Enhanced Stability of Surface-Tethered Diblock Copolymer Brushes with a Neutral Polymer Block and a Weak Polyelectrolyte Block: Effects of Molecular Weight and Hydrophobicity of the Neutral Block

Yuanchao Li,[†,‡] Yeongun Ko,[†] Yiliang Lin,[†] Douglas Kiserow,[†,‡] and Jan Genzer*,[†]

[†]Department of Chemical &Biomolecular Engineering, North Carolina State University, Raleigh, North Carolina 27695, United States

[‡]US Army Research Office, Research Triangle Park, North Carolina 27709, United States

Ⓢ *Supporting Information*

ABSTRACT: We study the stability of diblock copolymer brushes featuring a bottom neutral block, poly(methyl methacrylate) (PMMA) or poly(poly(ethylene glycol) methacrylate) (PPEGMA), and a top poly(acrylic acid) (PAA) block on flat silicon substrate. The polymer brushes are prepared by surface-initiated atom transfer radical polymerization (SI-ATRP). We use a combinatorial design featuring a molecular weight gradient in the bottom neutral block to investigate systematically the effect of the molecular weight of that block on the stability of the copolymer brush. We measure variations in dry thickness of the diblock copolymer brush by ellipsometry after different incubation times in aqueous buffer (pH = 9.0) as a function of thickness of the neutral block,

indicating degrafting of the mechanically activated copolymer chains via hydrolysis of ester groups in the initiator and/or Si−O bonds that attach the polymer to the substrate. The stability of the diblock copolymer brushes is higher than that of PAA homopolymer brushes of the same molecular weight as the copolymer. Moreover, we establish that increasing the molecular weight of the neutral bottom PMMA block in PMMA-*b*-PAA brush shows higher stability than increasing the molecular weight of the bottom PPEGMA block in PPEGMA-*b*-PAA brush. Partial swelling of the bottom PMMA block (due to addition of a small amount of acetone) makes the degrafting of PMMA-*b*-PAA more pronounced. These findings suggest that the bottom water-insoluble polymer block plays an important role in governing the overall stability of the diblock copolymer brush.
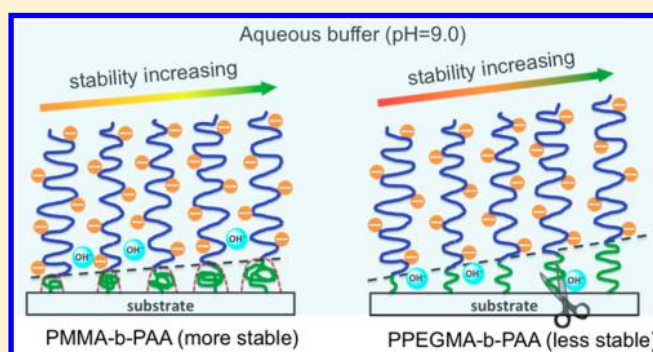
INTRODUCTION

Polymer brushes are long polymer chains attached by one end to a surface or interface with a high enough density of attachment points so that the chains are crowded and forced to stretch away from the surface or interface much farther than the end-to-end distance of an unperturbed chain.[1] Polymer brushes have been extensively studied both theoretically and experimentally for decades and possess wide range of applications in tuning surface properties (e.g., wettability and friction), creating "smart" surfaces and antifouling coatings, enabling cell culture, etc.[2−4] For many of the applications, long-term stability of polymer brushes is very important. Unfortunately, the stability of polymer brushes can be compromised under certain conditions (e.g., pH and ionic strength), resulting in degrafting and removal of polymer chains from the substrates.[5,6] Examples include degrafting of poly(poly(ethylene glycol) methacrylate) (PPEGMA) brushes in cell culture media,[7,8] surface-tethered hyperbranched polyglycidol during polymerization of glycidol,[9] polyacrylamide brushes in methanol with a strong base,[10] and polyelectrolyte (i.e., charged polymer) brushes in buffer solutions.[11−17] It is necessary to point out that the instability

occurs more often in polyelectrolyte brushes than neutral polymer brushes because additional tension can be generated along the grafted chain backbones in polyelectrolyte brushes due to strong swelling resulting from electrostatic repulsion and osmotic stress, which may make the weak bonds at the bottom-most portion of grafted chains close to the substrate, where the tension is ultimately focused,[18] more vulnerable to hydrolysis (or cleavage).

Since the stability of polyelectrolyte brushes may be compromised, it is important to seek strategies to enhance it. The two key factors contributing to the instability of polyelectrolyte brushes in aqueous systems are (1) weak linkages between grafted chains and the substrate (e.g., Si−O and Au−S bonds that hold the polymer attached to the substrate) and (2) tension exerted on the weak linkages (e.g., ester bond in the initiator) due to electrostatic repulsion and osmotic stress. Having identified the potential sources of
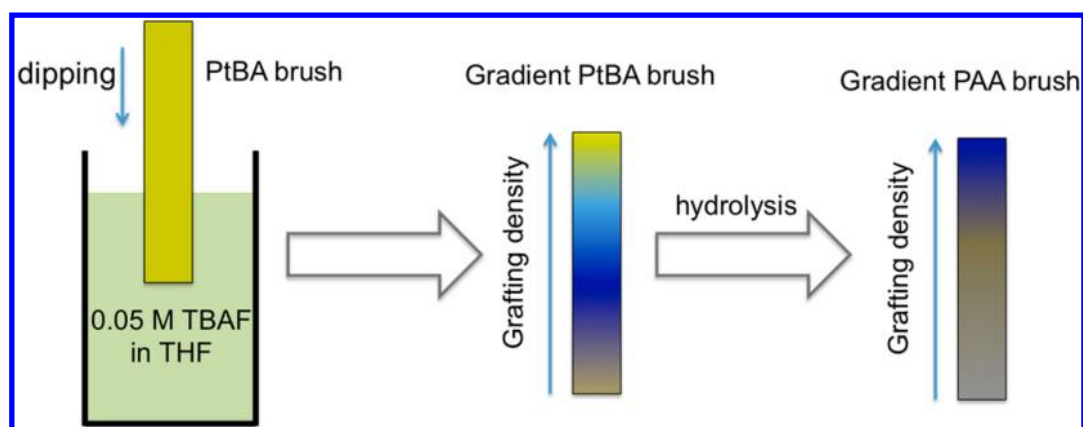
Figure 1. PtBA brush was dipped into 0.05 M TBAF solution at a controlled speed to partially remove PtBA chains from the substrate, resulting in a gradient in grafting density along the dipping direction.[20] The gradient PtBA brush specimen was then hydrolyzed to yield PAA brush with a gradient in grafting density.

instabilities, one can think of viable strategies that would enhance stability of polyelectrolyte brushes. Those include (1) minimizing the number of weak linkages that may be susceptible to cleavage and (2) reducing the tension that can further activate the weak linkage. For example, our group has recently synthesized a novel, ester-free and trichlorosilane-based initiator for surface-initiated free radical polymerization (SI-FRP) and used it to grow poly(2-dimethylaminoethyl methacrylate) (PDMAEMA) brushes which showed higher stability in phosphate-buffered saline (PBS) than those formed from ester-based initiator analogues.[14] Regarding the second strategy, one may think of diluting charge density of polyelectrolyte brushes by random copolymerization with a neutral monomer. However, surface properties of the random copolymer brushes may differ from those of the homopolyelectrolyte brushes. Therefore, an ideal approach is to introduce a short and neutral polymer block between the substrate and the polyelectrolyte brush that can act as a spacer to separate the charged units from the weak linkages without changing its surface properties. This strategy was first reported by Paripovic et al., who introduced a short neutral and hydrophobic block between the surface initiator layer and the hydrophilic polymer brush, and it was proved to be successful.[17] However, the role of the neutral block was not explored in detail.

Here, we focus on the second strategy and study the stability of block copolymer brushes with a neutral block and a polyelectrolyte block incubated in buffer solutions. The role of the neutral block is explored with respect to its molecular weight and hydrophobicity. We use surface-initiated atom transfer radical polymerization (SI-ATRP) to prepare the block copolymer brushes.[3,19] Poly(acrylic acid) (PAA) was chosen as a model polyelectrolyte. To investigate the effect of hydrophobicity of the neutral block, hydrophobic poly(methyl methacrylate) (PMMA) and hydrophilic PPEGMA were chosen as the neutral bottom block of the copolymer. The role of the length of the bottom block on polymer brush stability was elucidated systematically by creating and employing a combinatorial setup that features a gradient in molecular weight of the neutral bottom block.

■ EXPERIMENTAL SECTION

Materials. Ethanolamine, dimethylformamide (DMF), ethanol, methyl methacrylate (MMA), *tert*-butyl acrylate (tBA), poly(ethylene glycol) methyl ether methacrylate (PEGMA, ∼300 g/mol), N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA), CuBr (99.999%), CuCl (99%), 2,2′-bipyridine (BiPy), tetrabutylammonium fluoride (TBAF) solution in THF (1.0 M), trifluoroacetic acid (TFA, 99%), and inhibitor removers were purchased from Sigma-Aldrich and used as received (unless otherwise noted). MMA, tBA, and PEGMA were passed through an inhibitor remover column before use. Methanol, acetone, tetrahydrofuran (THF), dichloromethane (DCM), toluene, and sodium chloride (NaCl) were purchased from Fisher Scientific. [11-(2-Bromo-2-methyl)propionyloxy]undecyl-trichlorosilane (eBMPUS) was purchased from Gelest. Silicon wafers, with orientation [100], diameter 100 mm, and thickness 0.5 mm, were purchased from Silicon Valley Microelectronics. Water used for reaction, rinsing, and buffer preparation was taken from a Millipore Progard 2 purification system.

Sample Preparation. *Initiator Deposition.* Silicon wafers were cut into 45 mm × 8 mm strips and sonicated in methanol, dried with a stream of N_2 gas, and treated in a UV-ozone chamber for 8 min. The wafers were then placed into a solution of 20 μL of 5 wt % eBMPUS in anhydrous toluene and 20 mL of anhydrous toluene and incubated at −18 °C for 24 h. After removing from the toluene solution, the wafers were rinsed with ethanol and acetone and dried with a stream of N_2 gas.

Synthesis of PAA Brush. Surface-initiated ATRP of tBA was carried out using a reaction system consisting of tBA (15 mL, 102.4 mmol), CuBr (143 mg, 1.0 mmol), PMDETA (420 μL, 2.0 mmol), and DMF (10 mL). The solution was degassed by bubbling argon gas for 20 min and then charged to a crimp top vial containing two substrates functionalized with eBMPUS (placed back to back), and the reaction was allowed to proceed at 60 °C. After a certain reaction time (*vide infra*), the reaction mixture was removed and the substrates were rinsed thoroughly with acetone and sonicated in acetone for 20 min, followed by drying with a stream of N_2 gas. The poly(*tert*-butyl acrylate) (PtBA) brushes were characterized using ellipsometry, followed by hydrolysis by a solution of TFA in DCM (volume ratio of TFA to DCM = 1:10) at room temperature with stirring overnight to yield PAA brushes, which were then rinsed thoroughly with ethanol and water and dried with a stream of N_2 gas.

Preparation of PAA Brush with Grafting Density Gradient. As shown in Figure 1, a PtBA brush sample was dipped vertically into 0.05 M TBAF solution in THF at 40 °C at a constant rate of 0.3 mm/min. The resulting gradient PtBA brush sample was then characterized by ellipsometry, followed by hydrolysis by a solution of TFA in DCM (volume ratio of TFA to DCM = 1:10) at room temperature with stirring overnight to yield PAA brush with gradient in grafting density.

Synthesis of PMMA-b-PAA Block Copolymer Brushes. Surface-initiated ATRP of MMA for the first block was carried out using a reaction system consisting of MMA (10.8 mL, 101.4 mmol), CuBr (143 mg, 1.0 mmol), BiPy (312 mg, 2.0 mmol), methanol (12 mL), and water (4 mL). The solution was degassed by bubbling argon gas for 20 min. Two substrates functionalized with eBMPUS (placed back
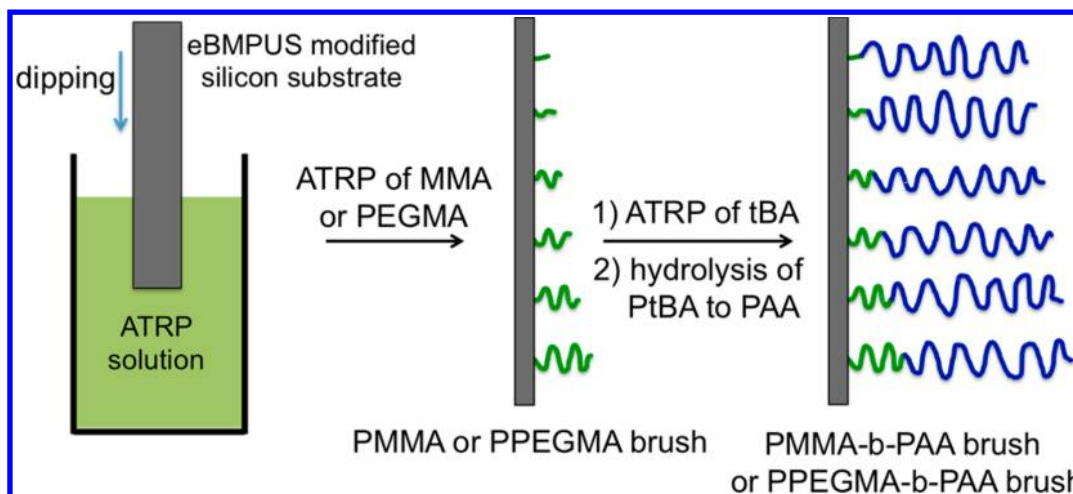
Figure 2. Preparation of surface-grafted PMMA-*b*-PAA or PPEGMA-*b*-PAA diblock copolymer brushes with molecular weight gradient in PMMA or PPEGMA block.

Scheme 1. Synthetic Route for the Preparation of Surface-Grafted PMMA-*b*-PAA or PPEGMA-*b*-PAA Diblock Copolymer Brushes
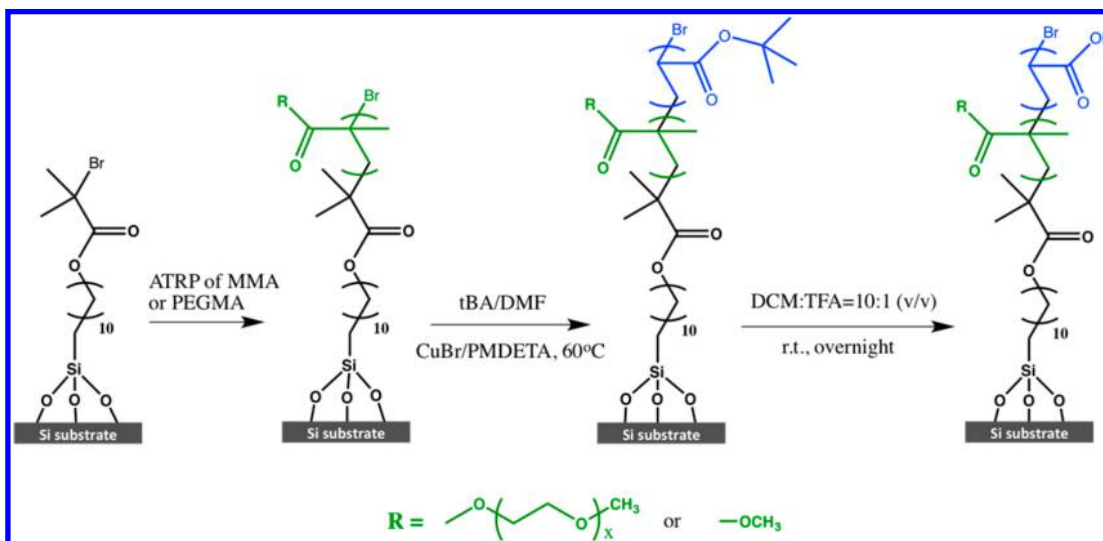

to back) were dipped into the degassed solution at a constant rate of 1 mm/min under an argon atmosphere at room temperature. The resulting PMMA brushes with molecular weight gradient were rinsed thoroughly with acetone and sonicated in acetone for 20 min, followed by drying with a stream of N$_2$ gas. The gradient PMMA brushes were characterized by ellipsometry. Polymerization of the second block was carried out in the same reaction system used for ATRP of PtBA homopolymer brushes as described above. After polymerization for 20 h, the reaction mixture was removed, and the substrates were rinsed thoroughly with acetone and sonicated in acetone for 20 min, followed by drying with a stream of N$_2$ gas. The PMMA-*b*-PtBA brushes were characterized using ellipsometry, followed by hydrolysis by a solution of TFA in DCM (volume ratio of TFA to DCM = 1:10) at room temperature with stirring overnight to yield PMMA-*b*-PAA brushes. The procedures are illustrated in Figure 2 and Scheme 1.

Synthesis of PPEGMA-b-PAA Block Copolymer Brushes. Surface-initiated ATRP of PEGMA for the first block was carried out using a reaction system consisting of PEGMA (5.7 mL, 20.0 mmol), CuBr (143 mg, 1.0 mmol), BiPy (312 mg, 2.0 mmol), methanol (20 mL), and water (5 mL). The solution was degassed by bubbling argon gas for 20 min. Two substrates functionalized with eBMPUS (placed back to back) were dipped into the degassed solution at a constant rate of 0.5 mm/min under an argon atmosphere at room temperature. The resulting PPEGMA brushes with molecular weight gradient were

rinsed thoroughly with water and ethanol and sonicated in ethanol for 20 min, followed by drying with a stream of N$_2$ gas. The gradient PPEGMA brushes were characterized by ellipsometry before growing the second block. The following procedures were the same as those used to prepare PMMA-*b*-PAA block copolymer brushes.

Incubation Experiments. Ethanolamine buffer solution (0.1 M) with 0.05 M NaCl was adjusted to pH 9 using minute quantities of HCl and NaOH. The pH was measured using an Accumet AB15 pH meter (Fisher Scientific) equipped with a platinum pH electrode. In a typical experiment, a polymer brush sample was placed into a glass vial containing the buffer solution, and the vial was sealed and stored in the dark at room temperature. After every 24 h, the sample was removed, rinsed thoroughly with ethanol and water, dried with a stream of N$_2$ gas, and characterized by ellipsometry. After characterization, the sample was incubated again until a total incubation time of 120 h.

Spectroscopic Ellipsometry. Measurements were performed using a variable angle spectroscopic ellipsometer (J.A. Woollam Co.) controlled by WVASE32 software (J.A. Woollam Co.) at a fixed incident angle of 70° and a wavelength range of 400−1000 nm. The thickness was derived from the fitting of ellipsometric data.
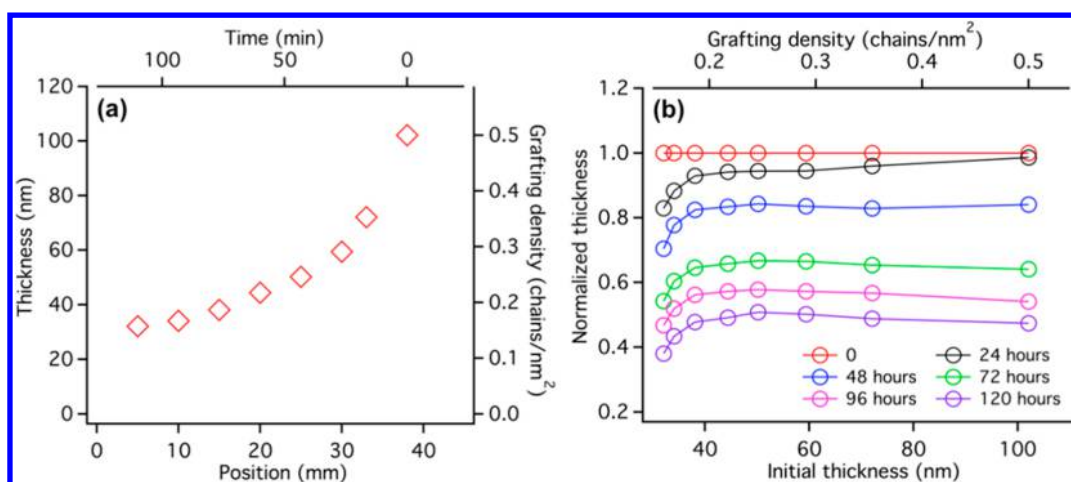
Figure 3. (a) Thickness and grafting density of PAA brush as a function of the position on the substrate (bottom axis); the top axis is the corresponding exposure time of its precursor PtBA in 0.05 M TBAF solution. (b) Ellipsometric thicknesses normalized by initial thicknesses (h_0 at 0 h) after incubation for various times in 0.1 M ethanolamine buffer (pH = 9.0) with 0.05 M NaCl as a function of the initial PAA brush thickness (or grafting density, top axis).

RESULTS AND DISCUSSION

The focus of this section is to discuss the incubation experiments of PMMA-*b*-PAA and PPEGMA-*b*-PAA diblock copolymer brushes. However, we will first present the incubation data for PAA brush with respect to its molecular weight and grafting density, which may help to better understand the incubation data for the diblock copolymer brushes.

Degrafting of PAA Brushes. The stability of PAA brushes was investigated to ascertain the role of the grafting density and molecular weight. To prepare a PAA brush sample with grafting density gradient, a PtBA brush sample with thickness of 222.3 nm was dipped into 0.05 M TBAF solution in THF at 40 °C at a constant rate of 0.3 mm/min. TBAF was chosen because it can selectively cleave Si−O bonds to remove the grafted PtBA chains from the substrate.[20] The resulting PtBA brush sample with grafting density gradient (Figure S1 in Supporting Information) was then subjected to hydrolysis to yield a gradient PAA brush sample. The dry thickness of a polymer brush (h) scales as the product of molecular weight (M_n) and grafting density (σ), i.e., $h = (M_n\sigma)/(\rho N_A)$, where ρ is polymer density and N_A is Avogadro's number. Since the gradient was generated by removing PtBA chains from a uniform brush (M_n was the same), the grafting density is proportional to the brush dry thickness. Recent measurements for PMMA brushes grown with an identical initiator and initiator deposition procedure provide a value of ∼0.5 chains/nm[2].[20] Assuming that the original PtBA brush had the same grafting density of ∼0.5 chains/nm[2], we can estimate the grafting density of PtBA/PAA for a given point on the substrate by its thickness, as shown in Figure 3a. This PAA brush sample with a grafting density gradient was then incubated in 0.1 M ethanolamine buffer (pH = 9.0) with 0.05 M NaCl at room temperature. Note that the effective bulk pK_a of PAA brushes is ∼6.5−6.6 and that the effective pK_a of the uppermost layer of PAA brush is ∼4.4;[21] therefore, its degree of dissociation is close to 1 at pH 9.0. The sample was removed from the buffer solution after every 24 h, rinsed thoroughly with water and ethanol, dried with N_2 gas, and then measured by ellipsometry. Figure 3b shows time evolution of PAA normalized thickness (h/h_0) with respect to its grafting density/initial thickness. The thickness reduction

decreases with increasing grafting density from ∼0.15 to 0.25 chains/nm[2], indicating increased stability. This is likely due to stronger charge regulation (less charged brush close to the attachment point at the substrate) at higher grafting density, leading to smaller tension along the chains during incubation.[15] However, PAA brushes with grafting density from ∼0.25 to 0.5 chains/nm[2] showed similar stability. To understand this behavior, we need to consider chain crowding effect as well as charge regulation.[22] At higher grafting densities, the crowding effect becomes more pronounced, which promotes brush degrafting. As the grafting density increases, the increase in crowding that favors degrafting may counterbalance the increase in charge regulation that suppresses degrafting. This then leads to a similar stability of PAA brushes with grafting density in the range of ∼0.25−0.5 chains/nm[2].

To investigate the effect of molecular weight on degrafting of PAA, five PAA brush samples with grafting density of ∼0.5 chains/nm[2] and thickness ranging from 10.5 to 102.1 nm were prepared (by varying the polymerization time for PtBA under identical conditions, as shown in Figure S2) and incubated in 0.1 M ethanolamine buffer (pH = 9.0) with 0.05 M NaCl at room temperature. The samples were removed from the buffer solution after every 24 h, rinsed thoroughly with water and ethanol, dried with N_2 gas, and then characterized by ellipsometry. Figure 4 displays the normalized brush thickness as a function of the initial PAA thickness after different incubation times. Generally, the stability of PAA brush decreases with increasing initial thickness (molecular weight), which is in good agreement with previous reports.[7,10] However, the stability of PAA brush with initial thickness larger than ∼60 nm levels off, which could be ascribed to saturation of crowding effect at high molecular weights.

Degrafting of PMMA-*b*-PAA and PPEGMA-*b*-PAA Diblock Copolymer Brushes. The diblock copolymer brushes were prepared by sequential SI-ATRP of MMA/PEGMA and tBA, followed by hydrolysis of PtBA into PAA. To investigate the effect of molecular weight of the neutral block on the stability of the diblock copolymer brush, molecular weight gradient was created when preparing the neutral block (PMMA or PPEGMA) by vertically dipping eBMPUS modified substrates into the ATRP solution at a controlled speed. As
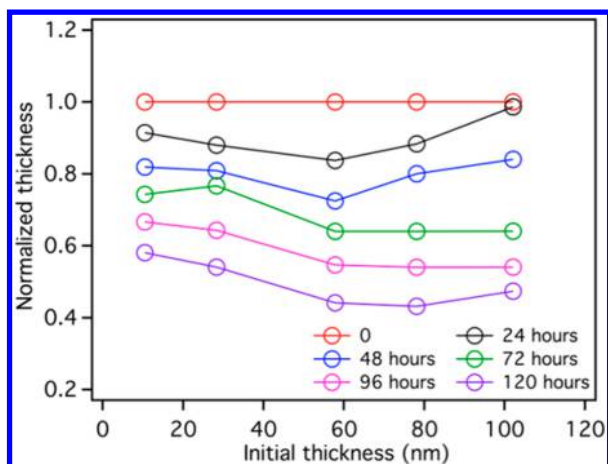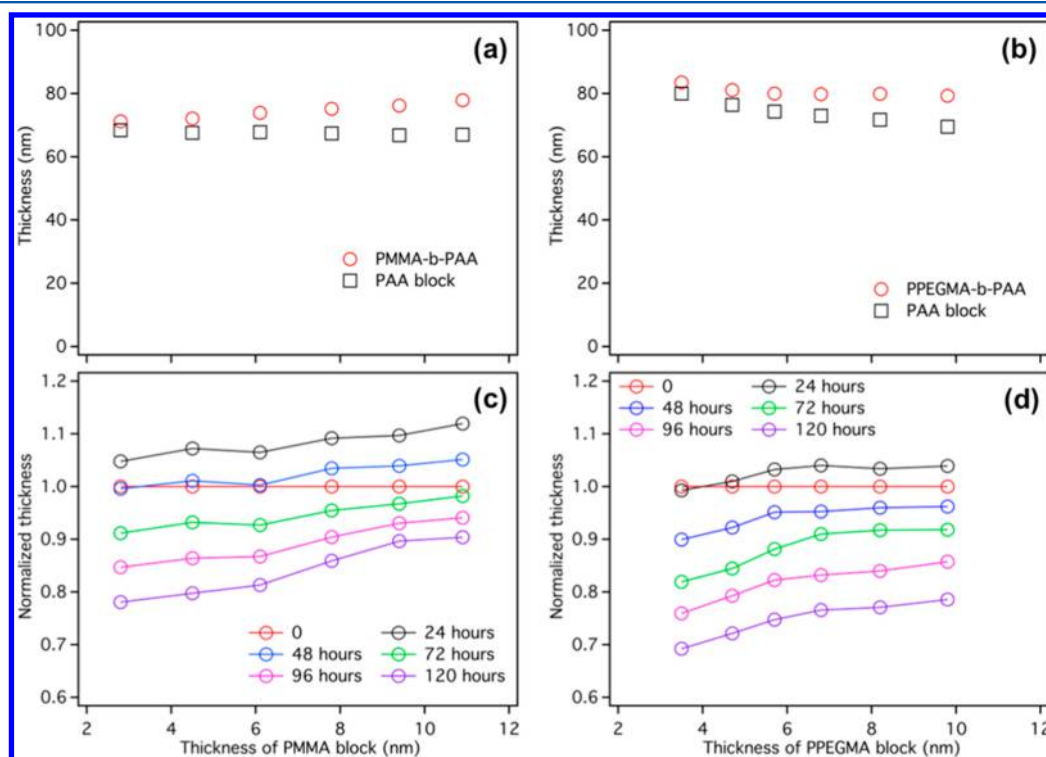
Figure 4. Ellipsometric thicknesses normalized by initial thicknesses after incubation for various times in 0.1 M ethanolamine buffer (pH = 9.0) with 0.05 M NaCl as a function of the initial PAA brush thickness (i.e., molecular weight).

shown in Figures 5a and 5b, the thicknesses of PMMA and PPEGMA were controlled in a similar range of ∼3−15 nm, which is much lower than that of PAA block (∼70 nm). There are two reasons for the thickness control: (1) minimizing the effects of PAA molecular weight and diblock copolymer molecular weight on the stability and (2) making it possible for cross-sample comparison with respect to hydrophobicity of the neutral block. It has to be pointed out that the thickness of PAA block for PMMA-*b*-PAA brush sample is about the same regardless of the thickness of PMMA block, while the thickness of PAA block for PPEGMA-*b*-PAA brush sample decreases

slightly with increasing the thickness of the PPEGMA block. This could be due to the fact that PEGMA is more bulky than MMA, leading to the decrease in the reinitiation efficiency of PPEGMA chains with increasing length. As we discussed earlier, the effect of this small difference in grafting density on the stability of the diblock copolymer brush can be neglected.

The diblock copolymer brushes (PMMA-*b*-PAA and PPEGMA-*b*-PAA) were incubated in 0.1 M ethanolamine buffer (pH = 9.0) with 0.05 M NaCl at room temperature. The samples were removed from the buffer solution after every 24 h, rinsed thoroughly with water and ethanol, dried with N_2 gas, and then characterized by ellipsometry. Figures 5c and 5d show the normalized thickness of PMMA-*b*-PAA and PPEGMA-*b*-PAA as a function of the thickness of the PMMA block and the PPEGMA block after different incubation times, respectively. It is prudent to mention that the change in brush thickness measured by ellipsometry is the outcome of two counter effects: (1) degrafting in the incubation solution that leads to decrease in grafting density and therefore decrease in thickness and (2) swelling due to residual charges and retained moisture[23] after removal from the incubation solution that causes increase in brush thickness. For both samples, an increase in brush thickness was observed after incubation for 24 h, which does not necessarily mean that degrafting did not occur. Instead, the decrease in brush thickness due to degrafting could not compensate for the increase in thickness by swelling due to residual charges and moisture, leading to a net increase in the film thickness. In addition, the increase in thickness for PMMA-*b*-PAA brush (up to ∼12%) is larger than that for PPEGMA-*b*-PAA brush (up to ∼4%) at similar thickness of the neutral block, suggesting that degrafting of PPEGMA-*b*-PAA chains was faster than that of PMMA-*b*-PAA chains. For

Figure 5. Thickness profiles of PMMA-*b*-PAA (a) and PPEGMA-*b*-PAA (b) brushes and their corresponding ellipsometric thicknesses normalized by initial thicknesses after incubation for various times in 0.1 M ethanolamine buffer (pH = 9.0) with 0.05 M NaCl as a function of the thickness of their neutral block: PMMA block (c) and PPEGMA block (d).
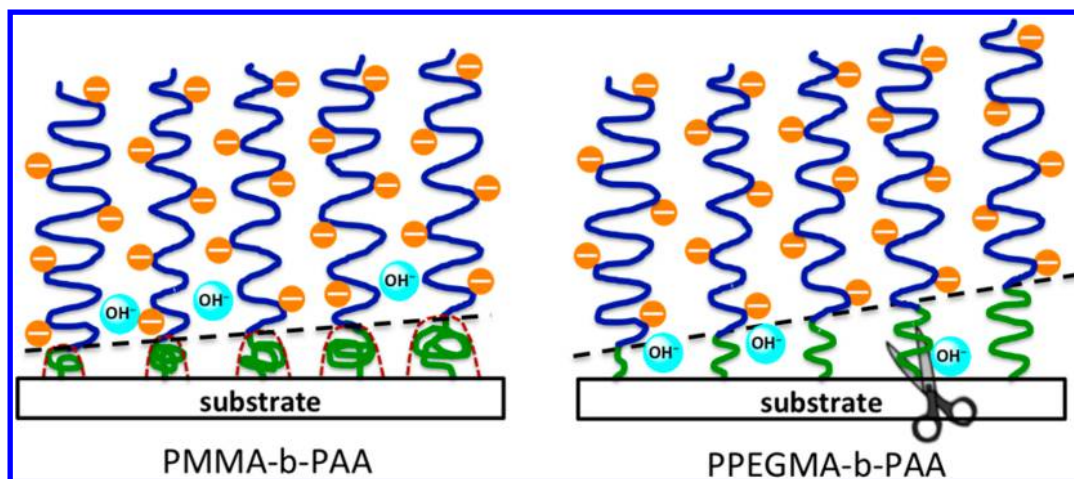
Figure 6. Neutral block (either PMMA or PPEGMA) separates the charged PAA block from the anchoring point. In contrast to hydrophilic PPEGMA block swelling in the incubation buffer, hydrophobic PMMA block could be in a collapsed state to form a shielding layer, leading to an increase in the barrier for hydroxide group to access the ester group and/or Si−O bond at the brush/substrate interface.

incubation times longer than 24 h, both samples show consistent decrease in thickness, indicating that degrafting took place. After a total incubation time of 120 h, the normalized thickness of PMMA-*b*-PAA is higher than that of PPEMGA-*b*-PAA by ∼10% at a similar thickness of the neutral block, which also suggests a higher stability of PMMA-*b*-PAA brush. Yet, the stability of PPEGMA-*b*-PAA brush may be affected by the lightly cross-linked nature of PPEGMA layer due to possible transesterification between neighboring chains.[8,24] From Figures 5c and 5d, we can see another distinct trend; i.e., the thickness for both PMMA-*b*-PAA and PPEGMA-*b*-PAA brush samples increases with increasing the thickness of the neutral block for all incubation times. Besides, the normalized thickness of PMMA-*b*-PAA brush at the lowest thickness of its PMMA block (2.8 nm) is higher by ∼35% than that of PAA homopolymer brush (with thickness of ∼78 nm; cf. Figure 4) after 120 h of incubation. We can thus deduce that the stability of PAA brush can be significantly enhanced by introducing a neutral block between PAA and the substrate and that its stability increases with increasing molecular weight of the neutral block, which is also in agreement with previous findings by Paripovic et al.[17] and Quintana et al.[25] It is necessary to point out that in the work done by Paripovic et al. no degrafting was observed for surface-grafted PMMA-*b*-PMAA diblock brushes, which is different from what we observed for PMMA-*b*-PAA diblock brushes. This is possibly because the thickness of the PMMA bottom block in their work is about 40 nm (i.e., ∼4 times as the highest PMMA block thickness in our work) and the thickness of PMAA block is much smaller than that of the PAA block used in this work.

To interpret the effects of the neutral block (PMMA or PPEGMA) on the stability of the diblock copolymer brushes, we hypothesize that the neutral polymer block may act as a spacer that separates the charged PAA block from the weak linkages in the initiator (i.e., ester group) and the bonding to the substrate (i.e., Si−O bond), which could weaken the transmission of tension due to electrostatic repulsion to the weak linkages and therefore improve the stability of tethered polymers. In addition, compared with the hydrophilic PPEGMA block, the hydrophobic PMMA block could collapse in the aqueous incubation solution to form a shielding layer

protecting the weak linkages from hydrolysis. These are illustrated schematically in Figure 6.

To validate our hypothesis, we estimate the size of PMMA block in an aqueous buffer. Considering only the bottom PMMA block in the absence of the top PAA block, we can use the equation $R_{gl} \approx b\left(\frac{N}{2\chi - 1}\right)^{1/3}$ to estimate the size of PMMA globules,[26] where N is the number of Kuhn monomers, $b \cong 1.5$ nm is the Kuhn monomer length[26] and $\chi \cong 3.6$ is the Flory interaction parameter of PMMA with water at room temperature.[27] For PMMA brush with dry thickness of about 2−10 nm, its molecular weight is in the range of about 2400−12 000 g/mol. This corresponds to 4−20 Kuhn monomers (molecular weight of Kuhn monomer for PMMA: 598 Da).[26] Therefore, we calculate radius of the globules (R_{gl}) to be in the range of 1.3−2.2 nm in aqueous buffer. The distance (d) between neighboring chains can be estimated as $d \cong 1/\sqrt{\sigma} = 1.4$ nm with grafting density σ of 0.5 chains/nm²,[20] Comparing the diameter of the PMMA globule ($2R_{gl}$) and the distance between neighboring chains (d), the collapsed PMMA globules may merge into a laterally uniform layer ($2R_{gl} > d$).

Now we consider whether the PMMA globules remain in collapsed state when the top PAA block is present. The critical force required to unfold the PMMA globules can be estimated as[28]

$$f_c \approx \frac{k_B T}{\xi_T} \approx \frac{|v|}{b^3}\frac{k_B T}{b} \approx (2\chi - 1)\frac{k_B T}{b}$$

where ξ_T is the thermal blob size, v is the excluded volume, and $k_B T$ is thermal energy. This yields $f_c \approx 17$ pN. We can also estimate the stretching force due to the charged PAA block with degree of dissociation ∼1 in the salted brush regime as (assuming that the monomeric unit size is equal to Kuhn segment size)[29]

$$f \cong \left(\frac{\sigma}{aC_S}\right)^{1/3}\frac{k_B T}{a}$$

where $C_S = 0.05$ mol/L is the salt concentration and a is the monomeric unit size. We use $a \approx 1$ nm to estimate the stretching force as $f \cong 10$ pN. Comparing f and f_c, we can conclude tentatively that the stretching force is not large
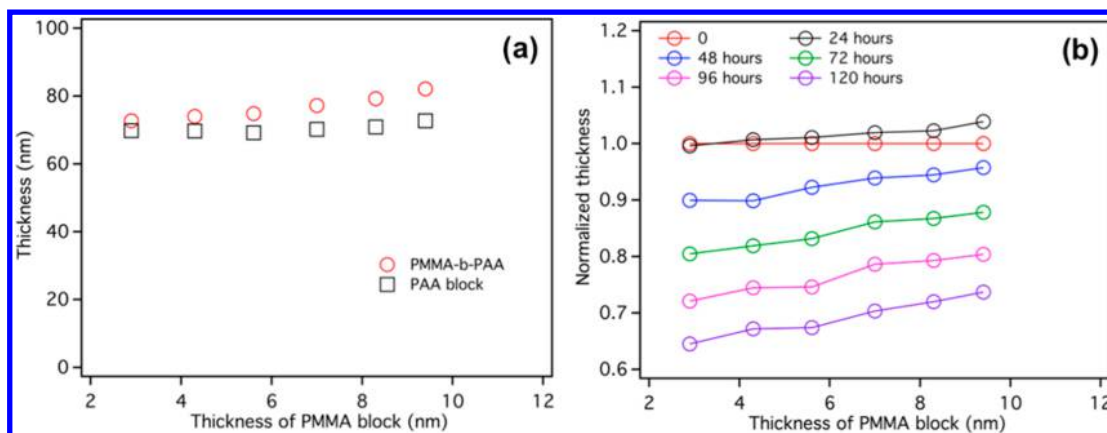
Figure 7. Thickness profile of PMMA-*b*-PAA (a) and its corresponding ellipsometric thickness normalized by initial thickness after incubation for various times in 0.1 M ethanolamine buffer (pH = 9.0) with 0.05 M NaCl and 5% acetone as a function of the thickness of the PMMA block.

enough to unfold the collapsed PMMA globules. Even if the PMMA globules were unfolded, the hydrophobic PMMA layer could still protect the weak linkages, just not as effectively as collapsed and dense layer of PMMA globules, but better than hydrophilic PPEGMA.

To further prove our hypothesis, we added 5 vol % acetone, a good solvent for PMMA, into the incubation solution and conducted the same incubation experiments for another PMMA-*b*-PAA brush sample that was made in the same batch as the one shown in Figure 5a. As shown in Figure 7b, the brush stability increases with increasing the PMMA block length, which is consistent with our observations reported in Figures 5c and 5d. However, by comparing the data in Figures 7b and 5c, one can clearly see that the PMMA-*b*-PAA brush showed reduced stability during incubation that involved a small amount of acetone in the incubation solution. Even a small amount of acetone in solution can cause (at least partial) swelling of the hydrophobic PMMA block. It is worth mentioning that ethanolamine may also swell PMMA a little, but the volume fraction of ethanolamine in the buffer solution is approximately 0.6%, which is much smaller than that of acetone (5%). We therefore neglect swelling of the PMMA block due to ethanolamine. Such swollen PMMA block cannot effectively protect the ester group and/or Si−O bond from hydrolysis, thus leading to the decrease in stability of the diblock copolymer brush. In this case, the PMMA-*b*-PAA brush behaves like the PPEGMA-*b*-PAA brush shown in Figure 5d during the incubation experiments, which supports our hypothesis illustrated in Figure 6.

CONCLUSIONS

We have investigated the stability of diblock copolymer brushes with a neutral block (PMMA or PPEGMA) and a PAA block and have demonstrated that the neutral block plays an important role in affecting the overall stability of the copolymer brush incubated in the buffer solution. Our findings suggest that the stability of both PMMA-*b*-PAA and PPEGMA-*b*-PAA diblock copolymer brushes increases with increasing length (i.e., molecular weight) of the neutral bottom block and that the diblock copolymer brushes showed significantly enhanced stability compared with PAA homopolymer brush. We attribute this to the introduction of the neutral block that acts as a spacer separating the charged PAA block from weak linkages (e.g., ester group and/or Si−O bond) close to the substrate and therefore weakens the transmission of tension due to

electrostatic repulsion to the weak linkages. PMMA-*b*-PAA brush shows higher stability than PPEGMA-*b*-PAA brush during incubation in the same aqueous buffer solution, suggesting that hydrophobicity of the neutral block also affects the stability of the diblock copolymer. These findings hold significant importance in the application of polyelectrolyte brushes in aqueous environments by shedding some light on how to improve the stability of polyelectrolyte brushes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.7b01825.

Thickness profiles of PtBA brush with grafting density gradient, PMMA-*b*-PtBA brush and PPEGMA-*b*-PtBA brush, and their corresponding ratios of PAA (block) thickness to PtBA (block) thickness; thickness of PtBA brush as a function of polymerization time (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail jgenzer@ncsu.edu (J.G.).

ORCID Ⓘ

Yuanchao Li: 0000-0002-8005-947X

Jan Genzer: 0000-0002-1633-238X

Present Address

Y.L.: Key Laboratory for Polymeric Composite & Functional Materials of Ministry of Education, School of Materials Science and Engineering, Sun Yat-Sen University, Guangzhou, Guangdong 510275, P. R. China.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Milner, S. T. Polymer Brushes. *Science* **1991**, *251*, 905−914.
(2) Zhao, B.; Brittain, W. J. Polymer brushes: surface-immobilized macromolecules. *Prog. Polym. Sci.* **2000**, *25*, 677−710.

(3) Barbey, R.; Lavanant, L.; Paripovic, D.; Schüwer, N.; Sugnaux, C.; Tugulu, S.; Klok, H.-A. Polymer Brushes via Surface-Initiated Controlled Radical Polymerization: Synthesis, Characterization, Properties, and Applications. *Chem. Rev.* **2009**, *109*, 5437−5527.

(4) Zoppe, J. O.; Ataman, N. C.; Mocny, P.; Wang, J.; Moraes, J.; Klok, H.-A. Surface-Initiated Controlled Radical Polymerization: State-of-the-Art, Opportunities, and Challenges in Surface and Interface Engineering with Polymer Brushes. *Chem. Rev.* **2017**, *117*, 1105−1318.

(5) Li, Y.; Sheiko, S. *Molecular Mechanochemistry: Engineering and Implications of Inherently Strained Architectures*; Springer: Berlin, 2015; pp 1−36.

(6) Klok, H.-A.; Genzer, J. Expanding the Polymer Mechanochemistry Toolbox through Surface-Initiated Polymerization. *ACS Macro Lett.* **2015**, *4*, 636−639.

(7) Tugulu, S.; Klok, H.-A. Stability and Nonfouling Properties of Poly(poly(ethylene glycol) methacrylate) Brushes under Cell Culture Conditions. *Biomacromolecules* **2008**, *9*, 906−912.

(8) Ataman, N. C.; Klok, H.-A. Degrafting of Poly(poly(ethylene glycol) methacrylate) Brushes from Planar and Spherical Silicon Substrates. *Macromolecules* **2016**, *49*, 9035−9047.

(9) Deng, Y.; Zhu, X. Y. A Nanotumbleweed: Breaking Away a Covalently Tethered Polymer Molecule by Noncovalent Interactions. *J. Am. Chem. Soc.* **2007**, *129*, 7557−7561.

(10) Melzak, K. A.; Yu, K.; Bo, D.; Kizhakkedathu, J. N.; Toca-Herrera, J. L. Chain Length and Grafting Density Dependent Enhancement in the Hydrolysis of Ester-Linked Polymer Brushes. *Langmuir* **2015**, *31*, 6463.

(11) Zhang, Y.; He, J. A.; Zhu, Y.; Chen, H.; Ma, H. Directly observed Au-S bond breakage due to swelling of the anchored polyelectrolyte. *Chem. Commun.* **2011**, *47*, 1190−1192.

(12) Lyu, B.; Cha, W.; Mao, T.; Wu, Y.; Qian, H.; Zhou, Y.; Chen, X.; Zhang, S.; Liu, L.; Yang, G.; Lu, Z.; Zhu, Q.; Ma, H. Surface Confined Retro Diels−Alder Reaction Driven by the Swelling of Weak Polyelectrolytes. *ACS Appl. Mater. Interfaces* **2015**, *7*, 6254−6259.

(13) Enomoto, K.; Takahashi, S.; Iwase, T.; Yamashita, T.; Maekawa, Y. Degradation manner of polymer grafts chemically attached on thermally stable polymer films: swelling-induced detachment of hydrophilic grafts from hydrophobic polymer substrates in aqueous media. *J. Mater. Chem.* **2011**, *21*, 9343−9349.

(14) Bain, E. D.; Dawes, K.; Özçam, A. E.; Hu, X.; Gorman, C. B.; Šrogl, J.; Genzer, J. Surface-Initiated Polymerization by Means of Novel, Stable, Non-Ester-Based Radical Initiator. *Macromolecules* **2012**, *45*, 3802−3815.

(15) Galvin, C. J.; Bain, E. D.; Henke, A.; Genzer, J. Instability of Surface-Grafted Weak Polyacid Brushes on Flat Substrates. *Macromolecules* **2015**, *48*, 5677−5687.

(16) Borozenko, O.; Godin, R.; Lau, K. L.; Mah, W.; Cosa, G.; Skene, W. G.; Giasson, S. Monitoring in Real-Time the Degrafting of Covalently Attached Fluorescent Polymer Brushes Grafted to Silica Substrates—Effects of pH and Salt. *Macromolecules* **2011**, *44*, 8177−8184.

(17) Paripovic, D.; Klok, H.-A. Improving the Stability in Aqueous Media of Polymer Brushes Grafted from Silicon Oxide Substrates by Surface-Initiated Atom Transfer Radical Polymerization. *Macromol. Chem. Phys.* **2011**, *212*, 950−958.

(18) Sheiko, S. S.; Panyukov, S.; Rubinstein, M. Bond Tension in Tethered Macromolecules. *Macromolecules* **2011**, *44*, 4520−4529.

(19) Matyjaszewski, K.; Xia, J. Atom Transfer Radical Polymerization. *Chem. Rev.* **2001**, *101*, 2921−2990.

(20) Patil, R. R.; Turgman-Cohen, S.; Šrogl, J.; Kiserow, D.; Genzer, J. Direct Measurement of Molecular Weight and Grafting Density by Controlled and Quantitative Degrafting of Surface-Anchored Poly(methyl methacrylate). *ACS Macro Lett.* **2015**, *4*, 251−254.

(21) Dong, R.; Lindau, M.; Ober, C. K. Dissociation Behavior of Weak Polyelectrolyte Brushes on a Planar Surface. *Langmuir* **2009**, *25*, 4774−4779.

(22) Gong, P.; Wu, T.; Genzer, J.; Szleifer, I. Behavior of Surface-Anchored Poly(acrylic acid) Brushes with Grafting Density Gradients on Solid Substrates: 2. Theory. *Macromolecules* **2007**, *40*, 8765−8773.

(23) Galvin, C. J.; Dimitriou, M. D.; Satija, S. K.; Genzer, J. Swelling of Polyelectrolyte and Polyzwitterion Brushes by Humid Vapors. *J. Am. Chem. Soc.* **2014**, *136*, 12737−12745.

(24) Desseaux, S.; Hinestrosa, J. P.; Schüwer, N.; Lokitz, B. S.; Ankner, J. F.; Kilbey, S. M.; Voitchovsky, K.; Klok, H.-A. Swelling Behavior and Nanomechanical Properties of (Peptide-Modified) Poly(2-hydroxyethyl methacrylate) and Poly(poly(ethylene glycol) methacrylate) Brushes. *Macromolecules* **2016**, *49*, 4609−4618.

(25) Quintana, R.; Gosa, M.; Jańczewski, D.; Kutnyanszky, E.; Vancso, G. J. Enhanced Stability of Low Fouling Zwitterionic Polymer Brushes in Seawater with Diblock Architecture. *Langmuir* **2013**, *29*, 10859−10867.

(26) Rubinstein, M.; Colby, R. H. *Polymer Physics*; Oxford University Press: Oxford, 2003.

(27) Davis, E. M.; Elabd, Y. A. Water Clustering in Glassy Polymers. *J. Phys. Chem. B* **2013**, *117*, 10629−10640.

(28) Polotsky, A. A.; Charlaganov, M. I.; Leermakers, F. A. M.; Daoud, M.; Borisov, O. V.; Birshtein, T. M. Mechanical Unfolding of a Homopolymer Globule Studied by Self-Consistent Field Modeling. *Macromolecules* **2009**, *42*, 5360−5371.

(29) Zhulina, E. B.; Birshtein, T. M.; Borisov, O. V. Theory of Ionizable Polymer Brushes. *Macromolecules* **1995**, *28*, 1491−1499.