GRADIENT POLYMER BRUSHES: PREPARATION AND APPLICATIONS

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Introduction
Continuous molecular gradients represent chief tools for combinatorial chemistry and materials science. These structures allow for systematic variation of one or more physico-chemical properties thus enabling multivariant exploration of the broad parameter space, improved efficiency, and lower cost. Surface confined polymer brushes represent effective design tools by which chemico-physical properties of surfaces can be tuned. Recently, techniques involving the patterning of polymer layers grafted to the substrate have been developed that utilize surface-initiated living-radical polymerizations. These technologies are based on decorating the material surfaces with monolayers of polymerization initiators and then performing the polymerization directly on the surface (“grafting from”). Here we outline our recent efforts in creating surface-grafted layers with a gradual variation of polymer grafting density and the molecular weight (or equivalently length).

Experimental
Preparation of surface initiator gradients. Molecular gradient of 1,3-bis(trichlorosilyl)-2-(m/p-chloromethylphenyl) ethane (CMPE) was prepared using the method of Chaudhury and Whitesides. In this methodology, CMPE was mixed with paraflin oil (PO) and the mixture was placed in an open container that was positioned close to an edge of a silicon wafer. As CMPE evaporated, it diffused in the vapor phase and generated a concentration gradient along the silicon substrate. Upon impinging on the substrate, the CMPE molecules were adsorbed on the substrate that do not contain the CMPE, we backfilled the unexposed regions on the substrate (containing unreacted −OH functionalities) with n-octyl trichlorosilane.

Synthesis of PAAm brushes. The polymerization of poly(acryl amide) (PAAm) was performed by atom transfer radical polymerization (ATRP), as described earlier. After the reaction, any physiosorbed monomeric and polymeric acrylamide was removed by Soxhlet extraction with deionized (DI) water for 48 hours and dried under nitrogen. In addition, PAAm brushes were grown on silica gels (Davisil™, grade 645, surface area = 300 m²/g) using the procedure outlined in Ref. 5. The PAAm polymers were grown and purified using the same conditions as described above. The PAAm chains were then cleaved from the silica support with a 10% (w/w) solution of HF for 2 hours, using the same conditions as described above. The PAAm chains were then cleaved from the silica support with a 10% (w/w) solution of HF for 2 hours, neutralized by adding sodium carbonate and filtered.

Results and Discussion
Formation of surface-anchored PAAm with grafting density gradients. Contact angle and NEXAFS experiments confirmed that the CMPE initiator formed a density-gradient on the substrate. VASE was used to measure the thickness of the dry PAAm film, h, as a function of the position on the substrate.

The data in Figure 1 reveal that h decreases gradually as one moves across the substrate starting at the CMPE edge. Note that the concentration profile of the polymer follows that of the CMPE initiator (solid line in Figure 1). Because the polymers grafted on the substrate have all roughly the same number of segments (see discussion below), the variation of the polymer film thickness can be attributed to the difference in the density, σ, of the CMPE grafting points on the substrate. The grafting density can be calculated from

σ = ρσN A/M w

where σ is the density of PAAm (=1.302 g/cm³), N A is the Avogadro’s number, and M w is the polymer molecular weight.

Figure 1. Dry (h, open squares) and wet (H, closed squares) thickness of the PAAm brush and the CMPE concentration (solid line) as a function of the position on the substrate (CMPE:PO concentration=1:1).

The wettabilities of both initiator- and polymer-covered substrates were probed using contact angle measurements (Ramé-Hart goniometer, model 100-00). We utilized near-edge x-ray absorption fine structure (NEXAFS) spectroscopy (U7A beamline at the NSLS, Brookhaven National Laboratory) to probe the concentration of the CMPE and BMPUS initiators on the substrate. Variable angle spectroscopic ellipsometry (VASE, J. A. Woollam, Co.) was used to measure the thickness of the initiator layer, and the surface-anchored polymer layers both in dry state and in solution.

Figure 2. Wet thickness of the PAAm brush (H) as a function of the PAAm brush grafting density (σ). The schematic illustrates the conformations of the surface-anchored PAAm as a function of the grafting density.
The substrates with the grafted PAAm were placed into a solution cell that was filled with DI water (pH=7), a good solvent for PAAm, and incubated for at least 5 hours. The wet thickness of grafted PAAm in DI water, \( H \), was measured using VASE. The values of \( H \) for samples prepared on CMPE:PO=1:1 gradients are shown as solid symbols in Figure 1. The data show that \( H \) decreases as one traverses across the substrate, starting at the CMPE side. Similar experiments were performed with PAAm brushes grown from gradient CMPE substrates prepared from various CMPE:PO concentrations.

In Figure 2 we plot the wet polymer thickness as a function of the PAAm grafting density on the substrate. The data in Figure 2 reveal that at low \( \sigma \), \( H \) is independent of the grafting density; hence the chains are in the mushroom regime. At higher polymer grafting densities, \( H \) increases with increasing \( \sigma \), indicating the brush behavior. The crossover between the two regimes occurs at \( \sigma=0.065 \text{ nm}^{-2} \). Fitting the data in the brush regime to \( H=\sigma n \) results in \( n \) equal to: 0.37±0.04 (CMPE:PO=1:1), 0.39±0.05 (CMPE:PO=1:2), and 0.40±0.06 (CMPE:PO=1:5). A remark has to be made about the possible variation of the chain length with grafting density. Jones and coworkers recently reported on studies of grafting from polymerization of PMMA using ATRP from substrates having various surface densities of the polymerization initiator, \( \alpha \)-mercaptoundecyl bromoisobutyrate. Their study revealed that the grafting density of the polymer depends on the grafting density of the initiator. However, based on the data presented in Ref. 10 it is uneasy to discern whether the kinetics of the polymerization also depends on the grafting density of the initiator. While we cannot exclude the possibility that the length PAAm chains polymerized on the various parts of the molecular gradient substrate varies with \( \sigma \), we note that the fact that the curves in Figure 2 superimpose on a single master curve indicates that the polymers have likely very similar lengths, which is not surprising for the rather short anchored polymers synthesized in this work.

Formation of PMMA brushes with molecular weight gradients. Poly(methyl methacrylate) with a variable degree of polymerization anchored to silica surfaces was synthesized following the room-temperature ATRP polymerization scheme described earlier. In the main part of Figure 3 we plot the variation of the dry PMMA thickness (measured by VASE) as a function of the position on the substrate. The inset depicts the variation of the same quantity but as a function of the polymerization time. The data in the inset illustrate that, as expected, the thickness increases linearly with polymerization time, in accord with previous reports. We have tested the effect of varying the solution removal speed on the polymer thickness variation. The arrows in Figure 3 mark the instances where the exhaust speed was reduced two times during the polymerization. As apparent from the data, the polymerization rate as a function of time was not affected (inset) but the “steepness” of the gradient increased correspondingly.

![Figure 3](image_url) Thickness of PMMA as a function of the position on the substrate. The inset shows the dependence of the PMMA brush length as a function of the polymerization time. The ATRP polymerization was performed at room temperature by mixing methyl methacrylate monomer (32.7 g), methanol (25.5 g), DI water (7.0 g), bipyridine (2.06 g), and CuCl (0.66 g). The arrows mark changes in the solution removal speed.

Figure 4. Dry PMMA brush thickness as a function of the room temperature polymerization time and various concentrations of CuCl\(_2\). The amounts of other reagents are: methyl methacrylate monomer (32.7 g), methanol (25.5 g), DI water (7.0 g), bipyridine (2.06 g), and CuCl (0.66 g). The lines are meant to guide the eyes.

Our experiments revealed that the parameters of the polymer brush – notably the polymer growth rate and polydispersity – are controlled by the amount of CuCl\(_2\) added to the reaction vessel (cf. Figure 4). This finding is not that surprising given the nature of the reaction. The key reaction in ATRP is the reversible activation-deactivation process using metal (M)/ligand (L) complexes: \( P-X + M/L \leftrightarrow P^* + M/LX_2 \), where \( M \) is usually Cu and X is either Cl or Br. The propagating radical, \( P^* \), produced by the halogen atom transfer from \( P-X \) to the \( M/LX_2 \) complex will undergo polymerization until it is deactivated by the \( M/LX_2 \) complex. The quick speed of the activation-deactivation cycles compared to rate of polymerization and the low concentration of the active species (relative to the \( P-X \) ones) lead to polymers with narrow polydispersities. MCl\(_2\) is usually added to the reaction mixture to regulate the reaction rate and chain polydispersity. We believe that the combinatorial design of our system is conveniently suited for such studies because it allows for complete probing of the anchored polymer properties and studying the polymerization kinetics in confined geometries.

Conclusions
We have presented two new fabrication methods leading to the formation of multivariate surface-grafted polymer layers. We have shown that polymer brushes with a gradient variation of their grafting densities on solid substrates can be generated by first depositing molecular gradients of polymerization initiators on solid silica-covered substrates, and performing polymerization from the substrate bound initiator centers (“grafting from”). We have also outlined a method for preparing assemblies comprising arrays of polymer brushes with a variable polymer molecular weight. We also note that the latter methodology can be extended to prepare complex combinatorial brush structures with variable chemistries and morphologies. Work on the latter topic is currently under way in our group.

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References