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Crucial Nonelectrostatic Effects on Polyelectrolyte Brush Behavior

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ABSTRACT: Polyelectrolyte brushes have received extensive attention due to their swelling behavior in aqueous solutions, which is a result of their ionic nature and nonelectrostatic (polymer-polymer and polymer-solvent) interactions. While the nonelectrostatic contributions are typically assumed to be negligible compared to the ion osmotic pressure, we present herein a systematic investigation of how the nonelectrostatic interactions dramatically affect the swelling behavior of polyelectrolyte brushes. Using a modular synthesis procedure, polyelectrolyte brushes with similar chain lengths, grafting densities and charge densities but with various side chains were synthesized. The swelling behaviors of the brushes were then thoroughly investigated as a function of grafting density and ionic strength using ellipsometry. A theoretical mean-field approach was also developed to quantify the contributions of the ion osmotic and nonelectrostatic effects. Accordingly, it was both experimentally and theoretically demonstrated how fundamentally different swelling behaviors can exist depending on the relative contributions of ion osmotic and nonelectrostatic effects. This new insight reveals new opportunities for applications of polyelectrolyte brushes based on their tunable hydrophobicity and provides new ideas for fundamental investigations of these systems.

1 INTRODUCTION

The swelling behavior of a polyelectrolyte brush in an aqueous medium is the result of a balance between various forces, such as the osmotic pressure of counterions (the ion osmotic effect), solvent-dependent excluded-volume effects (nonelectrostatic effects), and chain elasticity.¹⁻³ The swelling behavior of polyelectrolyte brushes has been theoretically described by scaling relations, which suggest various regimes depending on the brush grafting density (σ), chain charge fraction (f) and ionic strength (c_s) of the solution.⁴⁻⁸ These scaling relations are typically obtained for θ -solvent conditions and thus neglect the contributions of nonelectrostatic interactions and describe the brush thickness (h) within three regimes of swelling behavior with respect to ionic strength. The so-called osmotic brush regime (h ~ $c_s^0 \sigma^0$ and h ~ $c_s^{1/3} \sigma^{-1/3}$ for strong and weak polyelectrolyte brushes, respectively) is found at low ionic strength; the salted brush regime (h ~ $\sigma^{1/3} c_s^{-1/3}$) is found at intermediate ionic strength; and the "quasineutral" brush regime is found at high ionic strength. The scaling relations have been evaluated experimentally although, rarely under θ -solvent conditions.⁹⁻¹⁸ Thus, the results of those studies often show deviations from the theoretical predictions for both strong and weak polyelectrolyte brushes.¹⁰⁻¹⁶ In contrast to predictions based on the scaling laws, experimental studies of polyelectrolyte brushes demonstrate an increase in the thickness with the grafting density in the osmotic brush regime and further a more gradual variation in thickness with ionic strength in the osmotic and salted brush regimes.^{10-16, 18} Both quantitative and qualitative discrepancies between the theoretical and experimental data have mainly been attributed to an interplay between nonelectrostatic effects (which under most real conditions, cannot

be neglected) and the ion osmotic pressure (which was originally assumed to dominate the polyelectrolyte brush swelling behavior).^{2,11,13,19,20}

With respect to nonelectrostatic effects, theoretical studies of polyelectrolyte brushes predict a transition from the swollen to the collapsed state under poor solvent conditions.^{21,22} Further, the formation of lateral morphologies (e.g., cylindrical aggregates) has been shown under poor solvent conditions using molecular dynamics simulations.^{23,24} Several experimental studies have demonstrated an impact of nonelectrostatic effects by varying either the solvent quality for a certain polyelectrolyte brush²⁵⁻²⁷ or the brush chemistry.²⁸⁻³¹ Wang *et al.*²⁷ have shown that the swelling and collapse of a polyelectrolyte brush become less pronounced by increasing the methanol content in a water/methanol mixture. Willot *et al.*³⁰ investigated the swelling behavior of three weak polyelectrolyte brushes of varying monomer hydrophobicities. With enhanced monomer hydrophobicity, the thickness in the neutral brush regime was reduced, and the transition from the neutral to the osmotic brush regime was shifted to larger ionic strengths. However, despite these scattered observations, the interplay between the ion osmotic effect and the nonelectrostatic effects is still poorly understood. Thus, instead of providing additional experimental evidence for the deviation between the original scaling law and real brush behavior, we aim to deliver a full but relatively simple explanation for the swelling behavior of polyelectrolyte brushes.

In this study, we employed a modular synthesis method that enabled a systematic comparison of brushes with various chemical structures. The polyelectrolyte brushes were obtained by synthesizing poly(2-dimethylaminoethyl) methacrylate (PDMAEMA) brushes with controlled grafting densities followed by postpolymerization quaternization with various alkyl halides. Consequently, the chain length, chain dispersity, grafting density, and charge density were all fixed, whereas the side chains were systematically varied. This rational molecular design enables a direct experimental investigation of the nonelectrostatic effects on polyelectrolyte brushes. Additionally, a simple mean-field model was developed that accounts for both ion osmotic and nonelectrostatic effects. With this direct comparison between experimental data and theoretical predictions, we are able to quantify the relationships among the molecular structure, solvent quality and swelling behavior of polyelectrolyte brushes.

2 EXPERIMENTAL SECTION

2.1 Materials

(3-Aminopropyl)triethoxysilane (APTES), toluene, dichloromethane, tetrahydrofurane (THF), α -bromoisobutyrylbromide, triethylamine, methanol, 2,2'- bipyridine (BPy), (2-dimethylaminoethyl) methacrylate (DMAEMA), ethyl α -bromoisobutyrate (EBiB), copper (I) bromide (CuBr), iodomethane, 1-bromobutane, 1-bromodecane, hydrogen bromide (HBr), sodium hydroxide (NaOH), and sodium bromide (NaBr) were obtained from Sigma Aldrich and were used as received. Propionyl bromide was purchased from Tokyo Chemical Industry Co. (TCI) and used as received. Aqueous solutions were prepared using ultrapure water with a resistance of 18.2 M Ω .cm (Sartorius Arium Pro). Sodium bromide was used to adjust the ionic strength, and sodium hydroxide/hydrogen bromide was used to adjust the pH.

2.2 Synthesis of PDMAEMA brushes and quaternization

Thermally oxidized silicon wafers (Wafer Net, USA) were washed with acetone, ethanol, and deionized water 3 times followed by plasma cleaning for 3 minutes (Harrick Plasma) under 500 mTorr water vapor. Afterwards, a solution of APTES in toluene (volume ratio: 1:1) was used to functionalize the silicon wafers with amine groups via vapor deposition for 24 h. The samples were then washed with toluene, ethanol, and acetone and dried under a stream of argon. The grafting density of the samples was adjusted by using a mixture of an inactive acyl bromide (propionyl bromide) and an active initiator (α -bromoisobutyrylbromide).³²⁻³⁴ For the higher grafting density sample, a mixture of dichloromethane (20 mL) and triethylamine (960 mg, 9.5 mmol) was prepared, and then α -bromoisobutyrylbromide (1.85 g, 8.1 mmol) was added dropwise at 0 °C. For the lower grafting density sample, a similar procedure was employed, but a mixture of propionyl bromide (1.0 g, 7.3 mmol) and α -bromoisobutyrylbromide (185 mg, 0.8 mmol) was used instead of pure α -bromoisobutyrylbromide. The reaction mixture was stirred at room temperature overnight. After rinsing with dichloromethane, acetone, and ethanol, the initiator grafted surfaces were dried under argon and used immediately for the polymerization reaction.

PDMAEMA was synthesized using surface-initiated atom transfer radical polymerization (SI-ATRP).³⁵⁻³⁷ The monomer (DMAEMA) was purified by passing it through an alumina column. Initiator-grafted surfaces from the previous step were placed into a solution of DMAEMA (8.4 g, 53 mmol) in methanol (20 mL). Subsequently, the sacrificial initiator (EBiB) (11 mg, 0.06 mmol) and the ligand (BPy) (166 mg, 1.1 mmol) were dissolved, and the mixture was bubbled with argon for 40 minutes. Afterwards, the catalyst (CuBr) (77 mg, 0.54 mmol) was added to initiate polymerization. The reaction mixture was purged with argon for an additional 15 minutes and stirred under a positive pressure of argon at 25 °C. The molar ratio of reactants was [DMAEMA]:[EBiB]:[CuBr]:[BPy]=100:0.1:1:2.

Conversion of the weak polyelectrolyte brushes (PDMAEMA) to the strong polyelectrolyte brushes was carried out via quaternization of the amine groups by using excessive amounts of alkyl halides.^{31,38-40} The strong polyelectrolyte brush with the methyl side group (PDMAEMA-QC1) was synthesized using 1000 mM iodomethane in 10 mL THF at 40 °C for 18 hours. To employ bromide as the counterion, the sample was subsequently exposed to an ion exchange process using 3 cycles of immersion in a 100 mM NaBr solution for 10 minutes followed by rinsing and then 3 cycles of immersion in 3.0 M NaBr solution for 10 minutes followed by rinsing and then 3 cycles of polyelectrolyte brushes with longer side groups (PDMAEMA-QC4 and PDMAEMA-QC10) were synthesized using 100 mM 1-bromobutane and 1-bromodecane, respectively, in 10 mL THF at 40 °C. The quaternization reaction was continued until the samples showed no significant effect of unreacted basic groups, as verified by the pH response (Supporting Information, S2). Based on the dry thicknesses and the

estimation of the grafting density in a swollen brush, we confirmed that no degrafting occurs during the quaternization reaction (Supporting Information, S3).

In total, 8 samples were examined in this study, including two sets of samples with a lower or higher grafting density (L or H), and in each set, there were 4 samples (PDMAEMA, PDMAEMA-QC1, PDMAEMA-QC4, and PDMAEMA-QC10). To distinguish between the samples, the nomenclature PDMAEMA(-QCx)-L/H is used, where x denotes the number of carbon atoms in the side group (1, 4 or 10) and L and H stand for the lower grafting density and higher grafting density, respectively.

2.3 Ellipsometry

The thickness of the brushes was determined using spectroscopic ellipsometry (M-2000U, J. A. Woollam Co., Inc.). The instrument's standard liquid cell (5 mL heated liquid cell) was used for the measurements in solution. In situ measurements were conducted over a wavelength range between 245 and 1000 nm and at an angle of incidence of 75°. The brush was considered to be under equilibrium when the variation in thickness was lower than 0.2 nm over a 10-minute period. The ionic strength studies were conducted at pH 6.00 ± 0.05 unless otherwise stated. The data analysis was conducted using the instrument software (CompleteEASE, J.A. Woollam Co., Inc.). The employed optical model comprises a thick Si substrate, an intermediate roughness layer, a SiO₂ layer (99.0 nm, as obtained from the bare wafer data), and a transparent polymer layer with unknown thickness and optical constants. The Cauchy relation (n = A + B/ λ^2) was used to describe the optical dispersion of the hydrated brush. The optical dispersions of the saline solutions were estimated from measurements on a bare silicon wafer (Supporting Information, S4). The cross-correlation factors for the model parameters were always lower than 0.9, indicating that the free parameters (thickness, A, and B) are not coupled; in addition, the uniqueness of the estimated thickness was investigated using thickness-mean square error (MSE) plots, and the reproducibility of the ellipsometry results was verified (Supporting Information, S5).

3 RESULTS AND DISCUSSION

3.1 Experimental results

Figure 1 summarizes the synthesis route of the investigated brush samples. Two PDMAEMA brushes were first synthesized with an estimated number-average molecular weight (M_n) of 105 kg·mol⁻¹, one with a low grafting density (PDMAEMA-L, 0.086 chain·nm⁻²) and the other with a high grafting density (PDMAEMA-H, 0.257 chain·nm⁻²) (Supporting Information, S1). Next, each PDMAEMA brush was converted to strong polyelectrolyte brushes with varying side chains using postpolymerization quaternization with C₁, C₄, and C₁₀ alkyl halides (Supporting Information, S2). The employed synthesis design enables controlled variation of the side group hydrophobicity and bulkiness, which allows for a systematic investigation of nonelectrostatic effects on the swelling behavior of the polyelectrolyte brushes.

Figure 2 summarizes the swelling behavior of all the brushes studied as a function of ionic strength. Since PDMAEMA should be fully charged at pH 4, the number of charges are independent of ionic strength, and we can thus directly compare the swelling behavior of PDMAEMA brushes at pH 4 to the swelling behavior of the strong polyelectrolyte brushes (see details of the analysis of the PDMAEMA brushes at pH 4.0 as a function of pH and ionic strength in Supporting Information, S6). Figure 2a displays the thickness of PDMAEMA brushes at pH 4.0 as a function of ionic strength. Here, it is seen that both the PDMAEMA-H and PDMAEMA-L brushes are found in the swollen osmotic brush regime at ionic strengths lower than 10 mM. For ionic strength. Here, it should be noted that the thickness of PDMAEMA-H is greater than that of PDMAEMA-L regardless of the ionic strength, which contradicts the predictions from the simple scaling relations for the osmotic brush regime.⁶ This effect of grafting density can be explained by the interplay between the ion osmotic effect and the nonelectrostatic effects, which were not included in the original scaling relations. Thus, increased grafting density results in a higher local concentration of repeating units, leading to increased nonelectrostatic effects.

Next, PDMAEMA is converted to a strong polyelectrolyte brush with methyl side groups (PDMAEMA-QC1), as shown in Figure 2b. This conversion not only changes each of the



Figure 1. Synthesis route and schematic illustration of the polyelectrolyte brush samples; starting from the substrate, the initiator was grafted with two different grafting densities. SI-ATRP was conducted on the samples to obtain PDMAEMA brushes. Next, PDMAEMA brushes were converted to PDMAEMA-QC1, PDMAEMA-QC4, and PDMAEMA-QC10 brushes.



Figure 2. a) Thickness of PDMAEMA-H (solid line, \circ) and PDMAEMA-L (dashed line, \Box) as a function of ionic strength at pH=4.0, b) thickness of PDMAEMA-QC1-H (solid line, \circ) and PDMAEMA-QC1-L (dashed line, \Box) as a function of ionic strength and c) thickness of PDMAEMA-QC4-H (solid line, \circ), PDMAEMA-QC4-L (dashed line, \Box), PDMAEMA-QC10-H (solid line, \circ), and PDMAEMA-QC10-L (dashed line, \Box) as a function of ionic strength.

basic groups to have a permanent charge but also changes the polymer-polymer and polymer-solvent interactions in the brush. Thus, when comparing the swelling behavior of the PDMAEMA-QC1 brushes with the PDMAEMA brushes at pH 4 (when they are fully charged), we expect the differences to mainly be due to nonelectrostatic interactions. For each grafting density of the PDMAEMA-QC1 brushes, three brush regimes are observed, i.e., the osmotic brush regime, the salted brush regime, and the quasineutral brush regime. At the highest ionic strength studied (3.0 M), the thickness of PDMAEMA-QC1 is evidently greater than that of PDMAEMA for similar grafting densities (PDMAEMA-QC1-H (97 nm) > PDMAEMA-H (73 nm) and PDMAEMA-QC1-L (63 nm) > PDMAEMA-L (35 nm)). Since the ion osmotic effect is negligible in the quasineutral brush regime, the significant difference in the thickness could be attributed to a better solvent quality of PDMAEMA-QC1 than of PDMAEMA under aqueous conditions. Even in the osmotic brush regime, the thickness of PDMAEMA-QC1 is significantly higher than that of PDMAEMA, demonstrating the significant effect of solvent quality in the osmotic brush regime. To this end, it should be noted that the slightly bulkier repeating units in PDMAEMA-QC1 compared to in PDMAEMA are insufficient to account for the large difference in thickness of the two brushes.

Moreover, in the osmotic brush regime, the grafting density seems to have a minor effect on PDMAEMA-QC1 thickness, which suggests that compared to the case of the PDMAEMA brushes, in the case of PDMAEMA-QC1, the ion osmotic effect dominates significantly over nonelectrostatic contributions. To this end, we propose that PDMAEMA could have stronger intrachain and interchain interactions than those in PDMAEMA-QC1 due to its extensive ability to form hydrogen bonds. For PDMAEMA-QC1, this ability is partially lost, which is why the ion osmotic effect dominates. However, with increasing ionic strength, the ion osmotic effect is weakened, so the relative contribution of nonelectrostatic effects becomes progressively more pronounced. This is shown by a steeper collapse in the brush thickness in the salted brush regime for the sample with the lower grafting density than with the higher grafting density (where nonelectrostatic interactions naturally play a larger role). Similarly, in the quasineutral regime, the grafting density also has a notable effect, i.e., PDMAEMA-QC1-H shows a greater thickness.

Finally, strong polyelectrolyte brushes with longer alkyl side groups, i.e., PDMAEMA-QC4 and PDMAEMA-QC10 with butyl and decyl side groups, are investigated (Figure 2c). A longer alkyl side group is expected to affect the nonelectrostatic interactions in two ways: (i) an increased polymer hydrophobicity, favoring a collapsed brush conformation ("phase separation"), and (ii) an enhanced bulkiness, giving rise to larger steric effects and swelling. In general, our experimental results reveal that the ion osmotic effects on the brush thicknesses are negligible, suggesting that the first nonelectrostatic effect (hydrophobic collapse) is the controlling factor. However, while the collapse appears to be due to the hydrophobicity of the side groups, the actual collapsed brush thickness appears to be controlled by the second nonelectrostatic effect (steric repulsion), which first is shown by the higher grafting density brushes (PDMAEMA-QC4-H and PDMAEMA-QC10-H) having greater thickness than the lower grafting density brushes (PDMAEMA-QC4-L and PDMAEMA-QC10-L) at all ionic strengths and second is shown by the brush thickness increasing from PDMAEMA-QC4 with side groups that are less bulky to PDMAEMA-QC10 with side groups that are bulkier.

3.2 Mean-field approach including nonelectrostatic contributions

From the results presented in Figure 2, we demonstrate that nonelectrostatic effects, i.e., steric, polymer-polymer, and polymer-water forces, can notably contribute to the polyelectrolyte brush behavior. The original scaling relations of polyelectrolyte brushes were obtained by solving a force balance equation accounting for the ion osmotic effect and the chain elasticity.^{6,8} Later, an improved mean-field model was developed based on the original theory by taking into account the finite extensibility of chains and the excluded volume effects in a good solvent.⁴³ The results of the model were in good agreement with the data generated by the simulation methods. In this work, we extended this model by taking the full effect of nonelectrostatic contributions into account (a detailed discussion of the used assumptions, estimation and variables are provided in the Supporting Information, S7). Briefly, we introduce a pressure balancing equation including a term describing the nonelectrostatic contributions, which are based on the Flory-Huggins free energy for a semidilute polymer solution: ^{6,21,44-47}

$$\pi_{ion} + \pi_{NE} + \pi_{el} = 0 \tag{1}$$

with

$$\frac{\pi_{NE}}{k_B T} = \frac{1}{a^3} \left(-\frac{1}{2} \tau \phi_m^2 + \frac{1}{3} \omega \phi_m^3 \right)$$
(2)

Here, π_{ion} , π_{NE} , and π_{el} are the ion osmotic pressure, the osmotic pressure due to nonelectrostatic effects, and the elastic pressure due to chain stretching, respectively. τ is the excluded volume parameter (second virial coefficient) that is negative for good solvents and positive for poor solvents, ϕ_m is the polymer volume fraction, and ω is the third virial coefficient. Therefore, π_{NE} accounts for two contributions, i.e., the second and third virial terms. The latter term is always positive, whereas the former term could be positive or negative depending on the solvent quality. For small values of ϕ_m , the coefficients can be estimated by $\tau = 2\chi - 1$ and $\omega = 1$, where χ is the Flory-Huggins parameter, which accounts for the variation in solvent quality, i.e., χ increases with decreasing solvent quality. Rearranging eq. 1 after decoupling the two contributions of the nonelectrostatic effects and converting the pressure values to dimensionless contributions (C) gives the main balancing equation: 6,8,43,48,49

$$C_{ion} + C_{NE2} + C_{NE3} + C_{el} = 0$$
(3)

$$C_{ion} = \frac{\pi_{el}}{k_B T} \times \frac{r^2 a}{\sigma} = fr \left[\sqrt{\left(\frac{2c_s ar}{f\sigma}\right)^2 + 1} - \frac{2c_s ar}{f\sigma} \right]$$
(4)

$$C_{NE2} = -\frac{\tau \phi^2}{2a^3} \times \frac{r^2 a}{\sigma} = \frac{-(\chi - \frac{1}{2})\vartheta_m^2 \sigma}{a^4}$$
(5)

$$C_{NE3} = \frac{\omega \phi^3}{3a^3} \times \frac{r^2 a}{\sigma} = \frac{\vartheta m^3 \sigma^2}{3a^5 r}$$
(6)

$$C_{el} = \frac{\pi_{el}}{k_B T} \times \frac{r^2 a}{\sigma} = -r^3 \frac{3 - r^2}{1 - r^2}$$
(7)

Here, C_{ion} , C_{NE2} , C_{NE3} , and C_{el} represent the contributions of the ion osmotic pressure, the second virial term, the third virial term, and the polymer elasticity, respectively. Eq 4 is obtained based on the difference between the ion concentration inside the brush and in the medium assuming the absence of ion condensation, electro-neutrality in the brush, and Boltzmann distribution for the ions. The parameters f, r, c_s, a, σ , and ν_m are the charge fraction, the relative height (thickness/contour length), the salt concentration in the medium, the size of the polymer segment, the grafting density, and the volume of each repeating unit, respectively. By solving eq. 3 for a given grafting density and ionic strength, the relative height is then obtained as a function of χ .

Figure 3a shows the calculated relative brush height for a brush with and without the nonelectrostatic terms as a function of solvent quality in the osmotic brush regime (ionic strength of 1 mM) and for a grafting density of $\sigma = 0.086$ chain·nm⁻² (similar to the experimental samples with low grafting density). Accordingly, the nonelectrostatic effects could result in swelling or collapse of the brush in the osmotic brush regime, depending on the solvent quality. Under good solvent conditions (χ <0.5), the brush is found in a more swollen state compared to the pure ion osmotic brush. In contrast, the poorer the solvent, the more collapsed the brush is compared to the pure ion osmotic brush.

Since our experimental brush samples show partial hydrophobicity, we focus on the magnitude of the different relative contributions in the region of poor solvent conditions, $\chi > 0.5$ (see Figure 3b). At relatively low χ values (close to θ -solvent conditions), the ion osmotic and elastic terms dominate. However, with increasing χ , the relative contributions from the ionic and elastic terms notably decrease, whereas the contributions from the two nonelectrostatic terms progressively increase.

This means that the brush behavior is closer to the behavior predicted by the scaling relations for χ values approaching 0.5 (θ -solvent conditions). For high χ values ($\chi \approx 1.0$), nonelectrostatic effects dominate, and the brush collapses to a thickness where the second and third virial terms are balanced. However, at intermediate χ values, both the ion osmotic pressure and nonelectrostatic effects contribute significantly, and the brush swelling behavior becomes complex.

In an attempt to correlate this complex swelling behavior to our experimental observations (Figure 2), we use eq. 3 to predict the brush thickness changes as a function of ionic strength for three χ -values ($\chi = 0.5$, 0.75, and 1.0), which represent the three scenarios discussed above (see Figure 3c). With this approach, the modeling data enable a more quantitative evaluation of the experimental swelling data (Figure 2) in terms of ion osmotic and nonelectrostatic contributions. From this data, PDMAEMA appears to have a swelling behavior similar to the theoretical brush with an intermediate χ value (χ =0.75), where both the ion osmotic and nonelectrostatic effects comparably influence the brush thickness. PDMAEMA-QC1 demonstrates swelling behavior similar to the theoretical brush with a relatively small χ



Decreasing solvent quality

Figure 3. a) Relative height (r) as a function of χ for a polyelectrolyte brush with a grafting density of $\sigma_{LD} = 0.086$ chain·nm⁻² at an ionic strength of 1 mM and with nonelectrostatic interactions (red) and a pure ion osmotic brush (blue). b) Contributions of the ion osmotic effect (C_{ion}), the second virial term of nonelectrostatic effects (C_{NE2}), the third virial term of nonelectrostatic effects (C_{NE3}), and the chain elasticity (C_{el}) as a function of χ ($\sigma_{LD} = 0.086$ chain·nm⁻² and $c_s = 1$ mM). c) Relative height (r) as a function of ionic strength with $\chi=0.5$ (blue), $\chi=0.75$ (black), and $\chi=1.0$ (red) for brushes with grafting densities of $\sigma_{HD} = 0.257$ chain·nm⁻² and $\sigma_{LD} = 0.086$ chain·nm⁻².

value (χ =0.5), i.e., a significant contribution of the ion osmotic effects and a minor contribution of nonelectrostatic effects in the osmotic brush regime. Finally, the behavior of PDMAEMA-QC4 and PDMAEMA-QC10 brushes resembles that of the theoretical brush with a relatively large χ value (χ =1.0). Therefore, the various swelling behaviors of the brushes could be explained by the effect of solvent quality with the trend of PDMAEMA-QC1>PDMAEMA>PDMAEMA-QC4 \approx PDMAEMA-QC10. Last, in relation to the results presented in Figure 2, we speculated that the slightly higher thickness of PDMAEMA-QC10 than of PDMAEMA-QC4 is due to larger steric effects. This idea was also confirmed by the theoretical model, i.e., by varying the volume of the repeating unit (see the Supporting Information S8).

4 CONCLUSION

We systematically tuned the nonelectrostatic effects of a set of polyelectrolyte brushes while the charge fraction, chain length, chain dispersity, and grafting density (at two different values) were held constant to demonstrate the crucial impact of the nonelectrostatic effects on the swelling behavior of polyelectrolyte brushes. Additionally, we developed a simple mean-field

model to quantify the ionic and nonelectrostatic effects on a polyelectrolyte brush as a function of solvent quality. Overall, we showed that increasing hydrophobicity (decreasing solvent quality) in polyelectrolyte brushes not only causes brush collapse but also decreases the relative contribution of the ion osmotic effects. Based on the experimental and theoretical results, we observed regimes of hydrophobicities/solvent qualities in which either the ion osmotic effects or the nonelectrostatic effects or a combination of the two govern the brush behavior. We believe this new insight increases the general understanding of polyelectrolyte brush behavior and the importance of nonelectrostatic contributions to brush swelling behavior. Furthermore, this work offers both a simple theoretical tool to predict and an experimental route to tune the swelling behavior of polyelectrolyte brushes based on nonelectrostatic effects.

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Notes

The authors declare no competing financial interests.

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SUPPORTING INFORMATION

Determination of the molecular weight and grafting density, verification of the quaternization reaction, evaluation of possible degrafting, determination of the refractive index of the saline solutions, reproducibility of the experimental results, characterization of the weak polyelectrolyte (PDMAEMA) brush with respect to pH and ionic strength, theoretical model, and the effect of bulkiness of the repeating units

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