Microchannel Confined Surface-Initiated Polymerization

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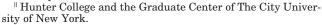
Surface-initiated polymerization is an attractive method used with increasing frequency to modify surfaces with grafted polymer brushes.^{1–8} Among many types of polymerization techniques available, atom transfer radical polymerization (ATRP)^{9–11} is of special interest because it is versatile, robust, and well controlled and possesses a living nature. The use of grafted polymer to control surface chemistry has become so appealing^{12–14} that research to understand the behavior of tethered chains at interfaces has become extensive. Recently, combinatorial methods have been demonstrated as tools to better understand the effects of graft density^{15,16} and molecular weight^{17,18} on polymer brush surfaces.

Use of microchannels as unique reaction environments has also become increasingly popular.^{19,20} In microchannels, only small volumes of reagents are necessary and the solutions can be manipulated rapidly into or out of the channels. Microchannels can also be used to impose certain lateral control of the reaction mixture within the channel depending on the flow conditions and fluid dynamics. Laminar flow inside microchannels has enabled spatial control of reaction mixtures, enabling microfabrication of structures much smaller than the width of the channel.²¹

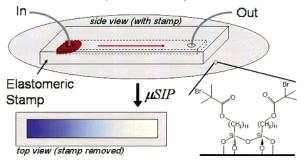
While ATRP in microchannels has been carried out previously to provide uniform coverage of surfaces,²² we are unaware of any use of the unique environment of microchannels to manipulate monomer/catalyst solutions on a flat surface and produce gradient and patterned specimen for further investigating the physical behavior of polymer brush layers. In this work, we report a microchannel-confined surface-initiated polymerization (μ SIP) technique. A microchannel is formed by placing a patterned poly(dimethylsiloxane) (PDMS) stamp onto an initiator-functionalized self-assembled monolayer on a silicon wafer (Scheme 1). A typical channel for demonstration was 300 μ m high by 8 mm wide by 4.5 cm long. After the channel was placed in a

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Scheme 1. Microchannel Confined Surface-Initiated Polymerization (µSIP)



sealed tank and flushed with argon, the polymerization solution was introduced into the channel from one end at a controlled rate. Because of its fast growth rate and reasonable control at room temperature, aqueous ATRP of 2-hydroxyethyl methacrylate (HEMA) was chosen as a model system to demonstrate the versatility of this technique.²³

To study the kinetics of brush growth on the surface, a solution with constant concentration of monomer and catalyst was gradually pumped into the channel at a fixed rate from the inlet, located at one end of the channel. After the reaction mixture reaches the outlet, the PDMS stamp was quickly removed and the silicon substrate was thoroughly rinsed with N,N-dimethylformamide (DMF). As a result, different regions on the surface have different polymerization times, which are directly proportional to the distance from the outlet and equal to the time of surface exposure to the monomer solution. Ellipsometry data taken along the length of the final specimen show that the thickness of the polymer brush increases linearly with the distance from the outlet (Figure 1a) and polymerization time (Figure 1b). By slowing down filling rate and thus the solution front advancing rate inside the channel, we were also able to generate polymer brushes with a steeper thickness gradient on the surface. The slope of the thickness gradient can be tuned, therefore, by adjusting the filling rate of the reaction mixture. As shown in Figure 1b, the thickness of the film as a function of exposure time is independent of the filling rate of the reaction mixture. Atomic force microscope images of the surfaces, confirming local coverage and uniformity of the resultant polymer layer are available in the Supporting Information. The entire region of the silicon wafer exposed to the monomer/catalyst solution was covered with grafted polymer.

During μ SIP, the initiator-functionalized regions are either exposed to the reaction mixture or in contact with PDMS. To evaluate the polymerization behavior of the surface after contact with PDMS and the reinitiation efficiency of the grafted layer, a channel was placed on the surface and quickly filled with the polymerization mixture. After 60 min of polymerization, the first PDMS stamp was removed and the surface was rinsed with DMF. The channel was then reapplied to the surface, but with its position shifted, such that the newly formed channel now covered part of the area that was previously in contact with the PDMS and part of the area that was inside the previous channel. Then the channel was again filled with the reaction mixture for 30 min.

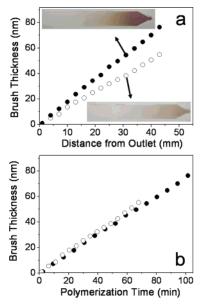


Figure 1. Kinetics of poly(2-hydroxyethyl methacrylate) brush growth with microchannel confined surface-initiated polymerization (μ SIP) and the formation of a gradient polymer brush on a surface: (a) profile of thickness across the gradient (insets are digital images of the gradient films); (b) brush thickness as a function of time as determined by the exposure time to the monomer/catalyst solution. Solution front advancing rate: $\bullet = 0.423$ mm/min; $\bigcirc = 0.634$ mm/min. Two standard deviations in the ellipsometry measurements are ± 1 Å.



Figure 2. Consecutive microchannel confined surface-initiated polymerization (μ SIP) on surface. The first channel includes region A and B, polymerization for 60 min. The second channel includes region B and C, polymerization for 30 min. Polymer brush thicknesses in regions A, B, and C are 43, 65, and 24 nm respectively.

Three distinct regions are formed as a result of these two consecutive polymerizations (Figure 2). Region A was exposed during the first polymerization and subsequently covered by PDMS during the second, while region B was exposed for both polymerizations, and region C was first covered by the PDMS and then exposed inside the second channel. Thus, the net polymerization times for regions A, B, and C were 60, 90, and 30 min, respectively. From ellipsometry measurements, the resulting thickness of the polymer brushes formed in regions A, B, and C were 43, 65, and 24 nm, respectively. Thus, it is clear that the surface covered by the PDMS stamp retains its initiating capacity.

This result suggests that multiple polymer brushes and/or multilayer copolymer brushes could be easily achieved with consecutive μ SIP steps by reinitiating the polymer-functionalized surface, without multistep patterning of different initiator segments, or the use of multiple polymerization chemistries, which may limit the types of polymers that can be produced.²⁴ Hence, μ SIP will enable patterning arrays of polymer brushes with a simplicity and uniformity not readily available with other techniques.

After the microchannel is filled with solution and the flow is stopped, the only mixing will be diffusive. In a channel with a gradient in composition, if the gradient is shallow enough, it is possible for the reaction to finish before any significant change in the composition profile

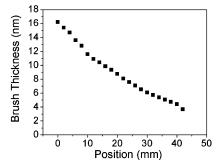


Figure 3. Influence of solvent composition on polymerization. The inlet of the channel was at 0 mm. Methanol content in the monomer/catalyst solution is highest at positions far from the inlet.

can occur (simple diffusion estimation provided in Supporting Information). Thus, by analyzing the tethered polymer brushes on the surface, we can continuously study the influence of a solution composition gradient on surface-initiated polymerization.

To this end, we employed μ SIP to investigate how the addition of methanol affects the polymerization throughout the channel. For ATRP of HEMA, it is known that the addition of methanol to the reaction mixture will reduce the polymerization rate.²⁴ Here two polymerization solutions were prepared. The only difference between these two solutions is that one (A) had methanol/ water (50/50 by volume) as the solvent and the other (B) had water as the solvent. Solution was added by first pumping solution A into the channel. Then the pumping rate of solution A was gradually decreased while the pumping rate of solution B was simultaneously increased. Through the course of infusion, the overall infusion rate was kept constant; however, the channel was filled quickly in this case (less than 2 min), such that the difference in exposure time along the channel was no longer a factor in the experiment and polymerization time was assumed to be uniform across the surface. Before the mixture entered the channel, it passed through a microstirrer to ensure complete mixing of the solutions. Before the experiment, the volume of the solution required to fill up the channel was calculated and the pumping rate of the two pumps was programmed so that a linear methanol concentration gradient was established from one end of the channel to the other and the flow was stopped before any solution could be flushed from the channel.

Figure 3 shows the result after 25 min of polymerization. The thickness of the polymer brush decreased from the channel end rich in water to the end enriched with methanol (50/50 v/v). Therefore, with a single μ SIP experiment, we confirmed that the substitution of methanol to water in the polymerization solution does slow the growth rate of polymer brushes from a surface and show that a concentration gradient within the solution can be trapped such that local regions of the surface are exposed to different polymerization solutions. It is precisely the ability to trap the solution as a gradient that remains a challenge using existing techniques and makes μ SIP unique.

In summary, surface-initiated atom transfer radical polymerization can be carried out inside microchannels to produce flat gradient and patterned surfaces. Compared with regular surface-initiated polymerization in a flask, μ SIP has several advantages: (1) As the microchannel height is only 300 μ m, only a small

amount of solution is necessary for the polymerization. (2) Since the flat surface in contact with the PDMS stamp retains initiating capacity, μ SIP can be used to pattern the surface sequentially with the same or block (co)polymer brushes. It is also possible to pattern the surface simultaneously with several brush configurations using multiple channels because the polymerization conditions can be varied from channel to channel. (3) By taking advantage of the composition gradients formed inside microchannels, it is possible to systematically investigate how the solution composition influences the formation of polymer brushes.

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Supporting Information Available: Text giving synthesis and methods as well as figures showing AFM of typical surfaces, water concentration profiles, and simple diffusion estimates. This material is available free of charge via the Internet at http://pubs.acs.org.

Note Added after ASAP Publication. This communication was released ASAP on 12/10/2004. Scheme 1 has been revised to include missing oxygen bonds between the silicon-silicon bonds in the chemical structure of Scheme 1. The revised version was posted on 12/15/2004.

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