

Charge State of Weak Polyelectrolyte Brushes Determines Salt-Dependent Swelling and Hysteretic Behavior

Farshad Safi Samghabadi, Shahryar Ramezani Bajgiran, Manuel Villegas Orellana, Jacinta C. Conrad,* and Amanda B. Marciel*



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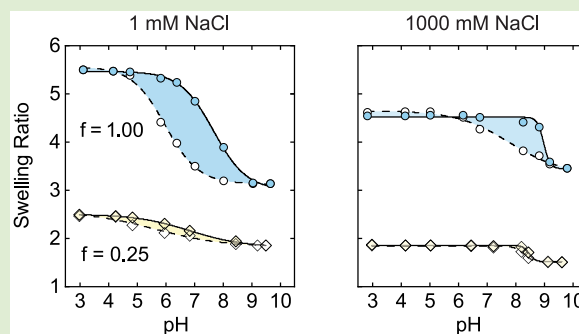
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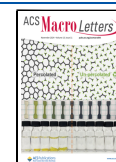
ABSTRACT: We investigate the combined effects of ionizable monomer fraction f , pH, and monovalent salt concentration C_s on the swelling of weak polyelectrolyte brushes (PEBs) by using in situ ellipsometry. Our system consists of random copolymers of basic (2-(dimethylamino)ethyl acrylate, DMAEA) and neutral (2-hydroxyethyl acrylate, HEA) monomers at varying fractions of ionizable monomer. Swelling of the brushes qualitatively follows the trends predicted by scaling laws for PEBs under different charge states but quantitatively deviates at specific ionic strengths and pH values. We posit these deviations stem from the lack of excluded volume effects and assumptions of strong chain stretching in current theoretical models. Most notably, we uncover a salt-dependent, nonmonotonic hysteretic behavior as weak PEB brushes are cycled from protonated to deprotonated and back. The nonmonotonic trend of hysteresis with salt can be explained by an interplay between the protonation facilitating effects of salt in the osmotic regime and the charge screening effects in the salted regime, which make charge distribution along weak PEBs more uniform. Our results provide insight into the mechanisms that determine whether polyelectrolytes exhibit weak versus strong polyelectrolyte behavior in various environmental conditions.



Polyelectrolyte brushes (PEBs) consist of charged polymers end-tethered to impermeable supports and are commonly used to modify the interfacial properties of multicomponent materials. Controlling the interfacial response requires understanding how structural and environmental parameters influence brush conformation, which is vital for applications requiring responsive behavior, such as separations,^{1–3} drug release,⁴ sensing,^{5–8} and actuation.⁹ These parameters include the polymer molecular weight distribution as well as the type and spacing of charges along the polymer. Despite their importance for myriad applications, the swelling behavior of polyelectrolyte brushes in varying salt and pH is not fully understood. PEBs may be described as strong or weak based on their response to varying pH conditions, where strong PEBs remain charged under all environmental conditions and weak PEBs exhibit reversible protonation/deprotonation events in response to varying pH and salt.¹⁰ Classical theories have predicted several conformation regimes for strong and weak PEBs, including the experimentally relevant osmotic and salted brush regimes.^{11,12} For weak PEBs, in the osmotic regime and below the crossover salt concentration C_s^* , the brush height is predicted to scale as $h \approx \left(\frac{\alpha_b}{1-\alpha_b}\right)^{1/3} NC_s^{1/3} \sigma^{-1/3}$, where α_b is the degree of ionization in the bulk, N is the number of monomer segments, C_s is salt concentration, and σ is the

grafting density.^{12,13} This scaling predicts that weak PEB brush height increases with salt concentration in the osmotic regime. By contrast, for strong PEBs the brush height is independent of salt and scales as $h \approx f^{1/2} N$ where f is the charge fraction. In the salted regime, however, the brush height for both weak and strong PEBs is predicted to decrease with salt concentration as $h \approx \beta^{2/3} NC_s^{-1/3} \sigma^{1/3}$, where β is α_b and f for weak and strong PEBs, respectively. The predicted scaling relationships for brush height with salt for weak PEBs imply a nonmonotonic trend between the two regimes. This nonmonotonic behavior has been verified experimentally; the scaling exponents observed in experiments, however, are inconsistent with theoretical predictions and generally exhibit lower absolute values in both regimes.^{14–22} In addition, it remains unclear why this nonmonotonic behavior is observed for weak PEBs at pH values where the charge state is high and strong PEB behavior is expected. This inconsistency opens questions regarding the conditions under which PEBs are expected to

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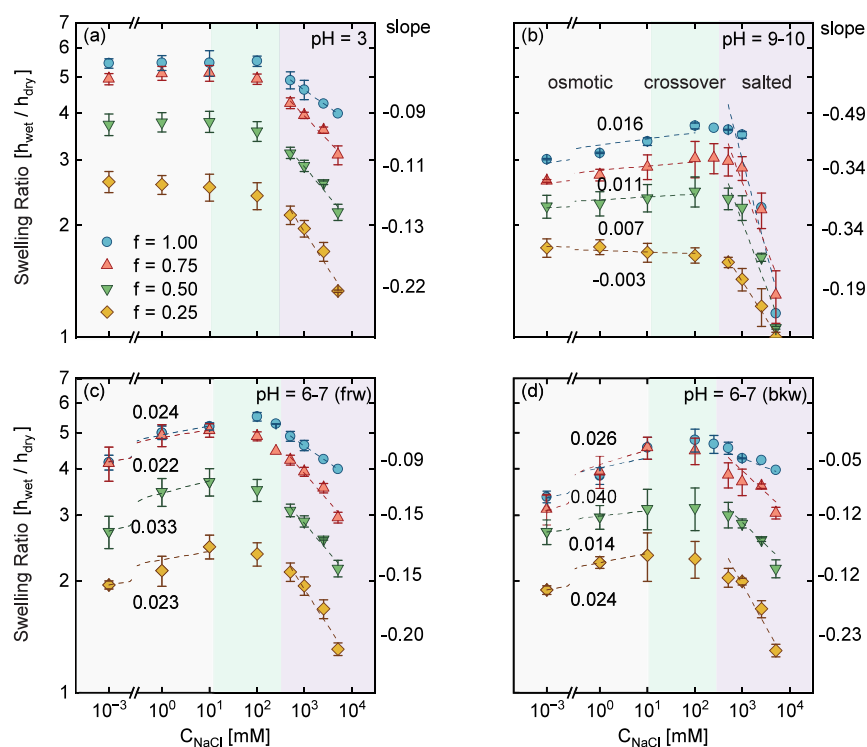


Figure 1. Effects of varying the DMAEA fraction, pH, and ionic strength on the swelling ratio of weak PEBs for (a) pH = 3, (b) pH = 9–10, (c) pH = 6–7 in the forward direction, and (d) pH = 6–7 in the backward direction. Error bars represent the standard deviation of three measurements across three distinct samples. Dashed lines indicate a linear fit in the osmotic and salted brush regimes. Shaded areas represent the osmotic (gray), crossover (green), and salted (purple) brush regimes.

exhibit weak scaling behavior and suggests a fundamental understanding of these systems is lacking. Thus, it is necessary to explore systems with chemistry and pH conditions close to neutrality to develop this fundamental understanding and thereby inform theoretical models describing weak PEB behavior.²²

Understanding the physical behavior of weak PEBs is further complicated by their theoretically predicted nonuniform degree of ionization (α) as a function of brush depth (decreasing exponentially toward the solid interface).¹² The distribution of α causes different segments of the weak PEB to have a range of pK_a values with the average value over all segments termed the apparent pK_a . The apparent pK_a for weak PEBs depends on the direction of pH change, resulting in an observed hysteretic behavior.^{23–26} As yet, no formal theory exists to explain this observed behavior. It has been proposed that the formation of a hydrophobic periphery inhibits ionization of deeper brush segments by hindering the transport of bulk solution into the brush.^{20,23,27,28} Thus, a higher chemical potential is required to achieve a specific overall degree of ionization in the direction of ionization, resulting in a shift in the apparent pK_a value, causing hysteresis. The extent of hysteresis in weak PEBs increases with both the degree of ionizable monomers²⁶ and dispersity.²⁴ The effect of salt on hysteresis, however, is unknown. It has been recently shown that the apparent pK_a of brushes is significantly affected by salt, shifting approximately one pH unit with a one decade increase in salt concentration.^{29,30} How these large shifts in pK_a affect the hysteretic behavior of weak PEBs is also not known. This understanding is vital for the performance of surfaces that require multiple pH cycles under salted conditions.

In this Letter, we show how the hysteretic pH response of weak PEBs is influenced by their charge state, which we adjust by varying the ionizable monomer fraction, solution pH, and ionic strength. In the strongly charged state at pH 3, the swelling behavior of weak PEBs qualitatively aligns with the theoretical predictions for strong PEBs, whereas under moderate to weakly charged states, it follows theoretical predictions for weak PEBs. However, the scaling exponents of the brush height with salt deviate from theoretical predictions in both the osmotic and the salted regimes. Notably, the acid dissociation constant pK_a of the brushes shifts toward more basic pH values as the salt concentration increases, differing significantly between the protonation and deprotonation directions, which contributes to the observed hysteretic behavior.

Random copolymer brushes of a weak basic monomer (2-(dimethylamino)ethyl acrylate, DMAEA) and a neutral hydrophilic monomer (2-hydroxyethyl acrylate, HEA) were prepared by surface-initiated copper(0)-controlled radical polymerization (SI-CuCRP).^{26,31} The fraction of DMAEA was varied from $f = 1.00$ to $f = 0.25$ at a fixed dry thickness of ≈ 30 nm and grafting densities in the range of 0.1 – 0.3 nm⁻² (constant for each fraction), as we have previously reported for similar weak PEBs.²⁶ Details on the brush synthesis and characterization can be found in the [Supporting Information](#). In situ ellipsometry was used to measure the brush thickness. The ionic strength of the solutions was tuned from 10^{-3} mM (no added salt) to 5×10^3 mM by adding the appropriate amounts of sodium chloride (NaCl). The pH was set by adjusting the HCl/NaOH concentration of the nonbuffered solutions from pH 3 to pH 10 in the forward direction and from pH 10 to pH 3 in the backward direction.

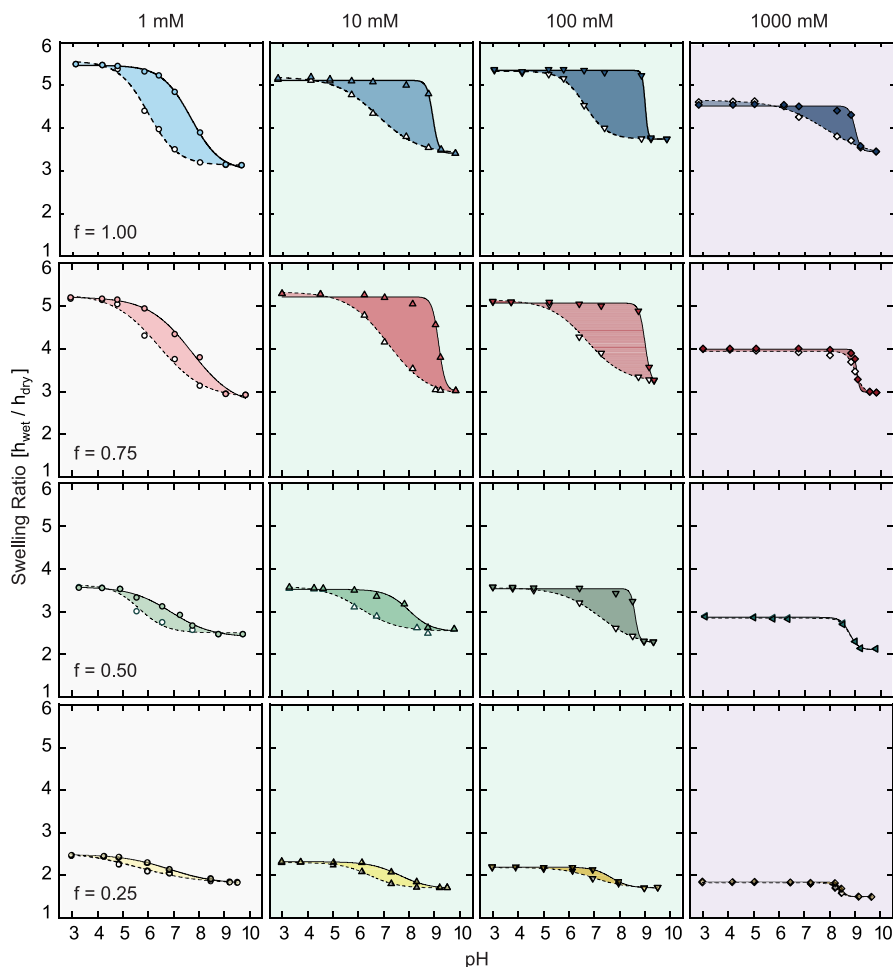


Figure 2. Swelling ratio of PEB fractions as a function of pH in solutions with various ionic strengths. pH was first increased from 3 to 10 (solid lines) and then decreased from 10 to 3 (short dashed lines). The shaded areas between the curves represent the hysteretic area. The background plot colors indicate the osmotic (gray), crossover (green), and salted (purple) brush regimes.

We first determine the swelling ratio (SR), $h_{\text{wet}}/h_{\text{dry}}$ (ratio of the solvated h_{wet} to dry h_{dry} brush thickness), as a function of salt concentration C_{NaCl} for each ionizable monomer fraction f at strong (pH = 3), moderate (pH = 6–7), and weak (pH = 9–10) charge states. The pH values were chosen based on our previous study detailing the charge state of P(DMAEA-*r*-HEA) brushes, with similar f values, in no-added salt conditions.²⁶ At pH 3, at low salt concentrations (10^{-3} –10 mM), the SR is independent of salt concentration across all f values, reflecting the characteristics of strong PEBs in the osmotic regime, where h is independent of salt concentration (Figure 1a).¹¹ Further increasing the salt concentration results in a decrease in the SR, indicating the onset of the salted regime. The swelling ratio scales as a power-law with C_{NaCl} , $\text{SR} \sim C_{\text{NaCl}}^m$ with $m < 1$, and the magnitude of the scaling exponent decreases with increasing f . All ionizable monomer fractions show weaker scaling with salt concentration in this regime compared to the theoretically predicted $m = -1/3$.^{13,32} This discrepancy has been observed in several experimental works^{15,20–22,33} and becomes more pronounced as the grafting density increases and the brushes possibly enter the concentrated brush regime,^{15,22,34} where the initial assumptions of the theories such as the negligible excluded volume interactions and strongly stretched brushes become invalid. Moreover, molecular dynamics (MD) simulations on strong PEBs have shown

that by including excluded volume effects and disregarding the strongly stretched brush assumptions, weaker scaling exponents between -0.15 and -0.12 for C_s are found, which better capture experimental results.^{35–37} Even at low ionizable monomer fractions, brush behavior is still akin to strong PEBs, further evidencing that weak PEB behavior stems from charge regulation.

To establish at what pH range, if any, these brushes behave like weak PEBs, we examine the SR at pH 9–10 where brushes are expected to be weakly charged (Figure 1b).²⁶ In the osmotic regime, we observe an increase in the SR with C_{NaCl} consistent with a facilitated protonation and theoretical predictions for weak PEBs. This dependence on C_{NaCl} increases as the fraction of DMAEA increases, yet all PEBs exhibit magnitudes of scaling exponents smaller than those of the theoretical prediction for weak PEBs. In particular, the height of the lowest ionizable monomer fraction brush ($f = 0.25$) remains largely unaffected by salt concentration within the fitting error (± 0.002) and exhibits behavior similar to neutral polymer brushes. Thus, both the pH value and ionizable monomer fraction may be used to tune swelling behavior in the osmotic regime.

Interestingly, all PEBs transition to the salted regime with increasing C_{NaCl} at pH 9–10. The magnitudes of the scaling exponents increase with ionizable monomer fraction and, for f

= 0.50 and 0.75, approach the classic theoretical predictions.^{12,13} The scaling exponent for $f = 1.00$, however, exceeds these predictions. Its exponent of $C_s^{-0.49}$ is close to the value determined from a correction on the classical theory of weak PEBs that accounts for electrostatic persistence length effects on the order of the Debye length, which predicts $C_s^{-3/7}$.³⁸ The effects of the electrostatic persistence length should also be present at pH 3 and should be even more pronounced as the net charge is larger, whereas we observe the opposite, and the scaling exponent is much weaker than the theoretical prediction of $C_s^{-3/7}$ at pH 3 ($C_s^{-0.09}$). It is possible that an interplay between the effects of excluded volume and electrostatic persistence length determine these scaling exponents at different charge states. For instance, at pH 3, the increased charge density may lead to stronger electrostatic repulsion between polymer chains, resulting in a more expanded brush conformation. This expansion may mitigate the effect of the electrostatic persistence length on scaling behavior by enhancing excluded volume interactions. Therefore, we posit that at higher charge states excluded volume interactions dominate, whereas at lower charge states, the reduced electrostatic repulsion allows for more pronounced electrostatic persistence length effects, resulting in closer alignment with the aforementioned theoretical predictions. Further experimental and theoretical works are necessary to test this hypothesis.

At intermediate charge states (pH 6–7), all fractions exhibit the characteristic nonmonotonic trend with added salt for weak PEBs in both the forward (Figure 1c) and backward (Figure 1d) direction. The height scales more weakly with salt concentration than the classic theoretical prediction for the osmotic regime. Compared to pH 9–10, however, the scaling exponent is slightly increased, which may be due to the moderate charge state and thus greater salt sensitivity in the osmotic regime. In the salted regime, the absolute scaling exponents for all fractions (in both directions) are comparable to those observed in the strongly charged state at pH 3. We posit that the differences in the experimentally measured and theoretically predicted exponents may arise due to theoretical assumptions, including neglecting excluded volume effects and asymptotic strong stretching, that do not hold in the experiments. While MD simulations^{35–37} did not find a grafting density dependency, experimental studies of weak PEBs have shown that scaling exponents decrease when grafting density is increased, especially at grafting density values similar to ours.^{21,22} This can further contribute to the weaker scaling exponents observed here.

Overall, the nonmonotonic dependence of the scaling exponents in Figure 1b–d with f is due to the free energy balance between increments in osmotic pressure difference due to enhanced protonation of the brush and decrements due to charge screening effects that govern the conformations of weakly charged PEBs. In the osmotic brush regime, the addition of salt facilitates the protonation of the brush as salt counterions replace hydroxide ions. This process reduces the local pH in the brush layer and promotes a larger degree of protonation. However, the concentration of salt is not large enough to substantially screen the electrostatic repulsion between chains and cause the observed swelling in this regime. In the crossover region, the brushes reach their maximum SR upon initially increasing the salt concentration. With further increase of C_{NaCl} into the salted regime, the extent of charge screening becomes large enough for the electrostatic potential

inside the brush layer to significantly decrease and cause the observed deswelling in this regime.¹²

Interestingly, at pH 6–7, the scaling exponents in the forward and backward directions are similar, yet at any given salt concentration the SR is different, which indicates the presence of hysteresis at moderate charge states. To elucidate salt effects on hysteresis, we subject the brushes to pH cycling from 3 to 10 (forward direction) and 10 to 3 (backward direction) across a salt concentration ranging from no added salt to 10^3 mM NaCl. In both the forward and backward directions, the pH-responsive swelling behavior of the brushes follows a sigmoidal trend (Figure 2). At a given salt concentration and f , however, the pH response is hysteretic and shifted to more acidic pH values, indicating that protonation becomes more difficult in the backward direction. Moreover, the maximum swelling ratios and the extent of hysteresis decrease with decreasing f . This observation aligns with our previous findings with no added salt, emphasizing a consistent effect of f across different ionic strengths.²⁶ As salt concentration increases, the hysteresis increases within the osmotic brush regime ($C_{\text{NaCl}} \approx 1\text{--}100$ mM) for a constant f . Upon further increasing the salt concentration $C_{\text{NaCl}} \gtrsim 100$ mM into the salted regime, the pH response in the forward direction does not experience a significant shift, whereas in the backward direction it shifts to more basic pH values; thus, the extent of hysteresis decreases. Notably, this pattern shows that the hysteretic behavior is nonmonotonic with salt, increasing in the osmotic regime and decreasing in the salted regime.

The shift in pH response and hysteresis is influenced by both the ionizable monomer fraction and salt concentration. To assess the protonation state of the brushes, we determined the apparent $\text{p}K_a$ from the inflection point of the SR–pH cycles fitted to sigmoidal functions (Supporting Information). For a given f , the apparent $\text{p}K_a$ in the forward direction increases monotonically with increasing C_{NaCl} before reaching a plateau (Figure 3a). Similar changes in apparent $\text{p}K_a$ with salt concentration have been observed for other weak PEBs and are attributed to the Donnan effect in high grafting density brushes, where the presence of charged groups causes an uneven distribution of ions between the brush and bulk solution.^{20,29,30} This behavior has also been observed for spherical brush-like micelles consisting of PDMAEMA coronas³⁹ and PDMAEMA solutions,⁴⁰ where the apparent $\text{p}K_a$ approaches the monomer $\text{p}K_a$ with increasing salt concentration, but to a lesser extent compared to weak PEBs.²⁹ The presence of a plateau, however, to the best of our knowledge, has not been previously observed. As salt concentration increases, the electrostatic screening effect becomes more pronounced, leading to a decrease in the free energy cost associated with ionization of the brush.^{12,29} The plateau in apparent $\text{p}K_a$ in the forward direction is similar to the $\text{p}K_a$ of the DMAEA monomers in solution ($\text{p}K_a \approx 8.4$),⁴¹ further supporting the description above. The onset of the plateau in $\text{p}K_a$ also shifts to lower salt concentrations for brushes with higher ionizable monomer fractions. This shift can be attributed to the inherent hydrophilic properties of brushes with higher charge fractions. At any given salt concentration, brushes with higher charge fractions are more hydrophilic, facilitating protonation compared to those with lower fractions and resulting in the plateau shifting to lower salt concentrations.

In the backward direction, the apparent $\text{p}K_a$ also increases with increasing C_{NaCl} (Figure 3b). Unlike the forward

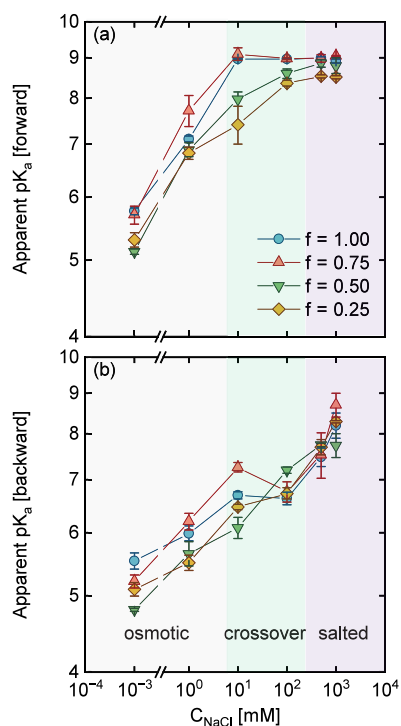


Figure 3. Apparent pK_a of random copolymer brushes of DMAEA and HEA with various ionizable monomer fractions f as a function of solution ionic strength when (a) pH was first increased from 3 to 10 (forward direction) and (b) pH was then decreased from 10 to 3 (backward direction). The background plot colors represent the osmotic (gray), crossover (green), and salted (purple) brush regimes.

direction, however, increasing C_{NaCl} does not lead to a discernible plateau. We posit this distinction is due to the hydrophobic periphery that forms upon brush deprotonation,^{24,26} which affects the ionization behavior in the backward direction, requiring higher salt concentrations to reach similar levels of protonation to those attained in the forward direction.

We can now examine the influence of the ionizable monomer fraction f on the apparent pK_a . It is expected that the apparent pK_a will be higher for brushes with lower f at any given ionic strength due to the larger spacing between charged groups, which facilitates protonation in the osmotic regime by reducing electrostatic repulsion. However, we observe non-monotonic behavior with f in both directions (Figure S1). We posit this is due to the hydrophobicity present in low ionizable monomer fraction brushes that hinders protonation and acts in direct opposition to any enhancement stemming from charge spacing. This is consistent with the observation that higher charge fraction brushes, which are more hydrophilic, have an earlier plateau onset compared with lower charge fraction brushes.

The shift in the pK_a ($\Delta pK_a = pK_{a,forward} - pK_{a,backward}$) is a nonmonotonic function of the salt concentration: it increases with C_{NaCl} , reaches a maximum, and then decreases to near zero values (Figure 4a). This behavior is almost independent of f , and the maximum occurs at salt concentrations between 10 and 100 mM NaCl. The values of ΔpK_a can reach ≈ 2 units of pH in the crossover region, indicating entirely different charge states at any specific intermediate pH between the two directions.

The trends in ΔpK_a are determined by a competition between the uniformity of the ion distribution along chains and

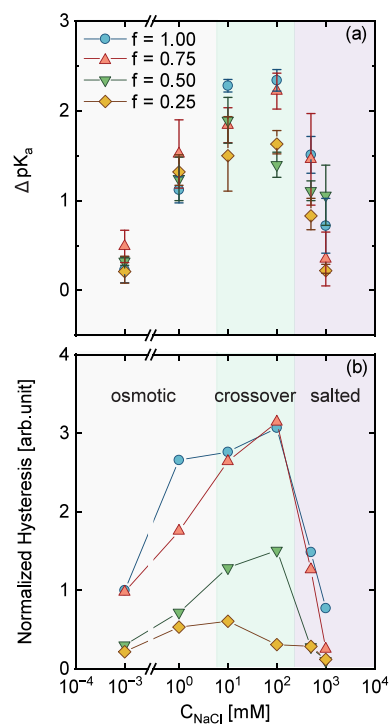


Figure 4. Effects of varying the ionizable monomer fraction f and the solution ionic strength on (a) the shift in apparent pK_a (ΔpK_a) and (b) the degree of hysteresis between the forward and backward direction. Shaded areas represent the osmotic (gray), crossover (green), and salted (purple) regimes.

the hydrophobicity of the brushes in their neutral state. In the osmotic regime, in the forward direction, the addition of salt enhances the protonation, as evidenced from the increased values of pK_a . In the backward direction, the addition of salt in this regime also facilitates the protonation but the salt concentration is not high enough to promote uniform ion distribution; due to the presence of hydrophobic periphery, the increase in pK_a is smaller compared to the forward direction and ΔpK_a increases. In the salted regime, the salt concentration is high enough to promote a uniform ion distribution along the chains. As a result, the hydrophobic effects of the neutral groups become less significant, the difference in α between the two directions becomes smaller, and ΔpK_a decreases. This hypothesis is consistent with a recent experimental study of the charge distribution in PAA brushes.⁴² In that study, the addition of salt increased the average degree of ionization in both regimes but did not significantly change the uniformity of charge distribution in the osmotic regime. As the salt concentration was further increased into the salted regime, however, the ion distribution became more uniform.⁴²

To quantify this hysteresis, we calculate the area enclosed by the forward and backward sigmoidal curves for each charge fraction and ionic strength (Supporting Information). The calculated hysteresis areas for $f < 1$ are then normalized by the hysteresis area for PDMAEA brush with $f = 1$ at no added salt condition (10^{-3} mM), as a reference (Figure 4b). This normalization provides a dimensionless quantity in arbitrary units, facilitating comparisons between various f and C_{NaCl} conditions. The normalized hysteresis trend aligns closely with the nonmonotonic behavior of ΔpK_a : it first increases with ionic strength up to a maximum and then decreases to near-zero values. The peak in hysteresis also corresponds to the

ionic strengths at which the largest pK_a differences occur, notably, at the transition from the osmotic to the salted regime. Moreover, brushes with greater f demonstrate larger extent of hysteresis across all ionic strengths, as observed in our previous study in no-added salt conditions.²⁶ This result suggests that the hysteresis area, unlike ΔpK_a , demonstrates the influence of the ionizable monomer fraction on brush swelling, especially in the osmotic regime, where hydrophobicity limits uniform ion distribution. Thus, two brushes with similar ΔpK_a values may exhibit different hysteresis areas. These nonmonotonic trends in both ΔpK_a and extent of hysteresis reflect the trends observed in swelling behavior at pH 6–7, underscoring that the transitions in brush behavior across varying salt concentrations directly correlate with hysteresis patterns: hysteresis intensifies with increasing salt in the osmotic regime, reaches its peak at the crossover regime, and then diminishes in the salted regime.

In conclusion, we demonstrate how the charge state significantly influences the hysteretic pH response of weak PEBs, adjusted by varying the ionizable monomer fraction, solution pH, and ionic strength. In the highly charged state, the swelling of the brushes aligns with the expected behavior for strong PEBs, whereas at moderate to low charge states it follows that of weak PEBs. Notably, deviations from theoretical scaling exponents observed in the osmotic and salted regimes suggest the influence of factors, such as excluded volume effects and chain stretching assumptions, that are not included in existing scaling theories. Finally, significant shifts in pK_a , with up to 4 pH units increase from no added salt to 5 M concentration, highlight the impact of salt on brush ionization. The qualitatively similar trends in apparent pK_a and hysteresis, which both exhibit a local maximum at the crossover between the osmotic and salted brush regimes, highlight the interplay between the uniformity of charge distribution and the hydrophobic tendencies of the brushes in their neutral state. Direction-dependent changes in brush conformation can be critical in applications requiring precise pH modulation, including drug delivery and purification of biologics.⁴³ The ability to predictably control brush conformation based on environmental conditions is essential for developing these responsive materials. Our findings provide critical insights into the behavior of weak polyelectrolyte brushes under varying pH and salt conditions. Specifically, we uncover a salt-dependent, nonmonotonic hysteretic behavior when transitioning between protonated and deprotonated states. This phenomenon not only challenges traditional understandings of polyelectrolyte dynamics but also highlights the complex interplay between charge distribution and osmotic effects.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmacrolett.4c00585>.

Experimental procedures for brush synthesis as well as ellipsometry, hysteresis, and fitting protocols (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Jacinta C. Conrad – Department of Chemical and Biomolecular Engineering, University of Houston, Houston, Texas 77204, United States; orcid.org/0000-0001-6084-4772; Email: jconrad@uh.edu

Amanda B. Marciel – Department of Chemical and Biomolecular Engineering, Rice University, Houston, Texas 77005, United States; orcid.org/0000-0001-9403-396X; Email: am152@rice.edu

Authors

Farshad Safi Samghabadi – Department of Chemical and Biomolecular Engineering, University of Houston, Houston, Texas 77204, United States; orcid.org/0000-0003-0556-000X

Shahryar Ramezani Bajgiran – Department of Chemical and Biomolecular Engineering, Rice University, Houston, Texas 77005, United States; orcid.org/0009-0007-9223-3838

Manuel Villegas Orellana – Department of Computer Science, University of Houston, Houston, Texas 77204, United States

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/acsmacrolett.4c00585>

Author Contributions

F.S.S. and S.R.B. contributed equally to this work, including the investigation, methodology, formal analysis, and validation of the experiments. M.V.O. contributed to the investigation of the experiments. J.C.C. and A.B.M. contributed equally to the conceptualization, funding acquisition, project administration, supervision, and resources. F.S.S., S.R.B., J.C.C., and A.B.M. contributed to the writing of the original draft and review and editing process. CRediT: Farshad Safi Samghabadi formal analysis, investigation, methodology, validation, writing - original draft, writing - review & editing; Shahryar Ramezani Bajgiran formal analysis, investigation, methodology, validation, writing - original draft, writing - review & editing; Jacinta C. Conrad conceptualization, funding acquisition, project administration, resources, supervision, writing - original draft, writing - review & editing; Amanda B. Marciel conceptualization, funding acquisition, project administration, resources, supervision, writing - original draft, writing - review & editing.

Notes

The authors declare no competing financial interest.

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