Preparing High-Density Polymer Brushes by Mechanically Assisted Polymer Assembly

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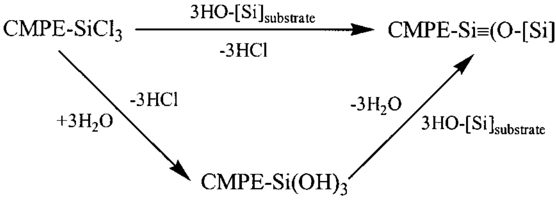
It is well-known that when polymers are end-anchored in a sufficient concentration to a substrate, they form a so-called polymer "brush" whereby the chains are stretched with respect to their preferred configuration away from the interface. The characteristics of polymer brushes have been analyzed using a variety of theoretical methods and experimental probes and are now fairly well established.[1−4] For example, the thickness of the brush layer, H, is known to depend linearly on the number of repeat units of the polymer, N, and on the power law of the brush grafting density at the substrate, σ, with the exponent of $^1/_3$ or 1, depending on the surface coverage.[1,2] To fine-tune the polymer brush properties, one needs to have a good control over H and σ. While H can be adjusted by simply varying the polymerization time, monomer concentration, and monomer conversion, σ depends on the methods by which polymer brushes are formed.

Previous reports established that polymer brushes with moderately high grafting densities can be prepared by harnessing the "grafting from" principle in which the polymer chains are synthesized using radical initiators that are covalently bound to the substrate. A vast majority of experiments involved classical radical growth methods with either azo- (e.g., AIBN) or peroxide-based initiators that either were created directly on the substrate or were attached to the substrate via self-assembly.[5−11] While the advantage of such methods is their ease of use and the ability to prepare brushes from a variety of monomers, a major disadvantage is a hard-to-control polymerization process, which usually leads to brushes with broad molecular weight distributions. Recently several reports appeared that described the formation of polymer brushes using surface-initiated "living" radical polymerization,[12] such as the atom transfer radical polymerization (ATRP).[13,14] Because of its simplicity, robustness, and the ability to synthesize polymers with narrow molecular weight distributions, ATRP has been the method of choice for most surface-initiated "living" radical polymerization processes.[15−21]

As mentioned previously, one of the crucial parameters governing the behavior of polymer brushes is their grafting density at the polymer/substrate interface. The "grafting from" techniques offer a fairly good control over the grafting density of the polymer brush—in the ideal case σ is simply equal to the surface density of the polymerization initiators. While a relatively high density of initiators can be achieved by assembling the molecules on the surface by means of Langmuir−Blodgett (LB) techniques[17,20] or by forming organized self-assembled monolayers (SAMs),[19] tailoring the grafting density of the SAM chains is not an easy task. SAMs are usually formed through self-assembly processes that are governed by the chemical and structural nature of the SAM molecules and the means of their attachment to the substrate. To overcome this limitation, one would need to seek another way of controlling the grafting density of the surface initiators that is independent of the system thermodynamics.

Recently, we have demonstrated that one can fine-tune the grafting density of molecules on surfaces by fabricating MAMs ("mechanically assembled monolayers"), structures that are based on the combination of natural self-assembly and mechanical manipulation of the grafted molecules on surfaces.[22] In this work we utilize the MAMs to adjust the surface density of the initiators and consequently that of polymer brushes grown by surface-initiated ATRP. Following the steps involved in the preparation procedure (see below), we call this technique MAPA ("mechanically assisted polymer assembly").

In this communication we illustrate the principles of MAPA on preparing dense polymer brushes of polyacrylamide (PAAm).[15] Figure 1 shows schematically how PAAm−MAPA works. First, a pristine PDMS network film was prepared (cf. Figure 1a) by casting a mixture of PDMS and a cross-linker[24] into a thin (≈1 mm) film and curing it at 70 °C for about an hour. The film was then cut into small strips ($\approx 1 \times 5$ cm^2) and mechanically uniaxially elongated by Δx (cf. Figure 1b). Subsequent exposure to UV/ozone (UVO) treatment produced hydrophilic PDMS surfaces (PDMS−UVO) composed mainly of hydroxyl groups (HO−[Si]$_{\text{surface}}$)[22,24] that served as attachments points for chlorosilane-based ATRP initiators. Following previous work on PAAm brushes, we used 1-trichlorosilyl-2-(*m*-*p*-chloromethylphenyl)ethane (CMPE) (United Chemical Technologies, Inc.) as the initiator. The CMPE molecules were deposited from vapor[25] onto this stretched substrate (cf. Figure 1d) and formed an organized CMEP−SAM following the well-known set of reactions:



(1)

After the CMPE−SAM deposition, any physisorbed CMPE molecules were removed by thoroughly washing the substrates with warm deionized water (75 °C, >16 MΩ·m) for several minutes. The PAAm ATRP on the PDMS−UVO/CMPE substrates was performed as described previously[15] by placing the samples into 120 mL of *N*,*N*′-dimethylformamide and by adding 0.3 g of CuCl, 1.0 g of bipyridine, and 16.0 g of acrylamide (all obtained from Aldrich and used as received). The flask was sealed under N_2 and placed into an oil bath, and the mixture was reacted at 130 °C for 45 h to form PAAm brushes on PDMS−UVO substrates (cf. Figure 1e). After the reaction, the strain was released from the PDMS−UVO substrate, which returned to its original size (cf. Figure 1f), causing the grafted PAAm polymers to form a densely organized brush. Any physisorbed monomeric

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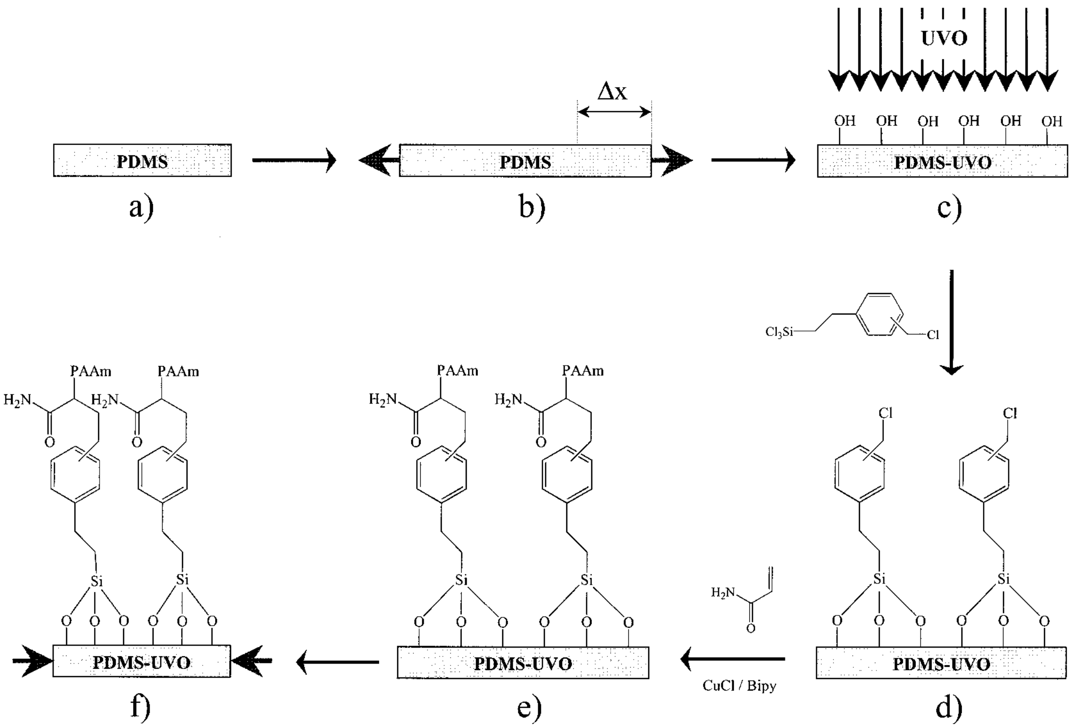

Figure 1. Schematic illustrating the principle of preparing high-density polyacrylamide bushes using MAPA ("mechanically assisted polymer assembly").

and polymeric acrylamide was removed by Soxhlet extraction with deionized water for 48 h.

We used near-edge absorption fine structure (NEXAFS) to examine the surface and bulk chemistry (including bond densities) of the samples. NEXAFS involves the resonant soft X-ray excitation of a K- or L-shell electron to an unoccupied low-lying antibonding molecular orbital of σ symmetry, σ^*, or π symmetry, π^*.[26] The initial state K-shell excitation gives NEXAFS its element specificity, while the final-state unoccupied molecular orbitals provide NEXAFS with its bonding or chemical selectivity. A measurement of the intensity of NEXAFS spectral features thus allows for the identification of chemical bonds and determination of their relative population density within the sample. The NEXAFS experiments were carried out on the NIST/Dow soft X-ray materials characterization facility at the National Synchrotron Light Source at Brookhaven National Laboratory (NSLS BNL).[27] The setup at NSLS BNL is capable of detecting both the partial electron yield (PEY) and the fluorescence yield (FY) NEXAFS spectra. Thus, by simultaneously collecting both the PEY and FY NEXAFS signals, whose probing depths are ≈2 and ≈100 nm, respectively, the surface and bulk chemical compositions of the sample can be probed in a single experiment. Figure 2 shows the PEY NEXAFS spectra taken at the nitrogen K-edge (left) and oxygen K-edge (right) of PDMS–UVO and PAAm–MAPA samples. The absence of any nitrogen signal for PDMS–UVO and strong absorption peaks detected at the nitrogen K-edge of the PAAm–MAPA samples verify that PAAm brushes were formed during the MAPA process. This finding is further supported by exploring the PEY NEXAFS spectra collected at the oxygen K-edge. While the broad peaks in the oxygen K-edge between 534 and 548 eV that are present in all spectra can be associated with various bonding environments of Si–O,[28] the peak at 531 eV corresponding to the 1s → $\pi^*_{C=O}$ transition is detected only in the PAAm–MAPA samples, providing an additional evidence for the presence of PAAm. A close inspection of the data in Figure 2 reveals that the intensity of the 1s → $\pi^*_{C=O}$ transition increases with increasing Δx, indicating that the density of the C=O bonds and thus the PAAm chains increases with increasing Δx, as expected. Furthermore, because no measurable nitrogen signal could be detected in the nitrogen K-edge FY NEXAFS spectra and also because the carbon K-edge and oxygen K-edge FY NEXAFS spectra were almost indistinguishable from that of bare PDMS, the NEXAFS measurements confirmed that the PAAm brushes were present only on the sample surface and not in the bulk.

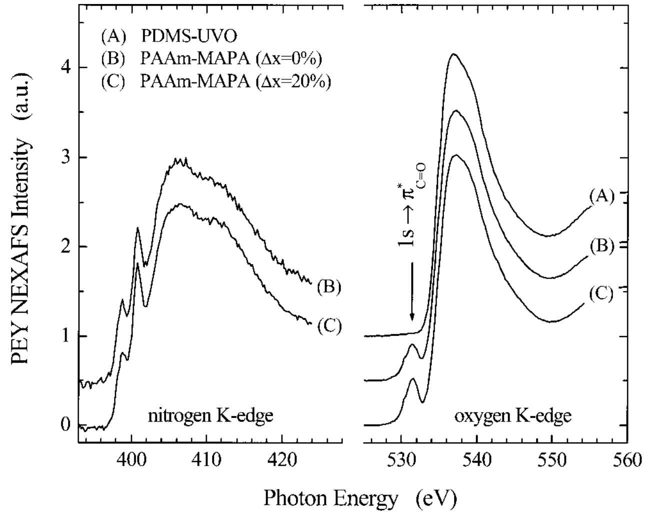

Figure 2. PEY NEXAFS spectra from PDMS–UVO (A), PAAm–MAPA ($\Delta x = 0\%$) (B), and PAAm–MAPA ($\Delta x = 20\%$) (C) samples. The spectra were collected at the nitrogen (left) and oxygen (right) K-edge. The arrow in the oxygen K-edge spectra indicates the position of the 1s → $\pi^*_{C=O}$ transition.

Further evidence for the observation elucidated from the PEY NEXAFS data was obtained from complemen-

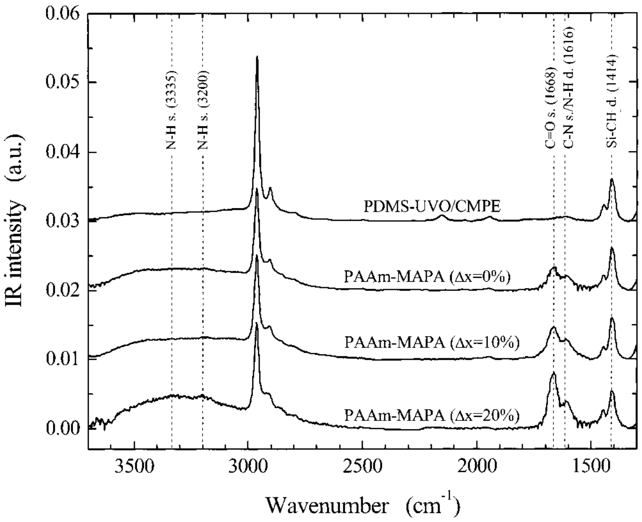

Figure 3. ATR-FTIR spectra from PDMS−UVO/CMPE, PAAm−MAPA ($\Delta x = 0\%$), PAAm−MAPA ($\Delta x = 10\%$), and PAAm−MAPA ($\Delta x = 20\%$) samples. A total of 2056 ATR-FTIR scans were collected with a resolution of 4 cm^{-1} and normalized to the Si−CH$_3$ deformation signal at 1414 cm^{-1}.

tary experiments using Fourier transform infrared spectrometry in the attenuated total reflection (ATR-FTIR). A total of 1024 scans were collected at a resolution of 4 cm^{-1} using a Digilab UMA-500 spectrometer equipped with a liquid nitrogen cooled MCT detector and a mirror speed of 0.3 cm/s. Figure 3 shows ATR-FTIR spectra measured on (top to bottom) PDMS−UVO/CMPE and MAPA−PAAm samples with Δx equal to 0%, 10%, and 20%. The spectra were normalized to the Si−CH$_3$ deformation mode at 1414 cm^{-1}.[29] Inspection of the data in Figure 3 reveals that there are several characteristic peaks in the ATR-FTIR data. Following previous studies on PAAm, we attribute the 1668 and 1616 cm^{-1} signals to the symmetric amide C═O stretching mode and the combination of the C−N stretching/N−H deformation modes, respectively.[29] Moreover, the bands at 3335 and 3200 cm^{-1} are assigned to the asymmetric and symmetric N−H stretching modes of the amide functionality, respectively.[29] As apparent from Figure 3, the intensity of both the C═O and N−H stretching modes increases with increasing Δx. This result thus demonstrates unambiguously that the polyacrylamide grafting density at the PDMS−UVO substrate increases with increasing elongation on the untreated elastic substrate.

While more work is needed to further characterize the physicochemical characteristics of polymer brushes grown by MAPA, the results reported in this communication clearly indicate that the MAPA method offers a unique and extremely simple means of tailoring the molecular properties of polymer brushes. Realizing that PDMS behaves as an ideal elastic material, the grafting density of the initiators and thus the polymer brush grafting density are directly proportional to Δx and can be varied smoothly (and with high precision) over a wide range. We predict that polymer brushes with extremely high grafting densities can be successfully prepared by MAPA.

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