for samples with shorter polymerization times after the same solvent treatment. For example, after 5 min of reaction, the polymerization mixture contains only 8 mol % HEMA. The sample taken out at this time has  $\theta_w$  of  $62^\circ$  after methanol treatment and  $68^\circ$  after  $\text{CH}_2\text{Cl}_2$  treatment. After 45 min, the HEMA concentration in the polymerization flask reached 44 mol % and the  $\theta_w$  of the sample taken out at this time are  $48^\circ$  after methanol treatment  $59^\circ$  after  $\text{CH}_2\text{Cl}_2$  treatment. These changes in



**Figure 4.** Water contact angle comparison of tapered copolymer brushes with different periods of polymerization time after methanol treatment (▲) and after methylene chloride treatment (●). Error bars represent standard uncertainty of six repeated measurements.

$\theta_w$  clearly reveal that the surfaces with longer polymerization time are more hydrophilic and contain higher HEMA composition. This result further confirmed that the copolymer brushes synthesized were tapered copolymer brushes that have a MMA-rich bottom layer and become progressively HEMA-rich as the polymer chains extended from the surface.

It is also worth noting that the  $\theta_w$  of the tapered copolymer brushes does not reach the value of pure PMMA after  $\text{CH}_2\text{Cl}_2$  treatment (Figure 4). Instead, it decreases with increasing brush thickness (or increasing HEMA content). After  $\text{CH}_2\text{Cl}_2$  treatment, the bottom MMA rich segments tend to migrate to the surface. However, for any segment of the tapered copolymer chain to be expressed at the surface, it must extend from the silicon substrate enough to accommodate the rest of the chain segments. Therefore, polymer chain segments formed at the early stages of the polymerization may not be able to penetrate the overlying polymer segments, even though they are favored by the solvent. With increasing thickness of the polymer brushes, only polymer segments formed at later stages of the polymerization are able to reach the surface. As a result, for the tapered polymer brushes,  $\theta_w$  after  $\text{CH}_2\text{Cl}_2$  treatment was observed to gradually decrease with increased polymerization time.

## Conclusions

In summary, by gradually increasing the HEMA concentration in the polymerization mixture, we synthesized poly-MMA-*tap*-HEMA copolymer brushes on surfaces via surface-initiated atom transfer radical copolymerization. Polymer segments formed at the later stage of the polymerization had increased HEMA composition, which is supported by the gradual decrease in  $\theta_w$  results. Due to the gradual composition change along the polymer chains, the tapered copolymer brush formed can reversibly respond to selective solvent treatment. Treating the tapered copolymer brush with  $\text{CH}_2\text{Cl}_2$ , a good solvent for PMMA, can bring MMA-rich segments to the surface and increase  $\theta_w$ . Treating the surface with methanol, a better solvent for PHEMA, can bring HEMA-rich segments to surface and reduce  $\theta_w$ . This rearrangement of the tapered copolymer brushes was also supported by AFM results. The formation of tapered copolymer brushes on a surface provides a one-pot synthesis method to fabricate surfaces with switchable properties, which can be readily tuned by adjusting the composition profile of the tethered polymer chains.

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