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Combinatorial Study of the Mushroom-to-Brush Crossover in Surface Anchored Polyacrylamide

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Polymers tethered to substrates represent a central part of a wide range of applications, including stabilization of colloids, adhesion promotes, and polymer coatings. In addition these systems are also attractive from the fundamental point of view: they provide unique means of probing the interplay between the polymer thermodynamics and the confinement effect due to the attachment to the substrate. The topic of neutral tethered polymer chains has received considerable attention, both theoretical and experimental.[1,2] The major findings of the various theoretical and experimental approaches have revealed that, depending on the grafting density of the polymers at the solution/substrate interface (σ), the anchored chains form either so-called mushrooms or so-called brushes. In good solvents, the thickness of the anchored polymer, H, in the low grafting density mushroom regime scales as $H \sim N\sigma^0$, where N is the degree of polymerization of the polymer; in the brush regime the chains become more crowded and the brush height scales as $H \sim N\sigma^{1/3}$.[1]

Multiple experimental studies appeared that attempted to test the above scaling relations and also the conditions for the mushroom-to-brush transition.[1−6] The typical hurdles experimental studies usually run into involve complications associated with (1) preparing brushes with high enough grafting densities and (2) exploring completely the broad σ space. In this Communication we present a method that circumvents these two obstacles simultaneously. Specifically, we show that by preparing density gradients of polymerization initiators on substrates and using "grafting from" polymerization from such substrates, arrays of anchored polymers with a gradual variation of grafting densities can be prepared. We demonstrate that this setup allows for a complete mapping of polymer behavior over a wide range of σ.

We formed a gradient of polymerization initiator on silica substrates using the methodology proposed about 10 years ago by Chaudhury and Whitesides.[7] Specifically, 1-trichlorosilyl-2-(*m-p*-chloromethylphenyl)ethane (CMPE) (United Chemical Technologies, Inc.) was mixed with paraffin oil (PO), and the mixture was placed in an open container heated at 88 °C 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 silica substrate. Upon impinging on the substrate, the CMPE molecules reacted with the substrate −OH functionalities and formed a self-assembled monolayer (SAM). The breadth and position of the CMPE molecular gradient can be tuned by varying the CMPE diffusion time and the flux of the CMPE molecules. The latter can be conveniently adjusted by varying the chlorosilane/PO ratio and the temperature of the CMPE/PO mixture and by utilizing flexible polymeric supports as substrates.[8] To minimize any physisorption of monomer and/or the polymer formed in solution on the parts of the substrate that do not contain the CMPE−SAM, we backfilled the unexposed regions on the substrate containing unreacted −OH functionalities with *n*-octyl trichlorosilane, (OTS) (Gelest, Inc.). After the OTS−SAM deposition, any physisorbed CMPE and OTS molecules were removed by thoroughly washing the substrates with warm deionized water (75 °C, >16 MΩ cm) for several minutes.

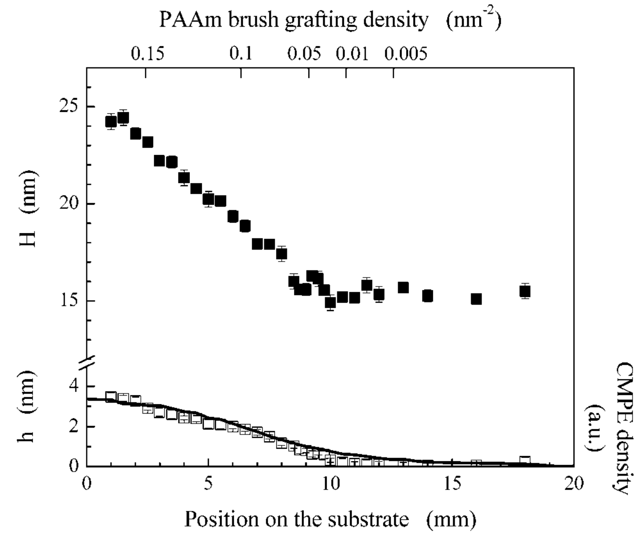

Figure 1. Dry (h, open symbols) and wet (H, closed symbols) thickness of the PAAm brush and the CMPE concentration (solid line) as a function of the position on the substrate.

We used near edge X-ray absorption fine structure (NEXAFS)[9] to study the chemistry and molecular orientation of the CMPE-SAMs surfaces. The NEXAFS experiments were carried out at the Soft X-ray Materials Characterization Facility at the National Synchrotron Light Source at Brookhaven National Laboratory (NSLS BNL). The NEXAFS spectra of CMPE−SAM and OTS−SAM collected in the partial electron yield (PEY) both contain peaks at 286.0 and 288.5 eV that correspond to the 1s → σ^* transition for the C−H and C−C bonds, respectively. In addition, the spectrum of CMPE also exhibits a very strong peak at 284.2 eV, which can be attributed to the 1s → π^* transition for phenyl C═C. The latter signal can thus be used as an unambiguous signature of the CMPE in the sample. With the X-ray monochromator set to 284.2 eV, we collected the PEY NEXAFS signal by scanning the X-ray beam across the gradient. The line in Figure 1 shows the variation of the PEY NEXAFS intensity measured at 284.2 eV across the gradient sample prepared by diffusing CMPE from the 1:1 CMPE/PO mixture for 2 min. The functional dependence indicates that the NEXAFS intensity from the C═C phenyl bond and thus the concentration of CMPE in the sample decreases as one moves from the CMPE side of the sample toward the OTS−SAM; the functional form closely resembles that of a diffusion-like profile. Experiments using variable angle spectroscopic ellipsometry (VASE, J. A. Woollam, Co.) confirmed that only a single monolayer was formed on the substrate.

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The surface-anchored polyacrylamide (PAAm) was prepared by atom transfer radical polymerization (ATRP), as described earlier,[10−12] by placing the initiator-containing samples into 100 mL of *N*,*N*′-dimethylformamide and by adding 0.3 g of CuCl, 1.0 g of bipyridine, and 24.0 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. After the reaction, any physisorbed monomeric and polymeric acrylamide was removed by Soxhlet extraction with deionized water for 48 h and dried with nitrogen. In addition, PAAm brushes were grown on silica gels (Davisil, grade 645, surface area $\approx$300 m^2/g) using the procedure outlined in ref 11. The PAAm polymers were grown and purified using the same conditions as described above. The PAAm chains were then cleaved from the silica support with a 10% (w/w) solution of HF for 2 h, neutralized by adding sodium carbonate, and filtered. Size exclusion chromatography was used to analyze the molecular weight of the cleaved PAAm macromolecules ($M_w = 17$ kDa, polydispersity index = 1.7). We note that Huang and Wirth reported a value of $M_w = 17.5$ kDa for the concentration of monomer, polymerization temperature, and time that were the same as in our experiments.[11]

VASE was used to measure the thickness of the dry polymer film, *h*, as a function of the position on the substrate. The details of the measurement and data interpretation will be disclosed elsewhere.[13] The results for the 1:1 CMPE/PO gradient are shown in the bottom part of Figure 1. 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 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 $\sigma = h\rho N_A/M_w$, where ρ is the density of PAAm (= 1.302 g/cm^3), N_A is the Avogadro's number, and M_w is the polymer molecular weight.

The substrates with the grafted PAAm were placed into a solution cell that was filled with DI water (pH $\approx$ 7), a good solvent for PAAm, and incubated for at least 5 h. The wet thickness of PAAm grafted polymer in DI water (*H*) was measured using VASE. The values of *H* for samples prepared on 1:1 CMPE/PO gradients are shown in the top part of Figure 1. The data shows that *H* decreases as one traverses across the substrate stating at the CMPE side. Similar experiments were performed with PAAm brushes grown from gradient CMPE substrates prepared from various CMPE/PO concentrations. We note that in all cases the diffusion time for the CMPE was 2 min. The results of the experiments are summarized in Figure 2.

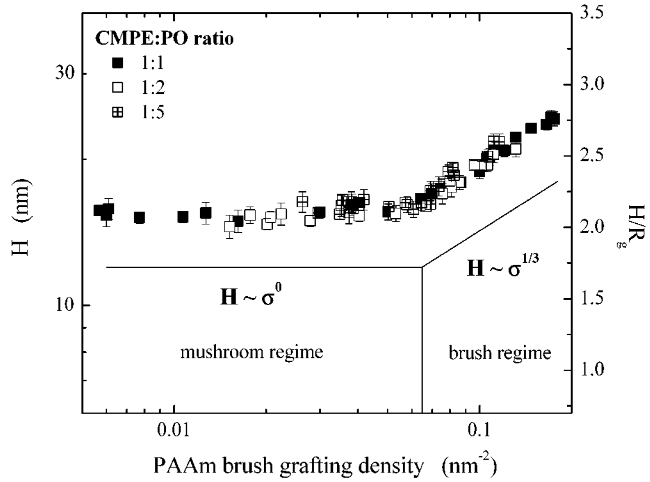

Figure 2. Wet thickness of the PAAm brush (*H*) as a function of the PAAm brush grafting density.

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 reveals that at low σ *H* is independent of the grafting density. Hence the chains are in the mushroom regime. At high polymer grafting densities, *H* increases with increasing σ, indicating the brush behavior. The crossover between the two regimes occurs at $\sigma \approx 0.065\ nm^{-2}$. By fitting the data in the brush regime to $H \sim N\sigma^n$ we obtain *n* equal to 0.37 ± 0.04 (1:1 CMPE/PO), 0.39 ± 0.05 (1:2 CMPE/PO), and 0.40 ± 0.06 (1:5 CMPE/PO). We note that *n* obtained by fitting the experimental data is slightly higher that the predicted value of $n = 1/3$; this observation is in agreement with recent reports.[14] 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 poly(methyl methacrylate) using ATRP from substrates having various surface densities of the polymerization initiator, ω-mercaptoundecyl bromoisobutyrate.[15] Their study revealed that the grafting density of the polymer depends on the grafting density of the initiator. However, on the basis of the data presented in ref 15 it is uneasy to discern whether the kinetics of the polymerization also depends on the grafting density of the initiator. Currently we have no means of measuring the molecular weight of the grafted brushes directly on the gradient substrate. While we cannot exclude the possibility that the length of PAAm chains polymerized on the various parts of the molecular gradient substrate varies with σ, 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.

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