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Electronic Supporting Information

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

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EXPERIMENTAL DETAILS

The synthetic and characterization procedures for PtBA brushes were previously published in Ref. ¹.

Materials. All chemicals were purchased from Sigma-Aldrich and used as received unless noted in the following. *tert*-butyl acrylate (*t*BA, 98%) was purified by passing through a silica gel column (60 Å pore size), dried, and distilled with calcium hydride (reagent grade, 95%) and a Schlenk line system. N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA, 99%) was degassed with a Schlenk line system with three cycles of free-pump-thaw. Copper (I) bromide (Cu^IBr) was purified with acetic acid, ethanol, and ether (see details below). Colloidal silica dispersed in methyl ethyl ketone was kindly provided by Nissan Co. (MEK-ST, 30-31wt%, supplier reported diameter of 10 – 15 nm) and used as received. Tetrahydrofuran (THF, JT Baker, low water HPLC grade, \geq 99.8%) and toluene (JT Baker, HPLC grade, \geq 99.7) were dried with a Pure Process Technology solvent purification system.

Synthetic procedures. The as-purchased Cu^IBr contains a trace amount of impurities of copper (II) bromide (Cu^{II}Br) due to oxidation during storage. We first purified 1 g of Cu^IBr with 30 mL of acetic acid (\geq 99.7%) under stirring overnight. After decanting the supernatant, the precipitate was stirred with 30 mL of fresh acetic acid for 10 min twice. The precipitate was separated from the supernatant and washed with an excessive amount of ethanol (\geq 99.5%) under stirring for 10 min several times until it became white. The white precipitate was thrice washed with 20 mL of ether (\geq 99.7%) under 10 min stirring. The final precipitate was collected and dried in a vacuum oven at 80°C overnight. The purified catalyst was then transferred into the glove box and stored under nitrogen.²

The monomer, *t*BA, was polymerized from the surface of the as-synthesized initiatorgrafted silica nanoparticles (see details of synthesis in ref.¹) by using surface-initiated atom transfer radical polymerization (SI-ATRP).³⁻⁸ Briefly, *t*BA, initiator-grafted silica nanoparticles (100 mg, 0.011 mmol of initiator), purified Cu^IBr (0.23 mmol), Cu^{II}Br (99%, 0.023 mmol, 10 mol% relative to Cu^IBr), anhydrous dimethylformamide (DMF, 99.8%), and PMDETA were mixed in a round bottom flask inside a glove box. The volume ratio of tBA to DMF was 1 : 1.75. After mixing, the flask was capped with a rubber septum and heated at 50°C in an oil bath under 375 rpm stirring. The ratio of [tBA] to [initiator] and the reaction time (≤ 5 h) were varied to tune the molecular weight of poly(*tert*-butyl acrylate) (PtBA). The reaction was quenched by addition of 200 mL THF, and the catalyst was removed by passing through an aluminum oxide column (80 g). The solution was then concentrated under reduced pressure by a rotary evaporator and precipitated in methanol/DI water mixture (50/50 by volume). The final precipitate was dried in a vacuum oven at room temperature overnight.

With addition of phenylhydrazine (PH, 97%) into the ATRP mixture, high-DPtBA brushes were obtained. The ratio of [PH] to [purified Cu¹Br] was 0.38 : 1, and the volume ratio of *t*BA to DMF was 1 : 1.75. The ratio of [*t*BA] to [initiator] and the reaction time (\leq 5 h) were also varied to control molecular weight. The reaction was quenched by addition of 200 mL THF. The product was purified by passing through an aluminum oxide column (80 g), concentrated under reduced pressure, and precipitated in a methanol/DI water mixture (50/50 by volume). The final product was dried in a vacuum oven overnight at room temperature.⁹

The as-synthesized PtBA chains were cleaved from the silica nanoparticles by hydrofluoric acid aqueous solution (HF_(aq), 49 wt%) to characterize the polymer molecular weight and its distribution by using gel permeation chromatography GPC. The PtBA-grafted silica nanoparticles (110 mg) were dissolved in 20 mL of THF in Teflon jars. 1.2 mL of HF_(aq) was added into the jars for 5 h without stirring, and 13 mL of KOH_(aq) (4M) was used to quench the remaining HF. The quenched solution was then dried by a rotary evaporator and a vacuum oven overnight at room temperature. The solid was dissolved in 50 mL of toluene and extracted by 100 mL of DI water for three times. The organic layer was collected and dried with excessive amount of anhydrous magnesium sulfate for 1 h under stirring. The magnesium sulfate and toluene were removed by gravimetric filtration and a rotary evaporator, respectively. The solid was dissolved in 3 mL THF and precipitated in a mixture of methanol and water (60/40 by volume). The precipitate was dried in a vacuum oven overnight at room temperature.

We note that kinetic information on the synthesis of PtBA in solution using SI-ATRP can be obtained from earlier studies.^{9, 10}

Thermogravimetric analysis (TGA). TGA was performed on a TA Instruments Model Q500 TGA for measurement of the mass of grafted P*t*BA, used in calculation of polymer grafting density σ . Between 10 and 30 mg of P*t*BA-grafted silica nanoparticles were placed on a platinum pan. TGA was set at an equilibrium temperature at 25°C and ramped to 800°C with 10°C min⁻¹ under 40 mL min⁻¹ air flow in the chamber.

Weight losses of bare silica nanoparticles and initiator-grafted silica nanoparticles arose from thermal degradation of the residual silanol and grafted initiator, respectively (Figure S1). The grafted PtBA experienced thermal degradation and formed carboxylic acid groups and alkene at 250° C.¹¹ At the elevated temperature, the carboxylic acid groups were further dehydrated to the six-member cyclic anhydride structure and water.¹¹ The reduction in weight of PtBA-grafted nanoparticles represented the thermal degradation of residual

silanol, grafted initiator and PtBA, where difference in degradation rate arose from variation of polymer chemical structures.

The initiation efficiency for the PtBA brushes was calculated by dividing σ (for the low N_w , low \mathcal{P} PtBA brush : 0.38 chains/nm²) with the initiator grafting density σ_I (for the low N_w , low \mathcal{P} PtBA brush : 0.54 molecules/nm²) (Table S1):¹

 $\frac{0.38 \text{ chains/nm}^2}{0.54 \text{ molecules/nm}^2} \times 100\% = 70\%$ (S1)

Table S1. Initiation efficiency of the selected PtBA-grafted silica nanoparticles for hydrolysis

PtBA brushes	σ (chains nm ⁻²) ^c	σ_I (molecules nm ⁻²) ^c	Initiation efficiency (%)
Low N_w , Low Đ	0.38	0.54	70
Low N_w , High Đ	0.53	0.83	64
High N_w , Low \oplus	0.31	0.43	72
High N_w , High Đ	0.70	0.83	84



Figure S1. Weight percent as a function of temperature of the bare silica nanoparticles (black curve), initiator-grafted silica nanoparticles (red curve), and PtBA-grafted silica nanoparticles with weight-average degree of polymerization $N_w = 780 \pm 50$, dispersity D = 1.23, average brush length $l_b = 57.2 \pm 0.3$ nm, and $\sigma = 0.31$ chains nm⁻² (blue curve).

Elemental analysis (EA). EA was performed on an Exeter CE440 instrument at the Midwest Microlab Co. to characterize the bromine composition in initiator-grafted silica nanoparticles, used in calculation of initiator grafting density.

Gel permeation chromatography (GPC). The molecular weight distributions of the cleaved PtBA were characterized with a Viscotek GPC, equipped with two Agilent ResiPore columns at 30°C and a mobile phase of stabilized THF (OmniSolv, HPLC grade, > 99 %) with a flow rate 0.7 or 1 mL min⁻¹. With a triple detection system (differential refractometer, light scattering, and viscometer), the number-average degree of polymerization N_n , weight-average degree of polymerization N_w , and dispersity \overline{D} were calculated using dn/dc = 0.048±0.001 of PtBA.¹² Refractometer chromatographs obtained from four cleaved PtBA (Table 1) with injection volume 0.1 mL are provided in the Figure S2.



Figure S2. GPC refractometer chromatographs of the cleaved PtBA brushes in Table 1: (a) $N_w = 45 \pm 3$, D = 1.09, $l_b = 6.6 \pm 0.2$ nm, $\sigma = 0.38$ chains nm⁻² (black curve), (b) $N_w = 45.3 \pm 0.7$, D = 1.69, $l_b = 14.0 \pm 0.2$ nm, $\sigma = 0.53$ chains nm⁻² (red curve), (c) $N_w = 780 \pm 50$, D = 1.23, $l_b = 57.2 \pm 0.3$ nm, $\sigma = 0.31$ chains nm⁻² (blue curve), and (d) $N_w = 840 \pm 10$, D = 1.76, $l_b = 58.0 \pm 0.5$ nm, $\sigma = 0.70$ chains nm⁻² (green curve).

Proton nuclear magnetic resonance (¹H-NMR). The chemical structures of PtBA (Figure S3) and PAA (Figure S4) were characterized with ¹H-NMR from a JEOL ECA-400 NMR spectrometer. PtBA and PAA were dissolved in deuterated chloroform and deuterated dimethyl sulfoxide (DMSO, 99.0%), respectively. Chemical shifts were referenced to the solvent proton resonance (7.26 ppm for chloroform and 2.50 ppm for DMSO).¹³



Figure S3. ¹H-NMR spectrum of the P*t*BA-grafted silica nanoparticles: $N_w = 840 \pm 10$, $\overline{D} = 1.76$, $\sigma = 0.70$ chains nm⁻². The ratio of (peak d + peak f) / (peak e) was 12 (theoretical value = 11). ¹H-NMR peak assignments (CDCl₃, δ , ppm): 2.15-2.31 (br, methine CH of the polymer backbone), 1.77-1.89 (br, meso methylene CH₂ of the polymer backbone), 1.49-1.68 (br, meso and racemo methylene CH₂ of the polymer backbone), 1.38-1.48 (br, methyl (CH₃)₃C from the polymer.



Figure S4. ¹H-NMR spectrum of the PAA-grafted silica nanoparticles: $N_w = 840 \pm 10$, D = 1.76, $\sigma = 0.70$ chains nm⁻². The ratio of (peak a + peak b) / peak c was 2.6 (theoretical value = 3.0). ¹H-NMR peaks assignment (C₂D₆SO, δ , ppm): 1.2-1.8 (br, methine CH of the polymer backbone), 2.0-2.3 (s, meso methylene CH₂ of the polymer backbone), 12.0-12.4 (s, hydroxyl OH from the polymer).

DYNAMIC LIGHT SCATTERING (DLS)

The intensity-intensity correlation functions $g^2(q, t) - 1$ of the PAA brushes hydrolyzed from the PtBA brushes in Table 1 in aqueous solutions of pH 3, 7, and 10 are shown in Figure S5, Figure S6, and Figure S7, respectively.



Figure S5. Intensity-intensity correlation functions $g^2(q, t) - 1$ as a function of delay time for the PAA brushes with N_w and varying \overline{D} dispersed in the aqueous solution with pH 3. Solid lines represent method of cumulant fits.¹⁴ (a) $N_w = 45$, $\overline{D} = 1.09$ (yellow closed triangles), $N_w = 45$, $\overline{D} = 1.69$ (green closed squares); (b) $N_w = 782$, $\overline{D} = 1.23$ (red open triangles), $N_w = 837$, $\overline{D} = 1.76$ (blue open squares).



Figure S6. Intensity-intensity correlation functions $g^2(q, t) - 1$ as a function of delay time for the PAA brushes with N_w and varying \overline{D} dispersed in the aqueous solution with pH 7. Solid lines represent method of cumulant fits.¹⁴ (a) $N_w = 45$, $\overline{D} = 1.09$ (yellow closed triangles), $N_w = 45$, $\overline{D} = 1.69$ (green closed squares); (b) $N_w = 782$, $\overline{D} = 1.23$ (red open triangles), $N_w = 837$, $\overline{D} = 1.76$ (blue open squares).



Figure S7. Intensity-intensity correlation functions $g^2(q, t) - 1$ as a function of delay time for the PAA brushes with N_w and varying \overline{D} dispersed in the aqueous solution with pH 10. Solid lines represent method of cumulant fits.¹⁴ (a) $N_w = 45$, $\overline{D} = 1.09$ (yellow closed triangles), $N_w = 45$, $\overline{D} = 1.69$ (green closed squares); (b) $N_w = 782$, $\overline{D} = 1.23$ (red open triangles), $N_w = 837$, $\overline{D} = 1.76$ (blue open squares).

NORMALIZED AVERAGE BRUSH LENGTH (l_b) as a Function of pH for PAA Brushes



Figure S8. $l_b/l_{b,max}$, where $l_{b,max}$ is the maximum l_b for each brush, as a function of pH for (a) high- N_w PAA brush pair with $N_w = 782$ and $\tilde{D} = 1.23$ (light blue closed triangles), $N_w = 837$ and $\tilde{D} = 1.76$ (dark blue closed squares), and PAA brushes from ref. ¹⁵ with $N_w = 250$ (black open diamonds) and $N_w = 1111$ (black open left-pointing triangles); (b) low- N_w PAA brush pair with $N_w = 45$ and $\tilde{D} = 1.09$ (light blue open triangles), $N_w = 45$ and $\tilde{D} = 1.69$ (dark blue open squares), and PAA brushes from ref. ¹⁵ with $N_w = 153$ (black closed diamonds).

POTENTIOMETRIC TITRATION

Four PAA brushes as hydrolyzed from the four PtBA brushes in Table 1 were titrated by 0.5 M HCl_(aq) from pH 12 (adjusted by adding NaOH) until the curves reached plateaus (Figure S9).



Figure S9. Low- N_w PAA brush pair with (a) $N_w = 45$ and $\overline{D} = 1.09$ (light blue open triangles) and $N_w = 45$ and $\overline{D} = 1.69$ (dark blue open squares) and high- N_w PAA brush pair with (b) $N_w = 782$ and $\overline{D} = 1.23$ (light blue closed triangles) and $N_w = 837$ and $\overline{D} = 1.76$ (dark blue closed squares) were dispersed in Milli-Q water at concentration 2 mg mL⁻¹ and titrated with 0.5 M HCl_(aq), starting from pH 12. Errors of pH were determined from three measurements.

During the titration, the titrant HCl can react in three different ways:¹⁶

1. Acid-base neutralization reaction: HCl reacted with the excess of the strong base NaOH, happening mainly at the beginning of the titration:

$$HCl + NaOH \rightarrow H_2O + NaCl$$
 (S2)

2. Association of acrylic acid (AA): HCl reacted with as-dissociated acrylic:

$$\mathrm{HCl} + \mathrm{AA}^{-} \to \mathrm{AAH} + \mathrm{Cl}^{-} \tag{S3}$$

3. HCl dissociation: when NaOH and AA were consumed by HCl, HCl started to dissociate by itself:

$$\mathrm{HCl} \to \mathrm{H}^{+} + \mathrm{Cl}^{-} \tag{S4}$$

The number of moles of NaCl n_{NaCl} was calculated as:

$$n_{\rm NaCl} = V_{\rm start} \times 10^{-14 + pH_{\rm start}} - (V_{\rm start} + V_{\rm HCl}) 10^{-14 + pH}$$
(S5)

The number of moles of dissociated HCl was calculated as:

$$n_{\rm HCl\,dissociated} = (V_{\rm start} + V_{\rm HCl}) \times 10^{-\rm pH} - V_{\rm start} 10^{-\rm pH}_{\rm start}$$
(S6)

Because HCl is a strong acid and fully reacted through the three mechanisms, the number of moles of the associated acrylic acid n_{AAH} was calculated as:

$$n_{AAH} = 0.5 M \times V_{\rm HCl} - n_{\rm NaCl} - n_{\rm HCl\,dissociated} \tag{S7}$$

The degree of dissociation of PAA α was calculated as:

$$\alpha = 1 - \frac{n_{AAH}}{n_{AAH,\text{max}}} \tag{S8}$$

where V_{start} and pH_{start} are the starting volume and pH of the solutions, respectively, V_{HCl} and pH are the added volume of $\text{HCl}_{(aq)}$ and pH after addition of $\text{HCl}_{(aq)}$, respectively, and $n_{AAH,\text{max}}$ is the maximum value of n_{AAH} .

From eqn. S5 to S7, number of moles of individual substance formed due to consumption of HCl during titration of four PAA brushes are shown as a function of volume of added HCl_(aq) (Figure S10). Nonmonotonic behavior for n_{AAH} indicates degradation of PAA at pH lower than two.



Figure S10. The number of moles of NaCl (green open circles), HCl dissociation (red open inverse triangles), and AAH (blue open triangles), calculated from eqns. S5, S6, and S7, respectively, for the PAA brushes with (a) $N_w = 45$ and D = 1.09, (b) $N_w = 45$ and D = 1.69,

(c) $N_w = 782$ and D = 1.23, and (d) $N_w = 837$ and D = 1.76.

The titration curves of α as a function of pH (Figure 3) were fit by

$$\alpha = A_2 + \frac{(A_1 - A_2)}{\frac{(pH - x_0)}{d_x}}$$
(S9)

where A_1 , A_2 , are initial and final values of α and fixed to 0 and 1, respectively; x_0 , and d_x are fitting parameters. Results for the PAA brushes are shown in Table S2.

PtBA brushes	<i>x</i> ₀	d_x
Low N_w , Low Đ	6.14±0.04	0.88±0.04
Low N_w , High $\overline{\mathcal{D}}$	6.28±0.04	0.83±0.04
High N_w , Low \mathbb{D}	5.68±0.02	0.85±0.02
High N_w , High Đ	5.96±0.01	0.82±0.01

Table S2: The parameters of sigmoidal fits for the PAA brushes titration curves

CONCENTRATION OF CONDENSED COUNTERIONS

The concentration of condensed counterions C_i of the PAA brushes was calculated at ionic strength I_s of 10⁻⁴ M (at pH 10).

The average charge density ρ_f in the brush layer is^{17, 18}

$$\rho_f = \frac{3er_0^2 \sigma L_c}{l_B[(r_0 + l_b)^3 - r_0^3]} \tag{S10}$$

where *e* is the electron charge $(1.6 \times 10^{-19} \text{ C})$, r_0 is the core radius, $L_c = N_w l_0$ is the contour length ($l_0 = 0.3$ nm is the length of two carbon-carbon bonds), and l_B is the distance between two charged groups along the polyelectrolyte chain, chosen as the Bjerrum length for PAA at pH 10, at which it is a strongly charged polyelectrolyte. C_i is then calculated as^{17, 18}

$$C_{i} = I_{s} \left[1 + \left(\frac{z\rho_{f}}{2eN_{A}I_{s}} \right)^{2} \right]^{1/2}$$
(S11)

where z is the valence of the ions and N_A is Avogadro's number.



Figure S11. C_i as a function of concentration of added ions I_s of low- N_w PAA brushes pair with $N_w = 45$ and $\overline{D} = 1.09$ (light blue open triangle) and $N_w = 45$ and $\overline{D} = 1.69$ (dark blue open square) and high- N_w PAA brush pair with $N_w = 782$ and $\overline{D} = 1.23$ (light blue closed triangle) and $N_w = 837$ and $\overline{D} = 1.76$ (dark blue closed square).

 $l_b/l_{b,\text{max}}$ as a Function of α for High- N_w PAA and PDMAEMA BRUSHES¹⁹



Figure S12. $l_b/l_{b,max}$ as a function of α for high- N_w PAA brush pair with $N_w = 782$ and $\overline{D} = 1.23$ (light blue closed triangles) and $N_w = 837$ and $\overline{D} = 1.76$ (dark blue closed squares); the PDMAEMA brushes with $N_w = 392 - 2541$ (black open symbols) from ref.¹⁹.

SCALING OF l_b with α



Figure S13. l_b as a function of α for low- N_w PAA brush pair with $N_w = 45$ and $\overline{D} = 1.09$ (light blue open triangles) and $N_w = 45$ and $\overline{D} = 1.69$ (dark blue open squares) and the high- N_w PAA brush pair with $N_w = 782$ and $\overline{D} = 1.23$ (light blue closed triangles), and $N_w = 837$ and $\overline{D} = 1.76$ (dark blue closed squares). Data were fit to a power-law equation log $l_b = b + c \times \log \alpha$, 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 high- N_w brushes, which collapsed onto a single curve and were fit together.

REFERENCES

- 1. T.-H. Li, V. Yadav, J. C. Conrad and M. L. Robertson, *ACS Macro Lett.*, 2021, **10**, 518-524.
- 2. K. Matyjaszewski, T. E. Patten and J. Xia, J. Am. Chem. Soc., 1997, **119**, 674-680.
- 3. T. von Werne and T. E. Patten, J. Am. Chem. Soc., 2001, 123, 7497-7505.
- 4. D. A. Savin, J. Pyun, G. D. Patterson, T. Kowalewski and K. Matyjaszewski, J. Polym. Sci. Part B: Polym. Phys., 2002, 40, 2667-2676.
- 5. K. Ohno, T. Morinaga, S. Takeno, Y. Tsujii and T. Fukuda, *Macromolecules*, 2007, **40**, 9143-9150.
- 6. F. Jiang, W. g. H. Meyer and J. Zhang, *Colloids Surf. A*, 2013, **436**, 302-308.
- N. J. Fernandes, H. Koerner, E. P. Giannelis and R. A. Vaia, *MRS Commun.*, 2013, 3, 13-29.
- 8. P. Chmielarz, M. Fantin, S. Park, A. A. Isse, A. Gennaro, A. J. D. Magenau, A. Sobkowiak and K. Matyjaszewski, *Prog. Polym. Sci.*, 2017, **69**, 47-78.
- 9. V. Yadav, N. Hashmi, W. Ding, T.-H. Li, M. K. Mahanthappa, J. C. Conrad and M. L. Robertson, *Polym. Chem.*, 2018, **9**, 4332-4342.
- 10. P. Kanhakeaw, B. Rutnakornpituk, U. Wichai and M. Rutnakornpituk, J. Nanomater., 2015, 2015, 121369.
- 11. M. Fernández-García, J. L. D. L. Fuente, M. L. Cerrada and E. L. Madruga, *Polymer*, 2002, **43**, 3173-3179.
- 12. V. Yadav, A. V. Harkin, M. L. Robertson and J. C. Conrad, *Soft Matter*, 2016, **12**, 3589-3599.
- 13. G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176-2179.
- 14. B. J. Frisken, *Appl. Opt.*, 2001, **40**, 4087-4091.
- 15. C. Zhang, T. Carlson, S. Yang and P. Akcora, *Adv. Mater. Interfaces*, 2018, **5**, 1701318.
- 16. O. Colombani, E. Lejeune, C. Charbonneau, C. Chassenieux and T. Nicolai, J. *Phys. Chem. B*, 2012, **116**, 7560-7565.
- 17. R. Hariharan, C. Biver and W. B. Russel, *Macromolecules*, 1998, **31**, 7514-7518.
- 18. X. Guo and M. Ballauff, *Langmuir*, 2000, **16**, 8719-8726.
- 19. D. Iqbal, J. Yan, K. Matyjaszewski and R. D. Tilton, *Colloid Polym. Sci.*, 2020, **298**, 35-49.