# Molecular Weight and Dispersity Affect Chain Conformation and pH-Response in Weak Polyelectrolyte Brushes

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# Molecular Weight and Dispersity Affect Chain Conformation and pH-Response in Weak Polyelectrolyte Brushes

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The impact of brush molecular weight distribution on the conformation and response of weak polyacid brushes was investigated. We show that weight-average degree of polymerization ($N_w$) and dispersity (Đ) alter the pH-responsive conformation of poly(acrylic acid) (PAA) brushes grafted to silica nanoparticles. We quantified the average brush length ($l_b$) at various pH using dynamic light scattering. The $l_b$ of low-$N_w$ PAA brushes ($N_w$ = 45) increased as Đ was increased from 1.09 to 1.69, but $l_b$ for the high-$N_w$ PAA brushes ($N_w$ ≈ 813) did not vary substantially when Đ was increased from 1.23 to 1.76. This result indicates that the presence of a small fraction of long chains in a broad dispersity brush has a greater impact on $l_b$ when $N_w$ is low. Additionally, the extent of pH-response in $l_b/l_{b,\max}$ increased with $N_w$ or Đ (when $N_w$ is low), where the maximum brush length ($l_{b,\max}$) was $l_b$ measured at pH 10. The scaling of $l_b/l_{b,\max}$ with degree of dissociation ($\alpha$), however, was influenced by $N_w$ but not Đ, indicating the low- and high-$N_w$ PAA brushes were in the quasi-neutral brush (q-NB) and salted brush (SB) regimes, respectively. Differing behaviors in the pH-response and $\alpha$-response of $l_b$ at low $N_w$ arose from subtle differences in dissociation behaviors among brushes of varying Đ. At low-Đ, the low-$N_w$ brush adopted a pH-independent extended conformation due to strong excluded volume interactions, whereas the conformation of the high-$N_w$ brush varied from collapsed to stretched with increasing pH arising from electrostatic interactions. At high-Đ, we suggest the brush conformation also varied from collapsed to stretched with increasing pH regardless of $N_w$.

## Introduction

Polyelectrolyte-grafted nanoparticles exhibit controllably reversible properties in response to pH change and are thus strong candidates for applications in colorimetric sensors,[1-3] filtration membranes,[4-7] and drug delivery.[8-11] The response of the brush conformation to environmental conditions, such as pH and added salt concentration $C_s$, is a key factor in the selection of materials for applications.[12, 13] The extent of dissociation as pH is varied, however, depends on the polyelectrolyte, leading to different conformational responses to pH. Quenched polyelectrolyte brushes are highly extended by electrostatic interactions because the brushes are strongly dissociated and ionized at all pH values.[14, 15] By contrast, for annealed brushes the degree of dissociation $\alpha$ varies with pH, leading to pH-responsive brush conformations induced by interchain and intrachain electrostatic interactions.[2, 16-21] In addition to the effects of environmental conditions, the brush properties (e.g. molecular weight and grafting density $\sigma$) can also affect pH-response of chain conformation. Thus, there is great interest in understanding how to predict the conformation of polyelectrolyte brushes.

The conformation of spherical brushes has been described using a model for star polyelectrolytes accounting for a variety of interactions in the brush layer.[22] This model has been successfully applied to experimental studies on spherical polyelectrolyte brushes when $l_b/r_0 \geq 1$, where $l_b$ is the average brush length and $r_0$ is the core radius.[23-26] The planar polyelectrolyte brush model, however, better predicts experimental results on spherical polyelectrolyte brushes when $l_b/r_0 < 1$.[27-29] The star polyelectrolyte model, which predicts conformation of salt-added (quenched, or annealed when $\alpha$=1) star polyelectrolytes as a function of the number of chains $f$ and $C_s$, can be adapted to spherical polyelectrolyte brushes using $\sigma = f/4\pi r_0^2$ (Fig. 1).[22] In the Pincus regime (low $\sigma$), $l_b$ is affected primarily by intrachain and/or interchain electrostatic interactions.[22, 30, 31] In the osmotic brush (OsB) regime (intermediate $\sigma$), counterions from the bulk solution are strongly condensed in the brush layer and the osmotic pressure of counterions controls brush conformation.[16, 22, 23, 31, 32] In the quasi-neutral brush (q-NB) regime (high $\sigma$), polyelectrolyte brushes are more strongly affected by excluded volume interactions than electrostatic interactions.[22, 31] In the salted brush (SB) regime, which occurs at high $C_s$, electrostatic

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Electronic Supplementary Information (ESI) available: Experimental details. TGA data of silica nanoparticles, initiator-grafted silica nanoparticles, P*t*BA brushes, and initiation efficiency. GPC refractometer chromatographs of cleaved P*t*BA. Proton NMR spectra of P*t*BA and PAA brushes. DLS intensity-intensity correlation curves of PAA brushes at pH 3, 7, and 10. $l_b/l_{b,max}$ of PAA brushes from this study and literature as a function of pH. pH titration data of PAA brushes including mole number of individual molecule and fitting titration curves. $C_i$ of the PAA brushes at ionic strength 10[-4] M. Scaling of $l_b$ of the PAA brushes with $\alpha$. $l_b/l_{b,max}$ of the high-$N_w$ PAA brushes and PDMAEMA brushes from literature as a function of $\alpha$. See DOI: 10.1039/x0xx00000x interactions are screened by added salts.[22, 23] In this regime, $l_b$ increases with $\sigma$ due to electrostatic excluded volume interactions, whereas it decreases with increasing $C_s$ because of charge screening:[22]

$$l_b \sim aN^{3/5}\alpha^{2/5}(C_s a^3)^{-1/5}\sigma^{1/5} \quad (1)$$

where $a$ is the monomer length and $N$ is the number of repeat units. Identical scaling behaviour is observed for annealed spherical polyelectrolyte brushes in the presence of added salt regardless of $\alpha$.[22, 24-26] Nonetheless, the impact of brush properties, e.g. $N$, $\sigma$, and dispersity Đ, on the applicability of the star polyelectrolyte model in spherical polymer brush systems with high curvature has been underexplored.

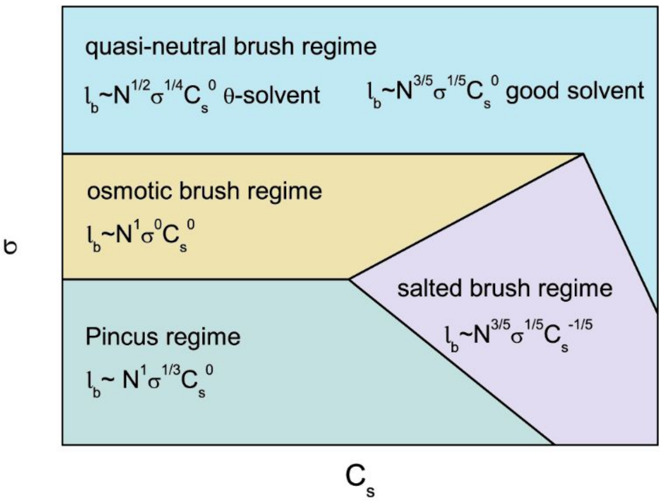


Figure 1. State diagram for high curvature ($l_b/r_0$ > 1) spherical polymer brushes, derived from a model for salt-added quenched and annealed (when $\alpha$ = 1) star polyelectrolytes with $\sigma$ in a solution of $C_s$. Adapted from ref. [22]

A recent experimental study examined the extent of pH-response on conformation and the scaling of $l_b$ of annealed polyelectrolyte poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) grafted on spherical nanoparticles across a range of $N$, $\sigma$, and Đ as a function of $\alpha$ at $C_s$ of 1 mM.[26] This study found that $l_b$ normalized by the maximum value for each brush collapsed onto a single curve as a function of pH, indicating that the extent of pH-response on brush conformation was independent of these properties.[26] Further, $l_b$ of all brushes scaled as $\alpha^{0.26 \pm 0.02}$, suggesting that the electrostatic interactions among the brush layers were not sensitive to $N$, $\sigma$, and Đ.[26] By contrast, in another study, the extent of pH-response in the conformation of annealed polyelectrolyte poly(acrylic acid) PAA grafted on spherical nanoparticles varied with both weight-average degree of polymerization $N_w$ and $\sigma$.[33] Therefore, it remains unclear how these brush properties affect the pH-response of the brush conformation and the driving forces for extension of the polymer chains.

Our prior study showed that Đ differently affected conformation of neutral brushes at low and high $N_w$.[34] Here, we extend this work to investigate the conformation of polyelectrolyte brushes of varying $N_w$ and Đ as a function of pH. We synthesized low-$N_w$ and high-$N_w$ pairs of PAA brushes hydrolyzed from poly(*tert*-butyl acrylate) P*t*BA-grafted silica nanoparticles in which Đ varied: in the first pair, $N_w$ = 45 and Đ = 1.09 and 1.69; in the second pair, $N_w$ ≈ 813 and Đ = 1.23 and 1.76. The brush conformation was assessed by measuring $l_b$ as a function of pH using dynamic light scattering. At $N_w$ = 45, $l_b$ of the high-Đ brush was markedly greater than that of the corresponding low-Đ brush for pH values ranging from 3 to 10, whereas at $N_w$ ≈ 813 the difference in $l_b$ with Đ was less pronounced. Increasing $N_w$ or Đ (when $N_w$ is low) led to a greater extent of pH-response of $l_b/l_{b,\max}$, where $l_{b,\max}$ is $l_b$ measured at pH 10. However, the scaling exponent of $l_b/l_{b,\max}$ with $\alpha$ increased with increasing $N_w$ but not Đ, suggesting the low-$N_w$ and high-$N_w$ brushes were in the q-NB and SB regimes, respectively (Fig. 1). Differences in pH- and $\alpha$-responses of $l_b/l_{b,\max}$ arose from subtle variations in the dissociation behaviour of the low-$N_w$ brushes. Together, our results indicate that the low-$N_w$, low-Đ brush adopted a pH-independent and extended conformation, whereas the conformation of brushes with higher $N_w$ and/or Đ varied from collapsed to extended with increasing pH.

Table 1. Variables and their symbols in the present study

| Variable | Symbols |
|---|---|
| Number-average degree of polymerization | $N_n$ |
| Weight-average degree of polymerization | $N_w$ |
| Dispersity | Đ |
| Grafting density | $\sigma$ |
| Brush length | $l_b$ |
| Degree of dissociation | $\alpha$ |
| Zeta potential | $\zeta$ |

## Experimental

### Materials

All chemicals were purchased from Sigma-Aldrich and used as received unless noted in the following. Dichloromethane (DCM, JT Baker, HPLC grade, ≥99.8%) was dried with a Pure Process Technology solvent purification system.

### Synthetic procedures

The synthesis of P*t*BA-grafted nanoparticles, where $r_0$ = 5.7 ± 0.2 nm, has been previously reported,[34] and is summarized in the ESI. Four P*t*BA-grafted nanoparticles were selected for hydrolysis to PAA-grafted nanoparticles (Table 2). The P*t*BA-grafted nanoparticles (110 mg) were transferred to a 100 mL round bottom flask and dissolved in 11 mL DCM under 375 rpm stirring at room temperature. 3 mL of trifluoroacetic acid was subsequently added to the solution for hydrolysis. The flasks were covered with aluminium foil and wrapped with Parafilm, and the reaction was allowed to proceed for 14 h at room temperature (Scheme 1). The solutions were dried under nitrogen purge and then dried in a vacuum oven at room temperature overnight. The remaining solid was dispersed in a minimum quantity of methanol (typically, 1 ml), precipitated into 100 mL DCM, and collected by centrifugation. The purification procedure was repeated three times and removal of unreacted monomer was confirmed by proton nuclear magnetic resonance ($^1$H-NMR). We note that the hydrolysis time is shorter than that used in earlier studies of planar PAA brushes, for which the hydrolysis did not appear to affect $\sigma$ or Đ;[35, 36] we therefore expect that Đ and $\sigma$ on the nanoparticles is not affected by the hydrolysis protocol.

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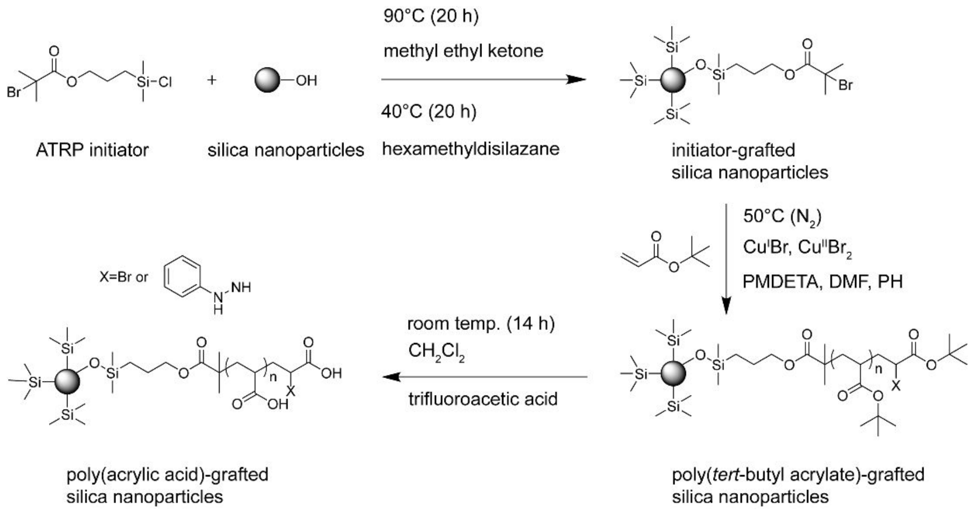


Scheme 1. Synthesis of PAA brushes

Table2. P*t*BA-grafted silica nanoparticles selected for hydrolysis

| P*t*BA brushes | $N_w$[a] | $N_n$[a] | Đ[a] | $l_b$ (nm)[b] | $\sigma$ (chains nm$^{-2}$)[c] |
|---|---|---|---|---|---|
| Low $N_w$, Low Đ | 45±3 | 41±4 | 1.09 | 6.6±0.2 | 0.38 |
| Low $N_w$, High Đ | 45.3±0.7 | 26±3 | 1.69 | 14.0±0.2 | 0.53 |
| High $N_w$, Low Đ | 780±50 | 630±40 | 1.23 | 57.2±0.3 | 0.31 |
| High $N_w$, High Đ | 840±10 | 480±30 | 1.76 | 58.0±0.5 | 0.70 |

[a] Characterized with GPC: $N_n$ and $N_w$ were calculated using $M_n/M_0$ and $M_w/M_0$, respectively, where $M_n$ is the number-average molecular weight, $M_w$ is the weight-average molecular weight, and $M_0$ = 128 g mol$^{-1}$ is the molecular weight of *t*BA; Đ $= N_w/N_n$. Standard deviations were calculated from 3 measurements.

[b] Characterized with DLS: $l_b$ was calculated using the method of cumulants (eqns. 2 and 3) to quantify the polymer-grafted nanoparticle $R_h$, followed by subtraction of $r_0$. Standard deviations were calculated from 10 measurements on the same sample.

[c] Characterized with TGA and EA.[34]

**Characterization procedures**

Procedures for thermogravimetric analysis (TGA), elemental analysis (EA), gel permeation chromatography (GPC), and $^1$H NMR have been previously reported[34] and are summarized in the ESI.

**Sample preparation**

The PAA-grafted silica nanoparticles were dispersed at concentrations of 0.5 and 2 mg mL$^{-1}$ for DLS/zeta potential and pH titration measurements, respectively, by stirring in Milli-Q water with varying pH for 3 h. pH was adjusted prior to dispersion by adding $HCl_{(aq)}$ and $NaOH_{(aq)}$ into Milli-Q water for acidic and basic conditions, respectively. The $HCl_{(aq)}$ and $NaOH_{(aq)}$ solutions were prepared using Milli-Q water to reduce the influence of unknown ionic strength from pre-existing ions. In addition, pH was measured thrice to confirm the stability of pH with 1 min stirring between individual pH readings. The samples were then filtered through a 0.2 or 0.45 µm Nylon syringe filter depending on the size of the nanoparticles.

**Dynamic light scattering (DLS).** $l_b$ was determined via DLS. The intensity correlation function $g^{(2)}(q,t)$ was measured on a DLS setup consisting of an ALV goniometer, a He-Ne laser (wavelength λ = 632.8 nm), and an ALV-5000/EPP Multiple tau digital correlator (ALV-GmbH, Langen, Germany). Each measurement was performed for 60 s at a constant scattering angle $\theta$ = 90°. $g^{(2)}(q,t)$ was fit using the method of cumulants,[37]

$$g^{(2)}(q,t) - 1 = \left[\mathrm{A}e^{\left(\frac{-t}{\tau(q)}\right)\left(1+\frac{\mu t^2}{2}\right)}\right]^2 \quad (2)$$

where $t$ is the lag time, which ranged from $2.5\times10^{-4}$ to $10^3$ ms; $q$ is the scattering vector ($q = 4\pi\sin(\theta/2)/\lambda$); $\tau^{-1}$ is the relaxation rate; and $\mu$ is the variance of the distribution. The hydrodynamic radius $R_h$ was calculated from the diffusion coefficient $D$ using the Stokes-Einstein equation

$$D = \frac{1}{\tau q^2} = \frac{k_B T}{6\pi\eta R_h} \quad (3)$$

where $n$ is the refractive index of water at 20°C, $\eta$ is the viscosity of water at 20°C, $k_B$ is the Boltzmann constant, and $T$ is the temperature.[38, 39] The $l_b$ was then obtained by subtracting $r_0$ from $R_h$. Three aqueous solutions were prepared from each brush on different days to determine the standard error on $l_b$. Measurements of $l_b$ were repeated consecutively ten times for each solution.

**Zeta potential ($\zeta$).** The $\zeta$ of PAA-grafted silica nanoparticles was measured using a NanoBrook ZetaPALs (Brookhaven Instruments) analyzer. Measurement of zeta potential was repeated 5 times on one solution for each brush to determine the standard deviation.

**pH titration.** pH values were measured by using a pH electrode InLab Micro Pro-ISM connected to a SevenCompact pH meter S220 (Mettler Toledo). To titrate the PAA brushes, the pH was adjusted to 12 by adding 0.5M $NaOH_{(aq)}$ with a micropipette. The solution was then titrated with 0.5M $HCl_{(aq)}$. The volume of the titrant was recorded from the micropipette, and the pH values were averaged from 3 measurements after each addition of the titrant.

## Results and discussion

To understand the effect of chain Đ on polyelectrolyte brush conformation, we measured $l_b$ as a function of pH for two pairs of PAA brushes grafted on silica nanoparticles of similar $N_w$ but different Đ. For the low-$N_w$ series ($N_w$ = 45), $l_b$ of the low-Đ PAA brush was independent of pH and was equal to the weight-average contour length $L_{c,w} = N_w l_0$, where $l_0$ = 0.3 nm is the monomer length (Fig. 2a). In sharp contrast, $l_b$ of the high-Đ PAA brush increased upon increasing pH and was markedly greater than both $l_b$ of the low-Đ PAA brush and $L_{c,w}$. The greater value of $l_b$ of the high-Đ PAA brush relative to that of the corresponding low-Đ PAA brush and to $L_{c,w}$ can be attributed to the presence of long chains,[26] which increase the brush length measured in DLS beyond that expected for a uniform chain of a given $N_w$. For the high-$N_w$ series ($N_w \approx 813$), $l_b$ of both PAA brushes increased with pH and gradually approached their $L_{c,w}$. At high $N_w$, differences in $l_b$ between the low and high-Đ brushes were less pronounced than for the low-$N_w$ brushes and were statistically insignificant at some pH values (Fig. 2b). Thus, Đ differently affected $l_b$ of brushes at low and high $N_w$. This result is consistent with the behaviour of neutral brushes observed in our previous study, in which $l_b$ increased with Đ at low $N_w$ but was independent of Đ for high $N_w$.[34] To examine the extent of pH-response, $l_b$ was normalized by $l_{b,\max}$. At low $N_w$, the high-Đ brush exhibited a greater change in $l_b/l_{b,\max}$ than the low- Đ brush as a function of pH. At high $N_w$, however, $l_b/l_{b,\max}$ of both low- and high- Đ brushes collapsed with that of the low-$N_w$, high-Đ brush (Fig. 2c). This comparison reveals that the extent of pH-response in $l_b$ can be enhanced by increasing either $N_w$ or Đ (when $N_w$ is low).

Prior studies report the pH-responsive $l_b/l_{b,\max}$ in polybasic PDMAEMA brushes ($N_w$ = 392 – 2541)[26] and polyacid PAA brushes ($N_w$ = 250 – 1111)[33]. $l_b/l_{b,\max}$ of PDMAEMA or PAA brushes as a function of pH collapsed onto a single curve for brushes of differing $N_w$,[26] which is consistent with the behaviour we observed in the high-$N_w$ PAA brushes ($N_w$ = 782 and 837) (Fig. S8a). We suggest the high-$N_w$ PAA brushes were in a high-$N_w$ regime where $l_b/l_{b,\max}$ was dependent on pH. However, $l_b/l_{b,\max}$ of the PAA brush with the lowest $N_w$ probed in ref. [33] ($N_w$ = 153) was independent of pH, consistent with the behaviour of our low-$N_w$, low-Đ brush ($N_w$ = 45) (Fig. S8b). We suggest the low-$N_w$ PAA brushes in our study were in a low-$N_w$ regime, where $l_b/l_{b,\max}$ was independent of pH and increased with increasing Đ. To explain the differences in the extent of pH response among the PAA brushes, we posit that the dominant parameter controlling the brush conformation, α, exhibited distinct sensitivities to changes in Đ in the two regimes of $N_w$ investigated.

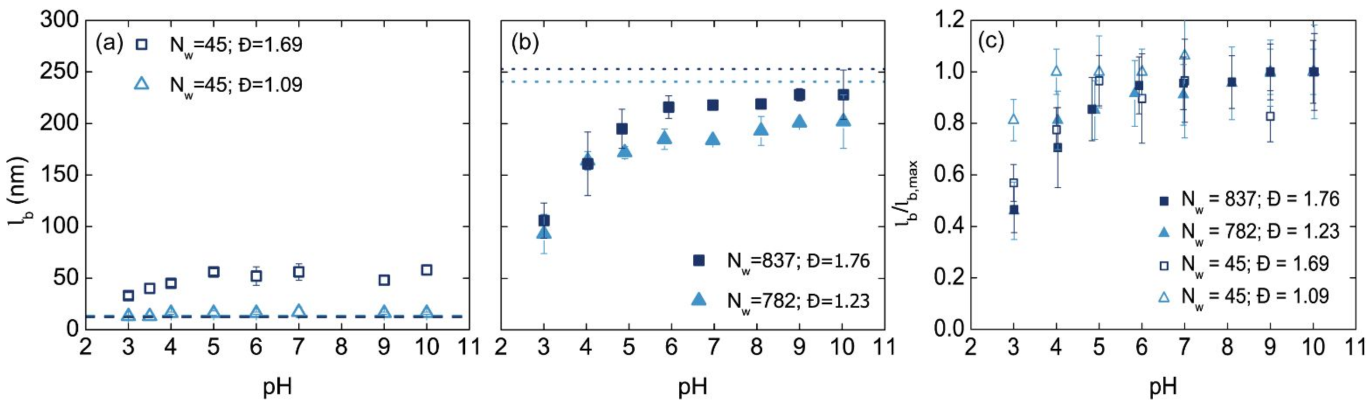


Figure 2. $l_b$ as a function of pH of the (a) low-$N_w$ PAA brush pair with $N_w$ = 45, Đ = 1.09 (light blue open triangles) and $N_w$ = 45, Đ = 1.69 (dark blue open squares) and (b) high-$N_w$ PAA brush pair with $N_w$ = 782, Đ = 1.23 (light blue closed triangles) and $N_w$ = 837, Đ = 1.76 (dark blue closed squares). (c) $l_b$ was normalized by $l_{b,\max}$ ($l_b$ measured at pH 10) as a function of pH for four PAA brushes. Dashed and dotted lines indicate $L_{c,w}$ of the low-$N_w$ and high-$N_w$ PAA brush pairs, respectively. Light blue and dark blue lines represent $L_{c,w}$ of the low-Đ and high-Đ PAA brushes, respectively. Error of $l_b$, smaller than symbols if not visible, was determined from 3 independent DLS measurements.

To test this idea, we determined α of the PAA brushes as a function of pH (Fig. 3) as assessed via titration curves upon decreasing pH (Fig. S9; procedures described in the ESI).[40] α monotonically increased with pH, in agreement with the previously reported behaviour of annealed polyacid brushes.[41-44] The titration curves of the PAA brushes were qualitatively similar for brushes of different Đ but similar $N_w$, indicating they were similarly dissociated and associated at high and low pH, respectively. To quantitatively examine the dissociation behaviour, the data were fit with sigmoidal curves, and the average acid dissociation constant $pK_a$ was obtained as the pH at α = 0.5 for each of the brushes.[45] At low $N_w$, $pK_a$ = 6.14±0.06 and 6.28±0.06 for low-Đ and high- Đ brushes, respectively; at high $N_w$, $pK_a$ = 5.68±0.03 and 5.96±0.01 for low-Đ and high- Đ brushes, respectively. These results indicate that the PAA brushes behave as annealed polyacids and bear an increasing number of negative charges as pH is increased. Further, increasing Đ slightly increased $pK_a$ whereas increasing $N_w$ decreased $pK_a$. The weak dependence of $pK_a$ on Đ is consistent with an earlier study on planar PAA brushes, when $pK_a$ was measured upon decreasing pH (as it was measured in the present study).[35] By contrast, $pK_a$ of the planar PAA brushes drastically increased with Đ when measured upon increasing pH.[35]

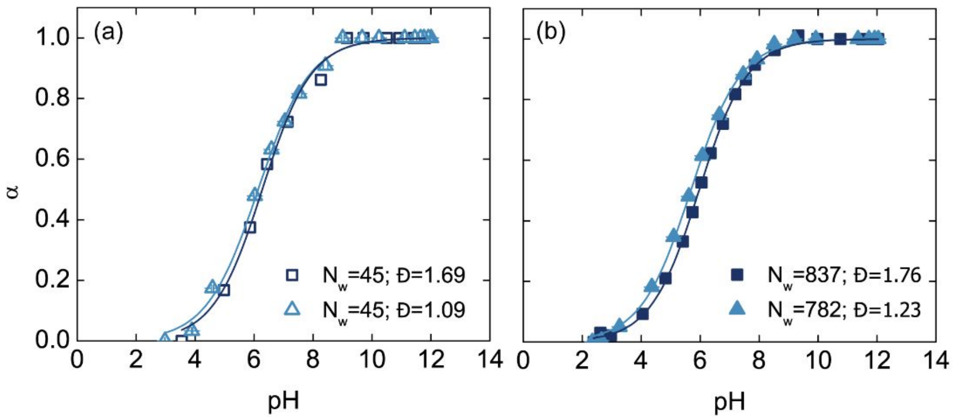


Figure 3. α as a function of pH of the (a) low-$N_w$ PAA brush pair with $N_w$ = 45, Đ = 1.09 (light blue open triangles) and $N_w$ = 45, Đ = 1.69 (dark blue open squares) and (b) high-$N_w$ PAA brush pair with $N_w$ = 782, Đ = 1.23 (light blue closed triangles) and $N_w$ = 837, Đ = 1.76 (dark blue closed squares). Light and dark blue solid lines are sigmoidal fits shown in the ESI (eqn. S8) of the low-Đ and the high-Đ PAA brushes, respectively, and the results of fitting parameters are shown in Table S1 in the ESI.

We characterized ζ as a function of pH (Fig. 4) to provide further insight into the dissociation behaviour of PAA brushes. The PAA brushes were negatively charged at all pH values tested and ζ monotonically decreased with increasing pH, indicating the number of charges increased for all brushes. The decrease in ζ with increasing $N_w$ arises from greater number of dissociated repeat units.[46] These results suggest that the counterions (i.e. positive charges) in the bulk solution could condense in the brush layer due to electrostatic interactions with negative charges on polyelectrolyte chains, but could not completely neutralize the negative charges.[16, 47] In addition, we calculated the concentration of condensed counterions $C_i$ at pH 10 (α = 1); $C_i$ was the largest for the low $N_w$, low Đ brush (due to differences in $l_b$) (Fig. S11, eqns. are shown in the ESI).

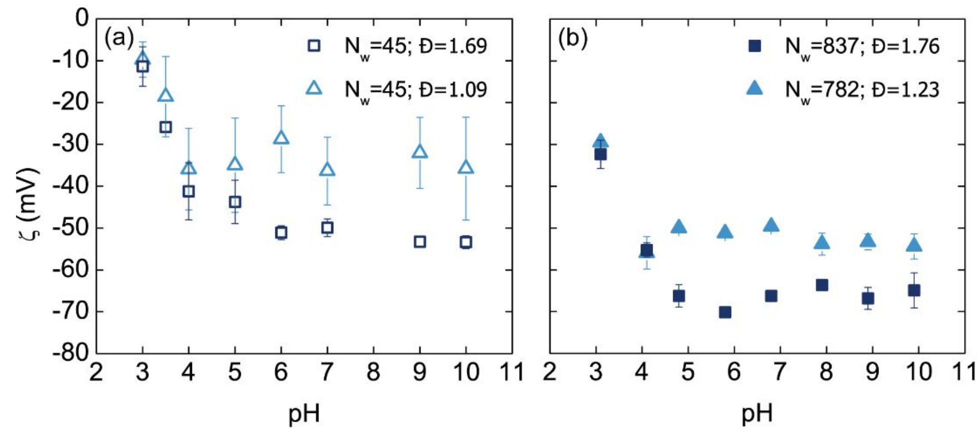


Figure 4. ζ as a function of pH of the (a) low-$N_w$ PAA brush pair with $N_w$ = 45, Đ = 1.09 (light blue open triangles) and $N_w$ = 45, Đ = 1.69 (dark blue open squares) and (b) high-$N_w$ PAA brush pair with $N_w$ = 782, Đ = 1.23 (light blue closed triangles) and $N_w$ = 837, Đ = 1.76 (dark blue closed squares). Error of ζ, smaller than symbols if not visible, was determined from 5 repeated measurements.

To probe PAA brush swelling, $l_b/l_{b,\max}$ was examined as a function of α, using the pH-dependencies of both $l_b/l_{b,\max}$ (in Fig. 2c) and α (in Fig. 3, along with sigmoidal fits to the data). $l_b/l_{b,\max}$ of the low-$N_w$ PAA brushes scaled weakly with α: $l_b/l_{b,\max}$

$\sim \alpha^{0.027 \pm 0.005}$ for the low-Đ brush and $l_b/l_{b,\max} \sim \alpha^{0.05 \pm 0.04}$ for the high-Đ brush (Fig. 5). Although Đ did not affect the scaling exponent for low-$N_w$ brushes, brushes with lower Đ had a greater degree of chain extension (e.g., greater $l_b/l_{b,\max}$) at a given value of $\alpha$ (Fig. 5). These scaling exponents indicate that the PAA brushes with $N_w$ = 45 were in the q-NB regime and were more affected by short-range excluded volume interactions than long-range electrostatic interactions.[22, 31] By contrast, $l_b/l_{b,\max}$ for high-$N_w$ brushes at both low- and high-Đ collapsed onto a single curve with that of PDMAEMA brushes (Fig. S12),[26] which had a larger scaling exponent: $l_b/l_{b,\max} \sim \alpha^{0.23 \pm 0.02}$ (Fig. 5), consistent with the scaling of the SB regime from prior studies.[24, 26] The transition from the q-NB to SB regimes upon increasing $N_w$ is consistent with expectations from the star polyelectrolyte model.[22] Overall, $l_b/l_{b,\max}$ collapsed as a function of $\alpha$ for the brushes with high but not low $N_w$ (Fig. 5), and $l_b/l_{b,\max}$ for the high-$N_w$ brushes and the low-$N_w$, high-Đ brush collapsed as a function of pH (Fig. 2c).

Increasing Đ led to distinct behaviours for low-$N_w$ brushes in the α- and pH-responses of $l_b/l_{b,\max}$. Whereas the pH-dependence of $l_b/l_{b,\max}$ showed a significant change as Đ increased (Fig. 2c), the scaling of $l_b/l_{b,\max}$ with α was unaffected by Đ (Fig. 5). At high-$N_w$, the pH- and α-responses of $l_b/l_{b,\max}$ each collapsed to a single curve as Đ was varied (Figs. 2c and 5). These differences in relationships of $l_b/l_{b,\max}$ with α and pH likely arise from subtle differences in dissociation behaviours among these brushes, quantified by the $pK_a$ (Fig. 3). We can identify different regimes of behaviour in low- and high-$N_w$ brushes using our data and that of a prior study. At high-$N_w$, the pH- and α-respsponses of $l_b/l_{b,\max}$ each collapsed onto a single curve for PDMAEMA brushes ($N_w$ = 392 – 2541; Đ = 1.31 – 2.10).[26] This behaviour is consistent with our data on high-$N_w$ PAA brushes ($N_w$ = 782 and 837; Đ = 1.23 and 1.76). Therefore, we suggest that these brushes were in the high-$N_w$ regime, where the pH- and α-responses of $l_b/l_{b,\max}$ each collapsed to a curve independent of $N_w$ and Đ. By contrast, $l_b/l_{b,\max}$ varied differently as a function of pH and α for the low-$N_w$ PAA brushes in our study ($N_w$ = 45; Đ = 1.09 and 1.16). We hypothesize the low-$N_w$ PAA brushes were in a low-$N_w$ regime, where the relationships of pH- and α-responses of $l_b/l_{b,\max}$ were affected by subtle differences in $pK_a$ (low-Đ : $pK_a$ = 6.14±0.06 and high-Đ : 6.28±0.06) (Fig. 3).

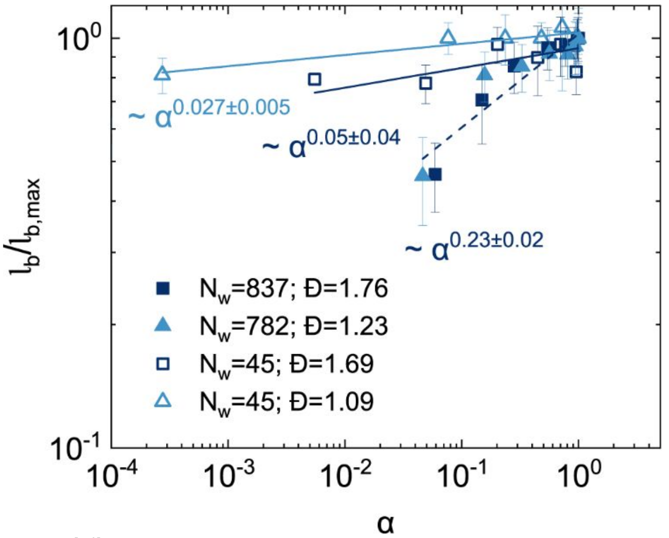


Figure 5. $l_b/l_{b,\max}$ as a function of $\alpha$ of the low-$N_w$ PAA brush pair with $N_w$ = 45, Đ = 1.09 (light blue open triangles) and $N_w$ = 45, Đ = 1.69 (dark blue open squares) and the high-$N_w$ PAA brush pair with $N_w$ = 782, Đ = 1.23 (light blue closed triangles) and $N_w$ = 837, Đ = 1.76 (dark blue closed squares). Data were fit to a power-law equation $\log l_b/l_{b,\max} = b + c \times \log \alpha$, where $b$ and $c$ were intercept and slope, respectively. Solid lines indicate the fits for low-$N_w$ brushes and the dashed line indicates the fit for the high-$N_w$ brushes, which collapsed onto a single curve and were fit together. Fig. S13 in the ESI shows $l_b$ as a function of $\alpha$.

We propose schematic representations for low-Đ (Fig. 6a) and high-Đ (Fig. 6b) annealed polyacid-grafted nanoparticles. Because $l_b$ of the low-$N_w$, low-Đ PAA brush was approximately equal to $L_{c,w}$, we suggest that the brush adopted a near-fully extended conformation at low pH due to strong excluded volume interactions (the q-NB regime). Although increase in pH induced electrostatic interactions, the brush could not further extend (Fig. 6a).[33] The gradual increase of $l_b$ to $L_{c,w}$ as pH increased for the high-$N_w$, low-Đ PAA brush indicates that the conformation transitioned from a relatively collapsed state to a near-fully extended state with increasing pH (Fig. 6a). In the collapsed state, the brush was stretched near the particle surface arising from the proximity of neighbouring chains. Further from the surface, the greater inter-chain distance allowed the brush to adopt an entropically favourable coiled conformation. In the extended state, the chain extension was induced by electrostatic excluded volume interactions.[22]

The gradual increase of $l_b$ to $L_{c,w}$ with increasing pH was also observed for the high-Đ PAA brushes, in which the conformation varied from collapsed to stretched with increasing pH (Fig. 6b). In the collapsed state, the shorter chains of the high-Đ brush adopted a “crown and stem" conformation at short distances from the surface, although the conformation at the periphery remained coiled.[48] We propose that the conformation of the high-Đ brushes in the extended state was similar to that of the high-$N_w$, low-Đ brush (Fig. 6b), evidenced by the collapse of $l_b/l_{b,\max}$ on a single curve as a function of pH for these three brushes (Fig. 2c).

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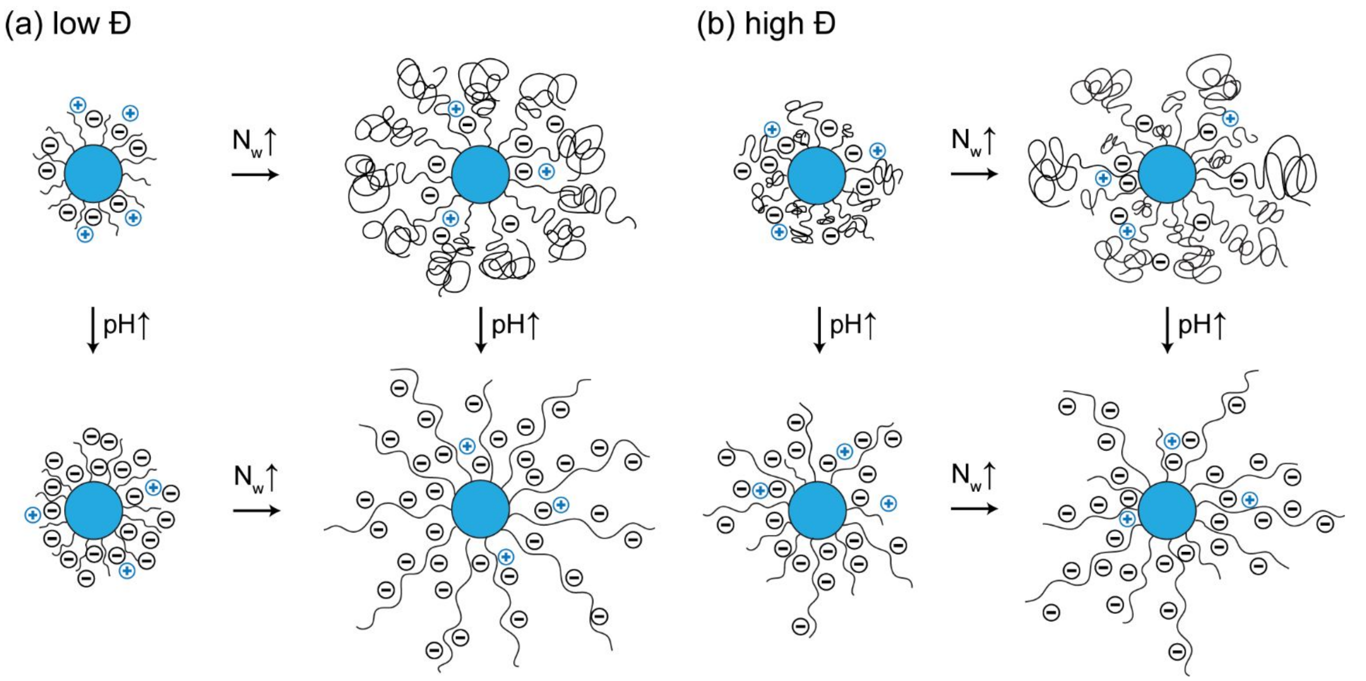


Figure 6. Schematic representation of the conformation of annealed polyacid-grafted nanoparticles: (a) low Đ and (b) high Đ with variation of $N_w$ and pH. The negative charges (black) are attributed to dissociated polyelectrolyte chains. The positive charges (blue) are attributed to counterions condensed from the bulk.

## Conclusions

We investigated the dependence of $l_b$ of annealed polyacid brushes and its pH-response on $N_w$ and Đ. $l_b$ increased with Đ for the low- but not high-$N_w$ PAA brushes. Increasing $N_w$ or Đ (in the case of low $N_w$ brushes) enhanced the extent of pH-response of $l_b/l_{b,\text{max}}$, whereas the extent of $\alpha$-response of $l_b/l_{b,\text{max}}$ increased with $N_w$ but not Đ. The scaling exponents of $l_b/l_{b,\text{max}}$ with $\alpha$ indicated the brush regime changed from q-NB to SB upon increasing $N_w$. Differences in pH- and $\alpha$-responses of $l_b/l_{b,\text{max}}$ at low $N_w$ were attributed to differences in the dissociation behaviours, quantified by $pK_a$. We propose that the low-$N_w$, low-Đ brush adopted a near-fully extended conformation at low pH arising from strong excluded volume interactions. Although increase in pH induced greater electrostatic interactions, the brush conformation did not change because the brushes were almost fully extended. By contrast, $l_b$ of brushes with higher $N_w$ and/or Đ greatly increased with pH. We hypothesize that the brush conformation transitioned from collapsed to extended with increasing pH. The pH-dependence of conformation of annealed polyelectrolyte brushes can therefore be tuned by varying $N_w$ or Đ (when $N_w$ is low). This understanding of the effects of brush properties on the extent of pH-responsiveness of the brush conformation can be leveraged for applications of annealed polyelectrolyte brushes. For example, short (<10 nm) brushes have been applied as adsorbents for water pollutants[43] and as colorimetric sensors;[1] we expect that modulating the length distribution of these brushes may lead to enhancements in efficacy. Indeed, we anticipate that different synthesis routes may lead to various distributions of brush molecular weight[49] and hence distinctive structure-property relationships[50]. Thus, we expect that tailoring the molecular weight distribution will provide additional control over the properties of responsive brushes.

## Conflicts of interest

There are no conflicts to declare.

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