Polymer Dispersity Affects Conformation of Brushes Grafted on Nanoparticles

by Tzu-Han Li

A thesis submitted to the Department of Materials Science of Engineering, Cullen College of Engineering in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in Materials Science of Engineering

Chair of Committee: Megan L. Robertson

Co-Chair of Committee: Jacinta C. Conrad

Committee Member: Alamgir Karim

Committee Member: Haleh Ardebili

Committee Member: Stacey Louie

University of Houston August 2021

ABSTRACT

Polymer-grafted nanoparticles (PGNPs) exhibit prominent performance in applications, such as tough thin films,¹⁻³ optics and electrics,⁴⁻⁷ ultrafiltration membranes,⁸ biomolecular and drug delivery vehicles,⁹⁻¹² colorimetric sensors,¹³⁻¹⁵ and lubrication,¹⁶⁻¹⁸ partly due to uniform dispersion and/or morphology of polymer brushes with varying chain conformation. Polymer brush properties, such as grafting density σ and degree of polymerization *N*, can drastically affect conformation of neutral and pH-responsive PGNPs and further influence their efficacy in applications. Surprisingly, how dispersity D (related to the breadth of the polymer molecular weight distribution) affects the brush conformation is still underexplored.

First, we examined the brush length l_b of neutral poly(*tert*-butyl acrylate) (P*t*BA) brushes in dilute solutions. l_b bifurcated as a function of weight-average degree of polymerization N_w : l_b increased with \mathcal{P} at low N_w in the concentrated polymer brush (CPB) regime but was less dependent on \mathcal{P} at high N_w in the semidilute polymer brush (SDPB) regime. We proposed that the variation of l_b with \mathcal{P} in the CPB regime was due to the presence of a stretched conformation of the stem near the particle surface in high- \mathcal{P} brushes.

SANS data obtained from low- and high-D PtBA brushes in the CPB and SDPB regimes were analyzed using a core-chain model and demonstrated the differences in l_b obtained from SANS and DLS increased with D in the SDPB regime due to the long chain effect. The monomer density ρ profiles at the periphery decayed in a linear and power-law for brushes in the CPB at low and high D, respectively. In the SDPB regime, ρ decayed in a power-law at the periphery regardless of D.

Next, we explored the conformation of pH-responsive poly(acrylic acid) (PAA) brushes, in which the extent of pH-response of l_b was enhanced with increased N_w or D (when N_w is low). We hypothesized the low- N_w and low-D brush adopted a highly extended conformation at all pH values, whereas the other brushes with higher N_w and/or D transitioned from a collapsed to extended conformations with increasing pH.

Together, these results suggest Đ is a tunable parameter to control chain conformation of PGNPs depending on brush molecular weight.

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Chapter 1. Introduction

1.1.Polymer-Grafted Nanoparticles

Polymer-grafted nanoparticles (PGNPs) have been widely applied as tough thin films,¹⁻³ optical and electrical devices,⁴⁻⁷ ultrafiltration membranes,⁸ biomolecular and drug delivery vehicles,⁹⁻¹² colorimetric sensors,¹³⁻¹⁵ and lubrication.¹⁶⁻¹⁸ The grafted polymers can be used to tune interactions between nanoparticles and polymer matrices or solvents, leading to different performance metrics and morphologies.¹⁹⁻²¹ In the case of grafting polyelectrolyte on nanoparticles, polyelectrolyte chains can bear charges, inducing interparticle electrostatic repulsions and allowing control over nanoparticle dispersion.²² In addition, grafted polyelectrolyte chains can be used to attract or repel molecules through electrostatic interactions by tuning pH and/or salt concentration C_s .⁹⁻

The functional properties of PGNPs are determined, in part, through conformation of the grafted polymer chains, which can be modified through control over brush parameters. In particular, polymer grafting density σ plays an important role in tuning chain conformation.^{23, 24} Increasing σ leads to increase in interchain interactions and extension of polymer chains.²⁴ In addition, the volume that polymer chains can occupy increases radially with the distance from grafting surfaces r. Therefore, polymer chains adopt a more extended conformation (the stem) near the surface due to interchain steric hindrance, but collapsed conformation (the crown) at the periphery.^{25, 26} However, when chain length is above a critical radius, polymer chains adopt an entropically favorable conformation (the coil) at the periphery.^{23, 24} Accordingly, the average chain length l_b of a polymer brush increases with the degree

of polymerization *N* of grafted chains, and, therefore, *N* is also a tunable parameter to control chain conformation.^{23, 24} Chain confirmation has been directly examined through small-angle X-ray and neutron scattering,²⁷⁻³² and is indirectly probed through analysis of l_b , often through dynamic light scattering (DLS).^{23, 24, 33-37}

While the chain conformation of polyelectrolyte brushes is influenced by σ and N, the brushes adopt different conformations as a function of pH and C_s .^{33, 38, 39} Two types of polyelectrolyte brushes with distinct pH-responses of conformation and dissociation behaviors have been observed. Quenched polyelectrolyte brushes are highly extended by electrostatic interactions because the brushes are strongly dissociated and bear charges at all pH values.^{40, 41} By contrast, for annealed brushes, degree of dissociation α varies with pH, leading to pH-responsive interchain and intrachain electrostatic interactions and brush conformations.^{14, 33, 35, 36, 42-44} Similar to neutral brushes, the chain conformation and l_b of polyelectrolyte brushes have been examined previously with scattering techniques.^{28, 45}

1.2.Conformation of Neutral Spherical Polymer Brushes: Scaling Theories and Experimental Validation

The modified Daoud-Cotton (DC) model quantitively examines conformation of grafted neutral polymer chains in good solvent conditions using a scaling theory in which l_b scales differently with σ and N in differing regimes (Figure 1-1).^{23, 24} At low σ , the distance between grafted sites is less than the size of grafted chains, and polymer chains adopt a mushroom-like conformation. As such, l_b is predicted to scale as²⁴

$$l_b \sim N^{3/5}$$
. (1-1)

At intermediate σ , above a threshold value, interactions between monomers are treated as pairwise and the brush is assumed to be in the SDPB regime. In the SDPB regime, the scaling behavior of l_b is^{23, 24}

$$l_b \sim \left(N \sigma^{\frac{1}{3}} \right)^{3/5}. \tag{1-2}$$

At sufficiently high σ , polymer chains experience higher-order segmental interactions and excluded-volume effects are screened. For brushes in this CPB regime, the scaling transitions to^{23, 24}

$$l_b \sim \left(N \sigma^{\frac{1}{2}} \right)^x,\tag{1-3}$$

where $3/5 < x \le 1$. To account for radial distribution of free volume, the conformation of spherical brushes is assumed to be transitioned from CPB to SDPB at a critical radius r_c .^{23, 24}



Figure 1-1. Conformation of polymer chains on spherical nanoparticle with a core radius r_0 in the (a) CPB and (b) SDPB regimes separated by r_c . The modified DC model has been successfully applied to understand experimental measurements of brush conformation. l_b of PGNPs was measured using

DLS in dilute good solvent conditions.^{23, 24, 34, 37} The scaling exponent of l_b with N and σ increased from 0.6 to 0.8 with increasing σ , indicating brush conformation transitioned from SDPB to CPB regimes.^{23, 24} However, the intermediate- σ brushes exhibited both scaling behaviors of CPB and SDPB regimes.²⁴ The theoretical calculation of r_c was then applied to quantitively define the l_b boundary between CPB and SDPB regimes.^{23, 24} Although the scaling theories and r_c were used to understand spherical brush conformation, this approach requires controllable syntheses of several brushes with different molecular weights to construct scaling curves.

The conformation of spherical polyelectrolyte brushes has been described using a model for star polyelectrolytes accounting for a variety of interactions in the brush layer.⁴⁶⁻⁴⁹ This model has been successfully applied to experimental studies on spherical polyelectrolyte brushes when $l_b/r_0 \ge 1$, where r_0 is the core radius.⁴⁷⁻⁵⁰ The planar polyelectrolyte brush model, however, better predicts experimental results on spherical polyelectrolyte brush model, however, better predicts experimental results on spherical polyelectrolyte brushes when $l_b/r_0 < 1.^{51-53}$ The star polyelectrolyte model, which predicts conformation of salt-added (quenched or high- α annealed) star polyelectrolyte as a function of the number of chains f and C_s ,^{46, 54} is adapted to spherical polyelectrolyte brushes using $\sigma = f/4\pi r_0^2$ (Figure 1-2). In the Pincus regime (low σ), l_b is affected primarily by intrachain and/or interchain electrostatic interactions.^{46, 55, 56} In the osmotic brush (OsB) regime (intermediate σ), counterions from the bulk solution are strongly condensed in the brush layer and the osmotic pressure of counterions controls brush conformation.^{33, 46, 50, 56, 57} In the quasi-neutral brush (q-NB) regime (high σ), polyelectrolyte brushes are more strongly affected by excluded volume interactions than electrostatic interactions.^{46, 56} In the salted brush (SB) regime, which occurs at high C_s , electrostatic interactions are screened by added salts.^{46, 50} In this regime, l_b increases with σ due to electrostatic excluded volume interactions, whereas it decreases with increasing C_s because of charge screening as⁴⁶

$$l_b \sim a N^{3/5} \alpha^{2/5} (C_s a^3)^{-1/5} \sigma^{1/5}, \tag{1-4}$$

where *a* is the monomer length. Identical scaling behavior was observed for annealed spherical polyelectrolyte brushes in the presence of added salt regardless of α .⁴⁶⁻⁴⁹



Figure 1-2. State diagram for high curvature $(l_b/r_0 > 1)$ spherical polymer brushes derived from a model for salt-added quenched and high- α annealed star polyelectrolytes with σ as a function of C_s . Adapted from ref.⁴⁶

1.3.Measurement of Brush Conformation Using Small-Angle Neutron Scattering

Small-angle neutron scattering (SANS) is an important technique utilized to measure the conformation of PGNPs in dilute solutions.^{29, 31, 32, 58} Neutron scattering occurs due to interactions between incident neutrons and atomic nuclei, and, therefore, neutrons are sensitive to different isotopes of a sample.⁵⁹ Different isotopes (*e.g.* hydrogen and deuterium) exhibit different scattering lengths, and therefore the contrast

between materials can be easily tuned through selective deuteration.⁵⁹ The contrast is quantified through the square of the scattering length density (SLD) difference of distinct domains present in the sample (such as the nanoparticle core, polymer brush, and solvent in the case of PGNPs), in which each SLD is calculated from the individual scattering lengths of the atoms comprising the molecules. The measured intensity of scattered neutrons is a function of scattering angle θ_n and wavelength λ_n .⁵⁹ The scattering intensity *I* is reported as a function of scattering vector *q*, in which $q = \frac{4\pi \sin(\theta_n/2)}{\lambda_n}$.⁵⁹ The size of domains probed in the experiment typically scales as q^{-1} , in which larger structures are measured at low *q* and smaller structures at high *q*.

The core-shell model was developed to predict I(q) of a spherical core surrounded by a polymer shell, in which the SLD of the solvent matched that of the core but differed from that of the shell to enhance I(q) from the polymer chains (Figure 1-3).⁶⁰⁻⁶² However, the core-shell model is not applicable to PGNP systems, because interchain excluded volume interactions and chain conformation are excluded from the core-shell model and the SLD of the shell is a constant. Because SLD is a function of ρ , the core-shell model assumes ρ in the shell is constant.

The core-chain-chain (CCC) model, adapted from the core-shell model, describes a core nanoparticle grafted by a block copolymer with two excluded volume parameters v for each block..^{32, 63} To validate the applicability of this model and probe conformation in the CPB regime, diblock copolymer chains with fully hydrogenated and partially-deuterated blocks were grafted from silica nanoparticles (with the fully hydrogenated block next to the silica nanoparticle surface), and the solvent was contrast

matched (i.e. same SLD) to the partially-deuterated block and core.³² The molecular weight of the fully hydrogenated block was fixed such that the distance from the core center to the periphery of the fully hydrogenated block was r_c .³² To probe conformation in the SDPB regime, the diblock polymer was grafted to the particle such that the partially-deuterated block was nearest to the particle surface.³² The predicted v (0.8 in CPB regime and 0.6 in SDPB regime) and r_c were consistent with the scaling theories.³² However, the CCC model assumes a constant SLD and ρ for each block similar to the core-shell model (Figure 1-3a).³² The constant ρ is inconsistent with the prediction from the DC model which predicts a decay in ρ as a function of r, arising from penetration of solvent into polymer layer.⁶⁴

To address this gap, a core-chain model was derived from the DC model, consisting of a core nanoparticle grafted by polymer chains with varying SLDs.^{31, 64, 65} For polymer chains nearest to the surface, the interchain crowding effect prevents penetration of solvent, and, therefore, SLD is constant (Figure 1-3b).^{31, 64, 65} Above the constant region, polymer chains are swollen by solvent, leading to linear variation in SLD as a function of *r* (Figure 1-3b).^{31, 64, 65} With further increase in *r*, polymer chains experience strong solvent swelling, and SLD scales as $r^{-4/3}$ (Figure 1-3b).^{31, 64, 65} This model was successfully applied to predict I(q) of PGNPs in dilute solutions in which the core and solvent had the same SLDs.^{31, 65} The SLD of polymer chains varied from the surface).^{31, 65}



Figure 1-3. The SLD profiles of a PGNP as a function of r predicted using (a) the core-shell and the CCC models and (b) the core-chain model. r_0 and R_p are the core size and the size of the PGNP, respectively.

1.4.Conformation of Broad Dispersity Spherical Polymer Brushes

The polymer molecular weight distribution is described by number- and weightaverage molecular weights (M_n and M_w , respectively), as well as the dispersity \overline{D} , defined as M_w/M_n and related to the breadth of the molecular weight distribution ($D = (s/M_n)^2 + 1$), where *s* is the standard deviation). While the impact of varying molecular weight has been previously explored in PGNPs,^{23, 24, 32} it is not immediately evident how to incorporate changes in brush conformation arising in a brush of even modest dispersity \overline{D} . To address this gap, the conformation of high \overline{D} neutral brushes was examined using theory and simulations.^{25, 26} In a high \overline{D} neutral brush, short chains were collapsed toward the surface, whereas long chains adopted a stretched stem conformation near the surface when surrounded by smaller chains, but collapsed at the periphery in the crown region.^{25, 26} Simulations on neutral brushes also showed change in ρ from parabolic to linear with increasing \overline{D} .²⁶

Synthetic techniques are now available to controllably vary Đ in PGNPs, such as surface-initiated controlled radical polymerization or ring-opening polymerization, enabling exploration of the conformation of broad dispersity brushes.^{37, 66} Although many experimental studies report brush \overline{D} , relatively few have examined its effect on brush conformation. A recent experimental study examining the conformation of polycaprolactone (PCL) brushes with $\overline{D} = 1.42 - 2.39$ showed that average brush thickness increased with increasing \overline{D} and σ .³⁷ The scaling exponents of l_b with N, however, were markedly greater than unity, the upper limit of the scaling theory in the CPB regime.²⁴ Differences in l_b in brushes of varying \overline{D} , and therefore the scaling exponents, were hypothesized to arise from differences in hydrodynamic interactions and brush conformation. Nonetheless, how these observations connect to predictions of scaling theory is not clear.

A recent experimental study examined the extent of pH-response of conformation and the scaling of l_b of annealed polyelectrolyte poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) brushes across a range of N, σ , and \overline{D} as a function of α at C_s of 1 mM.⁴⁹ 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 of brush conformation was independent of these properties. 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, σ , and \overline{D} .⁴⁹ By contrast, in another study, the extent of pH-response of the conformation of spherical poly(acrylic acid) PAA polyelectrolyte brushes varied with both weight-average degree of polymerization N_w and σ .⁶⁷ 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.

1.5.Objective of Dissertation

The objective of this dissertation is to understand the effect of \overline{D} on neutral and pH-responsive spherical brush conformations in dilute solutions. The findings of this thesis provide evidence that neutral and the pH-responsive brushes are affected differently by \overline{D} , which can be leveraged to improve nanoparticle dispersion in complex media. In Chapter 2, experimental methods of this dissertation are described, including syntheses and hydrolysis of poly(*tert*-butyl acrylate) P*t*BA brushes and instrumental characterizations.

In Chapter 3, neutral (PtBA) brushes were synthesized, using surface-initiated atom-transfer radical polymerization (SI-ATRP), in which both \overline{D} and N_w varied. The conformation of PtBA brushes was assessed from scaling of l_b using DLS. l_b of PtBA and various polymers (from literature studies) various \overline{D} could be collapsed onto a master curve as a function of $N_w \sigma^{1/3}$ in the SDPB regime, but fell on a bifurcated curve as a function of $N_w \sigma^{1/2}$ in the CPB regime. Therefore, we propose that the coiled conformation at the periphery was independent of \overline{D} in the SDPB regime. In the CPB regime, the conformation of the high- \overline{D} brushes was more extended than the low- \overline{D} brushes when $N_w \sigma^{1/2} < 470 \pm 30$. However, the difference in conformation at the periphery between the low- and the high- \overline{D} brushes was negligible at higher $N_w \sigma^{1/2}$.

In Chapter 4, SANS experiments were performed on a pair of low- N_w PtBA brushes (CPB regime) and two pairs of high- N_w PtBA brushes (SDPB regime), and Đ was distinct in each pair. The SLD of solvent (3.45 × 10⁻⁶Å²) matched that of the core (3.47 × 10⁻⁶Å²) but was different from the SLD of PtBA (0.55 × 10⁻⁶Å²). SANS

data were fit with the core-chain model, showing the variation of l_b and ρ profiles. l_b of the high-D brushes characterized from SANS was lower that that from DLS, and the difference in l_b was enhanced with increasing N_w . This suggested the presence of great among of long chains in the high- N_w , high-D brushes. At low N_w (CPB regime), the ρ profiles were different between low- (linear decay) and high-D (power-law decay) brushes nearly throughout the whole brush layer, indicating D had strong influence on the brush conformation. At higher N_w (SDPB regime), Although, the ρ profiles were different at the intermediate r, ρ scaled with $r^{-4/3}$ at the periphery. We hypothesized this D showed influence on the brush conformation, leading to different ρ profiles.

In Chapter 5, PAA brushes hydrolyzed from low- N_w PtBA brushes in the CPB regime exhibited different extents of pH-response of l_b when D was varied. For the high-D brush, l_b was greater than that of the low-D brush. However, in PAA brushes hydrolyzed from high- N_w PtBA brushes in the SDPB regime, l_b increased similarly with pH regardless of D. The extent of pH-response of $l_b/l_{b,max}$, where $l_{b,max}$ was the l_b measured at pH 10, weakly dependent on pH for the low- N_w , low-D brush, and it increased with increasing D and collapsed with the brushes with higher N_w . In addition, the scaling of $l_b/l_{b,max}$ with α increased with N_w but not D, indicating the low- and the high- N_w brushes were in the q-NB and the SB regime, respectively. The difference between the pH- and the α -responses of the low- N_w , low-D brush adopted a pHindependent extended conformation due to strong interchain excluded volume interactions, whereas the conformation of the other brushes with higher N_w and/or D varied from collapsed to extended with increasing pH arisen from electrostatic interactions.

In Chapter 6, key points of three studies in the chapter 3, 4, and 5 are summarized. For future work, the fitting results in the chapter 4 can be examined with addition of structure factor in the model, and the methods to probe brush conformation can be applied to study conformation of spherical brushes with different Đ dispersed in polymer matrices. In addition, the results in the chapter 5 can be extended to brush conformation in the presence of added salt probed by DLS and SANS.

Chapter 2. Experimental Details

2.1.Materials

All chemicals were purchased from Sigma-Aldrich and used without further purification unless otherwise noted. N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA, 99%) was degassed with three freeze-pump-thaw cycles before use. The inhibitor in *tert*-butyl acrylate (*t*BA, 98%) was removed using a silica gel column (60 Å pore size), then dried with calcium hydride (reagent grade, 95%), and distilled under reduced pressure. Dichloromethane (DCM, JT Baker, HPLC grade, \geq 99.8%), toluene (JT Baker, HPLC grade, \geq 99.7%), and tetrahydrofuran (THF, JT Baker, low water HPLC grade, \geq 99.8%) were dried with a Pure Process Technology solvent purification system. Copper (I) bromide (Cu^IBr) was purified before use (described in the next section).⁶⁸ Colloidal silica (MEK-ST, 30-31 wt% SiO₂ in methyl ethyl ketone, supplier reported diameter of 10 – 15 nm) was kindly provided by Nissan Chemicals Co. and used as received.

2.2.Polymer Syntheses

2.2.1. Purification of Cu^IBr

1 g of Cu^IBr and copper (II) bromide (Cu^{II}Br₂) mixture was stirred with 30 mL acetic acid (\geq 99.7%) overnight. The supernatant was decanted, and the precipitate was twice washed by fresh 30 mL acetic acid under 10 min stirring in a 100 mL round bottom flask. After the supernatant was removed, excess ethanol (\geq 99.5%) was used to wash the precipitate under 10 min stirring until it became white powder. 20 mL of ether (\geq 99.7%) was used to wash the resulting white precipitate for 3 times under 10 min stirring. Precipitate was then collected and dried in a vacuum oven at 80 °C

overnight. The pure Cu^IBr was directly transferred into a glove box from the vacuum oven.⁶⁸

2.2.2. Synthesis of ATRP Initiator

The ATRP initiator was synthesized by a hydrosilation reaction in the presence of platinum on carbon. (Scheme 2-1).^{69, 70} In a 500 mL round bottom flask wrapped with foil, platinum on carbon (110 mg) and dimethylchlorosilane (98%, 50 g, 0.528 mol) were mixed in the dark to avoid deactivating the catalyst. The flask was capped with a rubber septum, purged with nitrogen for 5 min, and placed in a 40°C oil bath. Allyl 2-bromo-2-methylpropionate (98%, 5 g, 0.024 mol) was subsequently transferred into the flask *via* a syringe under nitrogen purge. The solution was stirred at 40°C for 1 h and then at room temperature for 2 days. The catalyst in the solution was filtered through 0.2 μ m PTFE syringe filters. After removing excess dimethylchlorosilane under reduced pressure, a colorless oil-like product was obtained and used directly in the next step. The residual product was stored in a refrigerator.

Scheme 2-1 ATRP initiator synthesis



2.2.3. Synthesis of ATRP Initiator-Grafted Silica Nanoparticles

To immobilize the ATRP initiator on silica nanoparticles with $r_0 = 5.7 \pm 0.2$ nm measured with DLS, MEK-ST (30 g) was transferred into a 100 mL round bottom flask. While stirring, the ATRP initiator (1.2 g, 3.98 mmol) was added dropwise. The solution was placed in a 90°C oil bath and refluxed for 20 h.⁶⁹ Then, hexamethyldisilazane (HMDS, 99.9%, 1.77 mL, 8.55 mmol) was added at room temperature and subsequently heated to 40°C for 20 h.^{71, 72} HMDS terminated the remaining hydroxyl groups on the silica nanoparticles. The reaction mixture was precipitated into a methanol/deionized water solution (64 mL/16 mL). The initiator-grafted nanoparticles were isolated by centrifugation, precipitated in 200 mL hexane 3 times, and dried in a vacuum oven at room temperature overnight.

Scheme 2-2 ATRP initiator immobilization on silica nanoparticles



2.2.4. Synthesis of PtBA Brushes Grafted from Silica Nanoparticles

Low-Đ P*t*BA brushes were synthesized through surface-initiated atom transfer radical polymerization (SI-ATRP).^{23, 34, 70, 73, 74} The as-synthesized initiator-grafted silica nanoparticles (100 mg, 0.011 mmol), *t*BA, Cu^IBr (0.23 mmol) and Cu^{II}Br₂ (99%, 0.023 mmol, 10 mol% relative to Cu^IBr), and PMDETA (0.253 mmol) were mixed in a round bottom flask under nitrogen atmosphere inside the glove box with [initiator] : $[Cu^{I}Br]$: $[Cu^{II}Br_2]$: [PMDETA] = 0.05 : 1.00 : 0.10 : 1.10. Anhydrous dimethylformamide (DMF, 99.8%) was used to dilute the mixture with volume ratio 1.75 : 1 (vol. DMF : vol. *t*BA). The ratio of [initiator] to [*t*BA] and reaction time were varied to obtain polymer brushes with different molecular weights. The flask was capped with a rubber septum and transferred to a 50°C oil bath. Polymerization was performed between 1 to 5 h depending on targeted molecular weight. After polymerization, the septum was removed, and the reaction was quenched by the addition of 200 mL THF. The catalyst was then removed using an aluminum oxide column (80 g). The transparent solution was concentrated, precipitated in methanol/deionized water (50/50 by volume), and dried in a vacuum oven at room temperature overnight.

To vary \oplus of PtBA brushes, phenylhydrazine (PH, 97%) was added to select SI-ATRP syntheses. PH was added to the mixture prepared in the glove box containing initiator, Cu^IBr, Cu^{II}Br₂, and PMDETA, and the ratios of reagents were [initiator] : [Cu^{II}Br] : [Cu^{II}Br₂] : [PMDETA] : [PH] = 0.05 : 1.00 : 0.10 : 1.10 : 0.38. DMF was added as the solvent to dilute the mixture with the volume ratio 1.75 : 1 (vol. DMF : vol. *t*BA). The ratio of [initiator] to [*t*BA] and reaction time were varied to obtain polymer brushes with different molecular weights. The flask was capped with a rubber septum and transferred to a 50°C oil bath. Polymerization was performed between 1 to 5 h depending on targeted molecular weight. After polymerization, the products were quenched by 200 mL THF, purified with an 80 g aluminum oxide column, precipitated in methanol/deionized water (50/50 by volume), and then dried in a vacuum oven at room temperature overnight.⁶⁶

Scheme 2-3 Synthesis of PtBA brushes via "grafting from" surface initiated-ATRP



phenylhydrazine (PH)

2.2.5. Cleavage of PtBA Brushes from Silica Nanoparticles

To determine molecular weight and its distribution, aliquots of PtBA-grafted silica nanoparticles (110 mg) were dissolved with 20 mL of THF in Teflon jars followed by the addition of hydrofluoric acid HF aqueous solution (49 wt%, 1.2 mL).^{69, 75} The reaction was held at room temperature for 5 h without stirring. Then, the HF was neutralized by addition of KOH aqueous solution (4 M, 13 mL). The quenched solution was dried using a rotary evaporator, followed by drying in a vacuum oven at room temperature overnight. The cleaved samples were dissolved in 50 mL toluene and extracted with 100 mL deionized water three times. The organic layer was collected and stirred with excess anhydrous magnesium sulfate for 1 h. After removal of magnesium sulfate and toluene, the cleaved PtBA was dissolved by a minimal amount of THF, precipitated in methanol/deionized water (60 mL/40 mL), and dried in a vacuum oven at room temperature overnight.

2.2.6. Hydrolysis of PtBA to PAA

The PtBA-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 into the solutions for hydrolysis. The flasks were covered with aluminum foil and wrapped with Parafilm, and the reaction was allowed to proceed for 14 h at room temperature (Scheme 2-4). 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 (typical 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 (H¹-NMR).

Scheme 2-4 Hydrolysis of PtBA brushes



X= Br or

2.3. Characterizations of PtBA brushes

2.3.1. Dynamic light scattering (DLS)

Hydrodynamic radius R_h was measured using a DLS apparatus, which consisted of an ALV goniometer equipped with a He-Ne laser (wavelength 632.8 nm) and an ALV-5000/EPP multiple tau digital correlator (ALV-GmbH, Langen, Germany). Ten intensity correlation functions $g^{(2)}(q,t)$ were collected for 60 s at scattering angle 90° and temperature 20°C, where t is time and q is the magnitude of the wave vector (defined in eqn. 2-2). Samples were diluted in THF at 1 mg/mL and filtered through a 0.2 μ m PTFE syringe filter. The intensity correlation function was fit over the time range of 2.5 × 10⁻⁴ ms to 10³ ms to⁷⁶

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

and
$$q = \frac{4\pi n \sin\frac{\theta}{2}}{\lambda}$$
, (2-2)

where τ^{-1} and μ are the relaxation rate and the variance of the distribution, respectively. The diffusion coefficient *D* was calculated from the relaxation rate, and R_h was calculated from *D* using the Stokes-Einstein equation as

$$D = \frac{1}{\tau q^2} = \frac{k_B T}{6\pi \eta R_h},\tag{2-3}$$

where *n* is the refractive index of THF at 20°C, η is the viscosity of THF at 20°C, k_B is Boltzmann's constant, and *T* is the temperature in Kelvin.^{77, 78} l_b was then obtained by subtracting r_0 from R_h .

2.3.2. Thermogravimetric analysis (TGA)

TGA was performed on a TA Instruments Model Q500 TGA. The polymer nanoparticles (10 mg to 30 mg) were placed on a platinum pan and first equilibrated at 25°C, followed by ramping to 800°C at a rate of 10°C/min under a 40 mL/min air flow. The bare silica nanoparticles and initiator-grafted nanoparticles showed slight weight loss due to the residual silanol and grafted initiator, respectively.⁷⁹ The significant weight loss of the *Pt*BA-grafted nanoparticles arose from the degradation of *tert*-butyl groups, forming carboxylic acid groups and alkene at 250°C. At the elevated temperature, the carboxylic acid groups were further dehydrated to the six-member cyclic anhydride structure and water (Figure 2-1).⁸⁰



Figure 2-1. Weight percent as a function of temperature, obtained from TGA, of the bare silica nanoparticles (black curve), initiator-grafted silica nanoparticles (red curve), and PtBA-grafted silica nanoparticles sample L16 (Table A1) (blue curve).

2.3.3. Elemental analysis (EA)

Elemental analysis was performed using an Exeter CE440 instrument at the Midwest Microlab Co. for characterizing bromine composition in nanocomposite materials.

2.3.4. Gel permeation chromatography (GPC)

 M_n , M_w , and \overline{D} of the cleaved PtBA were characterized with a Viscotek GPC equipped with two Agilent ResiPore columns, using a mobile phase of stabilized THF (OmniSolv, HPLC grade, > 99 %) at 30°C. Refractometer data obtained from cleaved PtBA are shown in Figure 2-2 and Figure 2-3 (with sample characteristics summarized in Table A1 and A2). The flow rate was 1.0 mL/min for all data, except for Figure 2-3a, which was collected at 0.7 mL/min. The injection volume was 100 µL and the sample concentration was 1 mg/mL. A triple detection system, including a differential refractometer, light scattering, and viscometer, was employed to characterize the absolute molecular weight. The dn/dc value of PtBA was measured to be 0.048 \pm 0.001.⁸¹





Figure 2-2. GPC refractometer chromatographs of cleaved P*t*BA brushes (Table A1): (a) L1-L5; (b) L6-L10; (c) L11-L15; (d) L16-L20; (e) L21-L15; (f) L26-L30; (g) L31-L34.





Figure 2-3. GPC refractometer chromatographs of cleaved P*t*BA brushes (Table A2): (a) H1-H3; (b) H4-H8; (c) H9-H13; (d) H14-H18; (e) H19-H23.

2.3.5. Proton nuclear magnetic resonance (¹H-NMR)

The chemical structure of PtBA was characterized using a JEOL ECA-400 NMR spectrometer. Samples were dissolved in deuterated chloroform containing 0.03% v/v tetramethylsilane as an internal standard. Chemical shifts were referenced to the solvent proton resonance (7.26 ppm). A representative spectrum is shown in Figure 2-4.





Figure 2-4. (a) ¹H-NMR spectrum obtained from sample L10 cleaved from nanoparticles (Table A1). (b) and (c) show a closer view of selected regions of the data in (a).

2.3.6. Small-Angle Neutron Scattering (SANS)

SANS measurements were performed on the NGB 30 m beamline at the National Institute Standards and Technology Center for Neutron Research with a neutron source with 6 Å wavelength and 1 mm sample thickness. The PtBA brushes were dispersed in a mixed hydrogenated and deuterium THF (47/53 v/v) with concentration 0.3 wt%. The magnitude of *q* ranged from 0.001 to 0.310 Å⁻¹ by varying sample-to-detector distances at 13, 4, 1 m and addition of focusing refractive lenses at 13 m sample-to-detector distance. The *q*-dependent total scattering intensity I_{total} (*q*) was obtained by reduction of scattering neutron signal using Igor Pro 8 (WaveMetrics) to account for contributions from background, empty cell, sample transmission, and sample thickness.

2.4. Characterizations of PAA brushes

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. The samples were then filtered through a 0.2 or $0.45 \,\mu$ m Nylon syringe filter depending on the size of the nanoparticles.

2.4.1. ¹H-NMR

The chemical structure of PAA (錯誤! 找不到參照來源。) was characterized with ¹H-NMR from a JEOL ECA-400 NMR spectrometer. PAA was dissolved in deuterated deuterated dimethyl sulfoxide (DMSO, 99.0%). Chemical shifts were referenced to the solvent proton resonance (2.50 ppm for DMSO).⁸²



Figure 2-5 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).

2.4.2. DLS

The same DLS instrument and the fitting eqns. for PtBA brushes were utilized to characterize l_b of PAA-grafted silica nanoparticles solutions, where n and η become the refractive index and the viscosity of water at 20°C, respectively. 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.

The intensity-intensity correlation functions $g^2(q, t) - 1$ of the PAA brushes hydrolyzed from the PtBA brushes in Table 5-1 in aqueous solutions of pH 3, 7, and 10 are shown in Figure 2-6, Figure 2-7, and Figure 2-8, respectively.



Figure 2-6. Intensity-intensity correlation functions $g^2(q,t) - 1$ as a function of delay time for the PAA brushes with N_w and varying \mathcal{D} dispersed in the aqueous solution with pH 3. Solid lines represent method of cumulant fits.⁷⁶ (a) $N_w = 45$, $\mathcal{D} = 1.09$ (yellow closed triangles), $N_w = 45$, $\mathcal{D} = 1.69$ (green closed squares); (b) $N_w = 782$, $\mathcal{D} = 1.23$ (red open triangles), $N_w = 837$, $\mathcal{D} = 1.76$ (blue open squares).



Figure 2-7. Intensity-intensity correlation functions $g^2(q,t) - 1$ as a function of delay time for the PAA brushes with N_w and varying \mathcal{D} dispersed in the aqueous solution with pH 7. Solid lines represent method of cumulant fits.⁷⁶ (a) $N_w = 45$, $\mathcal{D} = 1.09$ (yellow closed triangles), $N_w = 45$, $\mathcal{D} = 1.69$ (green closed squares); (b) $N_w = 782$, $\mathcal{D} = 1.23$ (red open triangles), $N_w = 837$, $\mathcal{D} = 1.76$ (blue open squares).



Figure 2-8. 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.⁷⁶ (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).

2.4.3. Zeta potential (ζ)

The ζ 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.

2.4.4. 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, pH was adjusted to 12 by adding a 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.

Chapter 3. Effect of **Đ** on the Conformation of Spherical Polymer Brushes

In this chapter, we show that the effect of polymer \tilde{D} on the conformation of spherical polymer brushes depends strikingly on brush molecular weight. We synthesized PtBA brushes of $\tilde{D} = 1.03 - 1.98$ grafted to nanoparticles using SI-ATRP and determined l_b using DLS in a good solvent. The average lengths of brushes exceeded the number-average contour length $L_{c,n}$ predicted from the number-average degree of polymerization N_n , indicating that long chains contributed significantly to the measured l_b . In the SDPB regime, l_b of brushes of various \tilde{D} could be collapsed onto a master curve as a function of the scaling variable $N_w \sigma^{1/3}$. In the CPB regime, however, l_b collapsed onto a bifurcated curve as a function of the scaling variable $N_w \sigma^{1/2}$. Polymer brushes of various \tilde{D} from the literature also collapsed onto these curves.^{23, 24, 37, 83} To explain the bifurcation in the CPB regime, we propose that stretching of the stem region in disperse brushes leads to an increase in average l_b only when $N_w \sigma^{1/2}$ is low.

3.1. \mathbb{D} differently affects l_b of PtBA brushes at low and high N_w

PtBA brushes were grown from silica nanoparticles with an average r_0 of 5.7 ± 0.2 nm as measured by DLS *via* SI-ATRP, and brush \overline{D} was tuned between 1.03 and 1.98 with addition of phenylhydrazine to selected syntheses.¹⁵ Grafted polymer was cleaved from nanoparticles using aqueous HF for molecular weight and \overline{D} characterization *via* GPC. $\sigma = 0.5 \pm 0.2$ chains/nm² was calculated from the weight

percentage of grafted polymer, determined using TGA and EA (σ of individual samples are listed in the Appendix Table A1 and A2). From R_h of the PGNPs, characterized *via* the method of cumulants applied to DLS data, we calculated $l_b = R_h - r_0$.⁷⁶

Increasing the brush \mathbb{D} had different consequences for l_b , depending on N_w . At $N_w \approx 43$, the characteristic time scale extracted from the intensity-intensity correlation functions increased with \mathbb{D} (Figure 3-1a), indicating that R_h of the PGNP and hence l_b were greater. At higher $N_w \approx 833$, however, the intensity-intensity correlation functions obtained for brushes of two different \mathbb{D} were identical (Figure 3-1b), indicating that R_h did not change with increase in \mathbb{D} . This surprising result suggests that \mathbb{D} markedly alters l_b only in a range of N_w .



Figure 3-1. Intensity-intensity correlation functions $g^2(q, t) - 1$ as a function of delay time for PGNPs with similar N_w and varying \overline{D} were collected in a good solvent, THF, with concentration 1mg mL-1 at 20°C. Solid lines represent method of cumulant fits.⁷⁶.

3.2. l_b of PtBA Brushes with Varying \oplus Bifurcates as a Function of N_w

Prior studies on brush conformation examined l_b scaling behavior with both $N_n^{1, 26, 34, 37, 83-85}$ and $N_w^{3, 23, 24, 86}$, without clear consensus as to which molecular weight average governs brush behavior. To assess the effects of \mathbb{D} on l_b , we first examined l_b as a function of N_n . When \mathbb{D} was increased from low (1.03 - 1.29) to high (1.49 - 1.98), l_b increased at constant N_n , reflecting contributions from long chains in the broad molecular weight distribution (Figure 3-2a). At lower values of N_n , l_b of high- \mathbb{D}

brushes was greater than the number-average contour length determined as the full length of a PtBA chain adopting a linear conformation ($L_{c,n} = N_n l_0$) and the numberaverage fully-extended length determined as the length of the all-*trans* conformation ($L_{f,n} = N_n l_0 \sin \frac{\theta}{2}$), where $l_0 = 0.30$ nm (the length of two carbon-carbon bonds) and θ = 109.5° were the monomer length and carbon-carbon bond angle, respectively.⁸⁷⁻⁸⁹ This intriguing result confirms that long chains contribute substantially to l_b when the molecular weight distribution is broad. All l_b were greater than the radius of gyration ($R_g = 1.18 \times 10^{-2} M^{0.59}$, obtained from free PtBA in THF,⁹⁰ where *M* was the number-average and weight-average molecular weight in Figure 3-2a and Figure 3-2b, respectively), consistent with prior literature, demonstrating R_g of grafted chains was greater than that of free chains at high σ .⁹¹

To account for long chains in a broad molecular weight distribution, we compared the dependence of l_b on N_w with the weight-average contour length $(L_{c,w} = N_w l_0)$ and the weight-average fully-extended length $(L_{f,w} = N_w l_0 \sin \frac{\theta}{2})$.⁸⁷⁻⁸⁹ The l_b values of the high- θ series were commensurate with $L_{c,w}$ and $L_{f,w}$ when $N_w \leq 100$, and the l_b of the other brushes were between $L_{c,w}$ and R_g , regardless of θ and N_w (Figure 3-2b). To locate the crossover from CPB to SDPB brush regimes, r_c was calculated as³, 37,83

$$r_c = r_0 \sigma^{*0.5} v^{*-1}, \tag{3-1}$$

where $\sigma^* = \sigma b^2$ was the reduced grafting density, v was the excluded volume parameter, and $v^* = v/(4\pi)^{1/2}$. Eqn. 3-1 was previously applied to brushes grafted

from nanoparticles with r_0 varying from 5 – 65 nm.^{23, 24, 32, 37, 92} For P*t*BA brushes, $r_c = 32 \pm 5$ nm using eqn. 3-6 (b = 0.7 nm,^{93, 94} and $v = 0.23 \pm 0.06$, calculated using the MWC-WZ model below).²⁴ Thus, brushes with $l_b < 26$ nm were in the CPB regime, where l_b of high-D brushes was greater than that of low-D brushes. Brushes with $l_b > 26$ nm were in the SDPB regime, and l_b collapsed onto a master curve regardless of D.



Figure 3-2. l_b as a function of (a) N_n and (b) N_w . The dashed-dotted lines indicate $L_{c,n}$ in (a) and $L_{c,w}$ in (b). The dotted lines indicate $L_{f,n}$ in (a) and $L_{f,w}$ in (b). The dashed lines indicate R_g . The symbol's color shading indicates brush \mathcal{D} .

To obtain v of the spherical PtBA brushes, the MWC-WZ model, which only accounts for pairwise interactions, predicts the effective height (H_0) of a brush on a flat surface from l_b and r_0 of a brush on a spherical surface:²⁴

$$H_0 = \left[l_b^{\ 3} + \frac{3}{4} \left(\frac{l_b^{\ 4}}{r_0} \right) + \frac{1}{5} \left(\frac{l_b^{\ 5}}{r_0^{\ 2}} \right) \right]^{1/3} = \left(\frac{8}{\pi^2} \right)^{\frac{1}{3}} b N_w v^{\frac{1}{3}} \sigma^{*\frac{1}{3}}.$$
 (3-2)

v was calculated for selected low- \overline{D} spherical brushes in the SDPB regime, as determined by r_c from the scaling crossover ($l_b > 24$ nm), using eqn. 3-3, with N_w , the Kuhn length b = 0.7 nm, and σ (Table A1):

$$v = \frac{\pi^2 H_0^3}{8b^5 N_w^3 \sigma}.$$
 (3-3)

A representative calculation of v for sample L31 (Table A1) with $N_w = 780$, $\overline{D} = 1.23$, $l_b = 57$ nm, and $\sigma = 0.32$ chains/nm² is:

$$H_0 = \left[57.0^3 + \frac{3}{4} \left(\frac{57.0^4}{5.7}\right) + \frac{1}{5} \left(\frac{57.0^5}{5.7^2}\right)\right]^{1/3} = 174.3 \text{ nm}$$
(3-4)

and
$$v = \frac{\pi^2 \times 174.3^3}{8 \times 0.7^5 \times 782^3 \times 0.31} = 0.26.$$
 (3-5)

The value $v = 0.23 \pm 0.06$ reported in this chapter was determined as the average of v of the individual samples in Table A1

A representative calculation of r_c for sample L31 (Table A1) with $N_w = 780$, D = 1.23, $l_b = 57$ nm, and $\sigma = 0.32$ chains/nm² is:

$$r_c = 5.65 \times (0.32 \times 0.70^2)^{0.5} \left(\frac{0.26}{\sqrt{4\pi}}\right)^{-1} = 30.81 \text{ nm.}$$
 (3-6)

The value $r_c = 32 \pm 5$ nm reported in this chapter was determined as the average of r_c of the individual samples in Table A1. Finally, the critical brush length was calculated as

$$l_b = r_c - r_0 = (32 \pm 5) - (5.7 \pm 0.2) = 26 \pm 5 \text{ nm.}$$
 (3-7)

3.3. Đ
 Shows Different Influences on l_b for Brushes in the SDPB and the CPB
Regimes

Next, we examined l_b of brushes in the SDPB and CPB regimes as a function of $N_w \sigma^{1/3}$ and $N_w \sigma^{1/2}$, respectively.²⁴ The use of scaling theory allows us to compare multiple brush systems at different σ .²⁴ In the SDPB regime, l_b of PtBA brushes ($\theta =$ 1.03 – 1.96), as well as brushes composed of polystyrene (PS, $\theta = 1.05 - 1.13$)²⁴ and a poly(ethylene oxide-*block*-propylene oxide-*block*-ethylene oxide) triblock copolymer (PEO-*b*-PPO-*b*-PEO, D = 1.10 - 1.20)⁸³ collapsed cleanly onto a master curve as a function of $N_w \sigma^{1/3}$ (Figure 3-3a), independent of D. Thus, D does not markedly alter l_b in the SDPB regime.

In the CPB regime, however, short brushes of low- \mathcal{D} (PS, PMMA, PCL, and PtBA) and high- \mathcal{D} (PCL and PtBA) scaled onto a bifurcated curve as a function of $N_w \sigma^{1/2}$ (Figure 3-2b). l_b of brushes of varying composition and dispersity fell on two distinct curves that intersected at $N_w \sigma^{1/2} = 470 \pm 30$ (Figure 3-4). High- \mathcal{D} PtBA brushes ($\mathcal{D} = 1.49 - 1.98$) collapsed onto the high- \mathcal{D} branch along with the high- \mathcal{D} PcL brushes ($\mathcal{D} = 1.69 - 2.39$).³⁷ Low- \mathcal{D} PtBA brushes ($\mathcal{D} = 1.03 - 1.29$) collapsed onto the low- \mathcal{D} branch with PS ($\mathcal{D} = 1.06$ and 1.08)²⁴ and PMMA brushes ($\mathcal{D} = 1.19 - 1.28$).²³ Interestingly, PCL brushes with moderate \mathcal{D} ($\mathcal{D} = 1.42 - 2.06$) also collapsed on this branch (Figure 3-3b).³⁷ This result suggests that the σ -dependence of the scaling of higher- \mathcal{D} brushes may not follow that of uniform brushes. This idea, to be discussed later, is consistent with earlier Monte Carlo (MC) simulations, which revealed that l_b of brushes with $\mathcal{D} = 1.5 - 2.5$ scaled as $l_b \sim \sigma^{0.113 \pm 0.009}$.²⁶ Nonetheless, for each polymer composition, l_b in the high- \mathcal{D} branch was greater than that in the low- \mathcal{D} branch for $N_w \sigma^{1/2} < 470 \pm 30$; by contrast, l_b collapsed onto one curve at higher $N_w \sigma^{1/2}$ independent of \mathcal{D} (Figure 3-3b).



Figure 3-3. l_b as a function of (a) $N_w \sigma^{1/3}$ in the SDPB regime and (b) $N_w \sigma^{1/2}$ in the CPB regime, in which the color shading indicates \overline{D} .



Figure 3-4. l_b as a function of $N_w \sigma^{1/2}$ with color shading as an indicator for \mathbb{D} . Solid lines are fits for the upper and bottom branches, respectively, as $l_b = 1.29 (N_w \sigma^{1/2})^{0.72}$ and $l_b = 0.23 (N_w \sigma^{1/2})^{1.00}$.

Through a linear fit to P*t*BA brush data (Figure 3-5), we extracted the scaling exponents (eqns. 1-2 and 1-3). These exponents were 0.55 ± 0.03 in the SDPB regime and 0.90 ± 0.07 and 0.82 ± 0.07 for low-Đ and high-Đ branches, respectively, in the

CPB regime, consistent with scaling theory. PCL brushes exhibited a similar trend in scaling exponent to P*t*BA brushes in the CPB regime: the exponent of the low-D branch was higher than that of the high-D branch, though the exponent of the low-D branch exceeded 1.³⁷ Though the scaling theory was developed for low-D brushes, literature studies on high-D planar brushes confirmed their scaling exponents for *N* and σ were consistent with that of low-D brushes.²⁵



Figure 3-5. l_b of PtBA-grafted silica nanoparticles ($\theta = 1.03 - 1.98$, $\sigma = 0.5 \pm 0.2$ chains/nm²) as a function of (a) $N_w \sigma^{1/3}$ in the SDPB regime and (b) $N_w \sigma^{1/2}$ in the CPB regime, in which the color shading indicates θ . Solid lines represent linear fits to the data.

3.4.Polymer Conformation Varies Differently with N_w and \overline{D} in the SDPB and CPB Regimes

The independence of l_b with varying \overline{D} in the SDPB regime suggests that all brushes adopt a similar coiled conformation. In the CPB regime, however, at low $N_w \sigma^{1/2}$, higher- \overline{D} brushes adopt a more extended conformation than lower- \overline{D} brushes, whereas the brush conformation at the periphery is independent of \overline{D} at higher $N_w \sigma^{1/2}$. To explain these contrasting effects of \overline{D} , we propose physical pictures for brushes in the two regimes. The hypothesized conformation of brushes in the SDPB regime with varying \overline{D} is depicted in Figure 3-6a. At high l_b , the brush transitions from the CPB regime to the SDPB regime when l_b exceeds r_c , such that polymer chains adopt a coiled conformation at the periphery.^{23, 24} We propose that the coiled morphology at the periphery is not strongly influenced by \overline{D} (Figure 3-6a). Thus, the average l_b is relatively insensitive to \overline{D} in the SDPB regime.

The proposed conformation of brushes in the CPB regime with varying $N_w \sigma^{1/2}$ and D is depicted in Figure 3-6b. In the CPB regime, polymer chains in close proximity experience higher-order interactions.^{23, 24} For high-D brushes, based on earlier theories and simulations, we suggest that steric hindrance due to compressed short chains near the surface drives the extension of longer chains.^{25, 26} The long chains extend near the particle surface (the "stem") in the vicinity of shorter chains, but are less stretched at their free ends (the "crown").^{25, 26} It is this highly extended stem that leads to the experimental observation of greater l_b for the high-D brushes compared to the low-Dbrushes at low $N_w \sigma^{1/2}$. At higher $N_w \sigma^{1/2}$, however, we suggest that the conformation at the periphery is not strongly affected by D, and, hence, the difference in l_b between high-D and low-D brushes is negligible.



Figure 3-6. Schematic representation of conformation of PGNPs with core radius r_0 in different regimes. (a) Low-Đ and high-Đ brushes above r_c are in the SDPB regime at the periphery with similar l_b and coiled conformation. (b) Brushes below r_c are in the CPB regime with varying Đ and $N_w \sigma^{1/2}$.

This picture is consistent with earlier MC simulations, which found that the effect of \mathbb{D} on ρ varied with σ .²⁶ At constant N_n , when $\sigma = 0.65$ and 0.25 chains/ b^2 , the ρ at intermediate r decreased with increasing \mathbb{D} , indicating that the chains were extended near the surface.²⁶ When σ decreased from 0.25 to 0.1 chains/ b^2 , however, this ρ became less dependent on \mathbb{D} .²⁶ The nearly identical ρ profiles of brushes of various \mathbb{D} at the lowest σ suggests that these brushes do not adopt a stem configuration near the surface. This comparison suggests that the demarcation between high- and low- \mathbb{D} regimes is affected by σ . To test this idea, we compare σ (chains/ b^2) of the PCL brushes in Figure 3-3b (for which moderate- \mathbb{D} brushes collapsed onto the low- \mathbb{D} branch) with that of the MC simulations (Table 3-1). For PCL brushes, a grafting density of $\sigma = 0.21$ chains/nm² corresponded to $\sigma = 0.08$ chains/ b^2 (b = 0.6 nm),^{37, 95, 96} at which the effect of \mathbb{D} on PCL brush conformation was negligible in simulations.²⁶

Indeed, PCL brushes with $\sigma = 0.21$ chains/nm² adopted a similar conformation as that for low-D brushes, explaining the collapse of l_b for these brushes onto the low-Dbranch (Figure 3-3b). Likewise, the grafting density of moderate-D PCL brushes, $\sigma =$ 0.43 chains/nm² ($\sigma = 0.15$ chains/ b^2), was less than the $\sigma = 0.25$ chains/ b^2 at which stems were observed in simulations. We conclude that l_b of high-D brushes is controlled by the extended stem region, which is not present at low σ .

PCL σ (chains/nm ²) from ref. ³⁷	σ (chains/ b^2)
0.61	0.22
0.43	0.15
0.21	0.08

Table 3-1. Calculating σ of PCL brushes in chains/ b^2

3.5.Conclusions

We investigated the dependence of l_b of polymer brushes grafted to nanoparticles on \mathbb{D} . The transition from the CPB to the SDPB regimes was independent of brush \mathbb{D} , and l_b of PtBA brushes collapsed in the SDPB regime but fell on a bifurcated curve in the CPB regime. Significantly, l_b of brushes of various polymers (from literature studies) also collapsed onto the same master curve in the SDPB regime, and onto the same bifurcated curve in the CPB regime. We therefore propose that the coiled conformation is independent of \mathbb{D} in the SDPB regime. In the CPB regime, the high- \mathbb{D} brushes adopted a more extended conformation than the low- \mathbb{D} brushes when $N_w \sigma^{1/2} < 470 \pm 30$, yet brushes of differing \mathbb{D} adopted a similar conformation at the periphery at higher $N_w \sigma^{1/2}$. The more extended polymer brush conformation attained *via* increase in \overline{D} can be leveraged to control nanoparticle dispersion in complex media.

Chapter 4. \oplus Distinctly Affects ρ profiles in the CPB and SDPB Regimes

In this chapter, the ρ profiles of selected PtBA brushes from chapter 3 (Table 4-1) are assessed through SANS. We fit SANS data using a core-chain model derived from a scaling theory for star polymers established by Daoud and Cotton,⁶⁴ which was successfully applied to PGNP systems.^{31, 65, 97} This model assumes the ρ profile in the polymer layer varies from a constant region (inner layer) to a linear region (intermediate layer) and finally to a power-law region (outer layer) with increasing r (Figure 4-1).^{31,}



Figure 4-1. ρ profile of polymer chains grafted on nanoparticles consisting of a constant ρ region $\rho \sim r^0$ in the inner layer (pink curve), a lineardecay ρ region $\rho \sim r^{-1}$ in the intermediate layer (blue curve), and a power-law-decay region $\rho \sim r^{-4/3}$ in the outer layer (cyan curve).⁶⁵

PtBA brushes	N_w^{a}	N_n^{a}	${ m }{ m D}^{ m a}$	$l_b \ (nm)^b$	σ (chains nm ⁻ ²) ^c
Low N _w , Low Đ	67.2±0.3	58.2±0.2	1.15	9.6±0.2	0.44
Low N _w , High Đ	59 <u>±</u> 3	37±7	1.59	18.9±0.3	0.51
Intermediate N_w , Low Đ	390±30	330±20	1.19	33.5±0.2	0.28
Intermediate <i>N</i> _w , High Đ	360±20	220±20	1.60	36.4±0.3	0.56
High N _w , Low Đ	810±20	680±20	1.19	62.6±0.4	0.37
High N _w , High Đ	854	439	1.94	58.30±0.2	0.68

Table 4-1. PtBA-grafted silica nanoparticles selected for SANS measurements

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

^b Characterized with DLS: l_b was calculated from the method of cumulants (eqns. 2-1 and 2-3) and subtraction of R_h . Standard deviations were calculated from 10 measurements on the same sample.

^c Characterized with TGA and EA.⁹⁸

4.1.SANS Fitting Model

SANS data are fit to a core-chain model (using Sasview 4.2.2), which describes scattering from a spherical core and grafted polymers, and, in the polymer layer, the ρ varies with *r*. In addition, the SLD profile of the polymer layer is also dependent on *r*, because SLD is a function of ρ as³¹

$$SLD = \rho(r) \times b_{\text{coh,mono}} + \left[1 - \frac{\rho(r) \times m_{\text{mono}}}{N_A \times \rho_{\text{mono}}}\right] \times c_{\text{solvent}} \times b_{\text{coh,solvent}}, \quad (4-1)$$

where $b_{coh,mono}$ and $b_{coh,solvent}$ are the coherent scattering length of monomer and solvent, respectively; m_{mono} and ρ_{mono} are the molar mass and density of monomer, respectively; and $c_{solvent}$ is the number density of solvent molecules. $I_{total}(q)$ has contributions of q -dependent coherent scattering and q -independent incoherent (background) scattering B. The coherent scattering is a function of the structure factor S(q), representing inter-particle correlations, and form factors, describing intraparticle scattering and dependent on the shapes of the core, brush region, and individual polymer chains.⁵⁹ Under dilute conditions, the interparticle positions are not correlated and $S(q) \approx 1.^{59}$ The form factor from the spherical core $P_{\text{core}}(q)$ is³¹

$$P_{\text{core}}(q) = (\text{SLD}_{\text{core}} - \text{SLD}_{\text{solvent}}) \int_0^{r_0} r^2 \times \frac{\sin qr}{qr} dr, \qquad (4-2)$$

where SLD_{core} and $SLD_{solvent}$ are the SLD of core and solvent, respectively. The form factor of polymer chains $P_{polymer}(q)$, however, depends on r due to variation of SLD, and, therefore, $P_{polymer}(q)$ is separated into three regions. The form factor of the inner region (i.e. constant region) nearest to core surface $P_{polymer,inner}(q)$ is³¹

$$P_{\text{polymer,inner}}(q) = \left(\text{SLD}_{\text{polymer}} - \text{SLD}_{\text{solvent}}\right) \int_{r_0}^{r_2} r^2 \times \frac{\sin qr}{qr} dr, \qquad (4-3)$$

where $SLD_{polymer}$ and $SLD_{solvent}$ are the SLD of polymer and solvent, respectively. When the whole particle size $R_p > r_2$, the form factor from polymer in the intermediate region (i.e. linear region) $P_{polymer,inter}(q,r)$ becomes³¹

$$P_{\text{polymer,inter}}(q, r)$$

$$= \left(\text{SLD}_{\text{polymer}} - \text{SLD}_{\text{solvent}}\right) \int_{r_2}^{r_1} \frac{1 - (r - r_0)}{R_p - r_0} \times r^2 \times \frac{\sin qr}{qr} dr.$$
(4-4)

When $R_p > r_1$, the form factor from polymer in the outer region (i.e. power-law region) $P_{polymer,outer}(q,r)$ is

$$= \left(\text{SLD}_{\text{polymer}} - \text{SLD}_{\text{solvent}}\right) \int_{r_1}^{R_p} \left(\frac{r}{r_1}\right)^{-4/3} \times r^2 \times \frac{\sin qr}{qr} dr.$$
(4-5)

From the combination of these form factors (from eqn.4-2 to eqn. 4-5), the $I_{total}(q)$ is

$$I_{\text{total}}(q) = 44$$

$$\phi \times \frac{\left[4\pi \times \left(P_{\text{core}}(q) + P_{\text{polymer,inner}}(q) + P_{\text{polymer,inter}}(q,r) + P_{\text{polymer,outer}}(q,r)\right)\right]^{2}}{V_{\text{particle}}} + B, (4-6)$$

where ϕ and V_{particle} are volume fraction and volume of the whole nanoparticles, respectively.

4.2. Variation in l_b Between Low- and High- \oplus Depends on N_w

To enhance $I_{\text{total}}(q)$ from grafted polymer, the SLD of the solvent (3.45 × 10^{-6} Å^{-2}), a mixture of hydrogenated and deuterated THF (47%/53% v/v), is contrast matched to that of the silica core (3.47 × 10^{-6} Å^{-2}), whereas the SLD of P*t*BA is different from both (3.47 × 10^{-6} Å^{-2}). $I_{\text{total}}(q)$ of the high-D brushes is lower than that of the low-D brushes at low q region, showing the impact of D on structural features in SANS data (Figure 4-2). We hypothesize that the upturn in $I_{\text{total}}(q)$ of the low- and intermediate- N_w , high-D brush at low-q arises from nanoparticle aggregation, leading to deviation of the fitted curve from the data (Figure 4-2a and b). In addition, deviations from the model and data can also arise from lack of structure factor in the fitting model.



Figure 4-2. $I_{\text{total}}(q)$ for PtBA brushes with (a) $N_w = 67$, $\overline{D} = 1.15$ (black open squares) and $N_w = 59$, $\overline{D} = 1.59$ (blue open triangles), (b) $N_w = 389$, $\overline{D} = 1.19$ (black open squares) and $N_w = 357$, $\overline{D} = 1.60$ (blue open triangles), and (c) $N_w = 807$, $\overline{D} = 1.19$ (black open squares) and $N_w = 854$, $\overline{D} = 1.94$ (blue open triangles). Black and blue solid lines are fitted curves of low and high- \overline{D} PtBA brushes, respectively, using the core-chain model.

The SANS data are fit with the core-chain model by assuming $S(q) \approx 1$ due to the low concentration of PtBA brushes (0.3 wt%) (eqn. 4-6). During fitting, r_0 of the core is set to 5.7±0.2 nm (measured by DLS) and the SLDs of the core, solvent, and PtBA are set to the values mentioned above. ϕ is fixed and calculated from the known weight percentage of PtBA brushes in the solution, and *B* is fixed to the $I_{total}(q)$ at the high-*q* plateau (Table 4-2). The other parameters, r_2 , r_1 , and R_p , are allowed to float (Table 4-2). Optimized fitting results are obtained by reducing the goodness-of-fit χ^2 using the DiffeRential Evolution Adaptive Metropolis (DREAM) algorithm in SasView with the constraint $r_0 \leq r_2 \leq r_1 \leq R_p$.

PtBA brushes	ϕ	<i>B</i> (cm ⁻¹)	<i>r</i> ₂ (nm)	<i>r</i> ₁ (nm)	R_p (nm)
Low N_w , Low \mathbb{H}	0.00235	0.630	6.53±0.06	19.8±0.06	20.15±0.06
Low N _w , High Đ	0.00235	0.616	6.73±0.09	6.73±0.01	20.30±0.06
Intermediate N_w , Low Đ	0.002839	0.593	8.49±0.08	11.78±0.02	39.67±0.07
Intermediate N _w , High Đ	0.00247	0.532	8.86±0.06	8.86±0.02	34.2±0.1
High N _w , Low Đ	0.00305	0.648	6.2±0.3	16.25±0.04	63.8±0.2
High N _w , High	0.00258	0.606	6.2±0.3	16.25±0.04	62.6±0.4

Table 4-2 Fitting results of SANS data of PtBA brushes

The l_b of PtBA brushes is calculated by subtracting the core radius r_0 from the particle radius R_p (obtained from fitting the SANS data with the core-chain model). l_b of the high-D brushes obtained from SANS fitting is lower than that measured by DLS, and the difference between them increases with increasing N_w (Figure 4-3). However, for the low-D brushes, differences in l_b from SANS and DLS are less than the

differences for the high- \oplus brushes (Figure 4-3). Differences in l_b characterized by SANS and DLS is attributed to variation of ρ as a function of r. SANS is most sensitive to the layer with dense polymer chains, whereas DLS can also probe l_b of the dilute peripheral layer.⁹⁹ Therefore, we anticipate differences in l_b characterized by SANS and DLS are more pronounced with increasing \oplus and N_w as is observed in Figure 4-3, because of the presence of more long chains in the high- \oplus brushes.



Figure 4-3. l_b of the PtBA brushes with $N_w = 67$, $\theta = 1.15$ and $N_w = 59$, $\theta = 1.59$ and $N_w = 389$, $\theta = 1.19$; $N_w = 357$, $\theta = 1.60$ and $N_w = 807$, $\theta = 1.19$ and $N_w = 854$, $\theta = 1.94$ characterized using DLS (closed square) and SANS (open triangle). The symbol's color shading indicates brush θ .

4.3. Đ Differently Affects ρ Profiles of Low- N_w (CPB Regime) and High- N_w (SDPB Regime) Brushes

The ρ profiles of the PtBA brushes with different N_w and/or \overline{D} are calculated

from the fitting parameters $(r_2, r_1, \text{ and } R_p)$ of SANS data as a function of r (Figure 4-

4).

At low- N_w (CPB regime), the regions with constant ρ are narrow for low- \mathbb{D} (r

= 0.0 - 0.8 nm) and high-D (r = 0.0 - 1.0 nm) brushes (Figure 4-4a). Above the constant

 ρ region, ρ of the low- \overline{D} brush decays linearly as a function of r throughout nearly the whole brush layer (r = 0.8 - 14.1 nm), followed by a narrow power-law region (r = 14.1 - 14.5 nm) (Figure 4-4a). However, above the constant region, the ρ profile of the high- \overline{D} brush is composed of a power-law region (r = 1.0 - 14.6 nm) in the absence of the linear region, and the ρ of the high- \overline{D} brush is lower than that of the low- \overline{D} brush (Figure 4-4a). In addition, ρ of the high- \overline{D} brush reaches a plateau at high r and this is not observed in the low- \overline{D} brush.

At intermediate- N_w (SDPB regime), the regions with constant ρ extend up to 2.8 nm and 3.2 nm for the low- and high- \overline{D} brushes, respectively (Figure 4-4b). However, above the constant region, the ρ profile of the low- \overline{D} brush is composed of a narrow linear region (r = 2.8 - 6.1 nm) and a broad power-law region (r = 6.1 - 34.0 nm) (Figure 4-4b). The ρ of the high- \overline{D} brush above the constant region decays with the power-law only (r = 3.2 - 28.5 nm) (Figure 4-4b).

At high N_w (SDPB regime), the ρ profiles remain consistent with the intermediate- N_w brushes. For the low-D brush, ρ is constant (r = 0.0 - 0.5 nm) and follows a linear (r = 0.5 - 10.6 nm) and a power-law (r = 10.6 - 58.1 nm) decay. (Figure 4-4c). For the high-D brush, the ρ profile is constant (r = 0.0 - 6.8 nm) and then decays as a power-law (r = 6.8 - 44.2 nm).



Figure 4-4. ρ of the PtBA brushes as a function of r with (a) $N_w = 67$, $\theta = 1.15$ (solid curves) and $N_w = 59$, $\theta = 1.59$ (dashed curves); (b) $N_w = 389$,

D = 1.19 (solid curves); $N_w = 357$, D = 1.60 (dashed curves); (c) $N_w = 807$, D = 1.19 (solid curves) and $N_w = 854$, D = 1.94 (dashed curves).

4.4.Conclusions

We examined the ρ profiles as a function of \overline{D} at low, intermediate, and high N_w by analyzing the fitting results of SANS data using the core-chain model. The difference in l_b of the high- \overline{D} brush characterized from SANS and from DLS increased with increasing N_w due to the long chain effect. At low N_w (CPB regime), the ρ profiles were mostly composed of a linear region and a power-law region for the low-and high- \overline{D} brushes, respectively. At intermediate and high N_w (SDPB regime), the ρ profiles were composed of a power-law region at periphery of the low- and high- \overline{D} brushes. The variation of the ρ profiles could arise from the different conformations of low- and high- \overline{D} brushes.

Chapter 5. Molecular Weight and Dispersity Affect Chain Conformation and pH-Response in Weak Polyelectrolyte Brushes

To understand the effect of chain \tilde{D} 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 \tilde{D} (Table 5-1).

 N_w^a PtBA brushes N_n^a Ða $l_h (nm)^b$ σ (chains nm⁻²)^c 6.6±0.2 Low N_w , Low \overline{D} 1.09 0.38 45 ± 3 41 ± 4 Low N_w , High Đ 45.3±0.7 26 ± 3 1.69 14.0±0.2 0.53 High N_w , Low \overline{D} 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

Table 5-1. PtBA-grafted silica nanoparticles selected for hydrolysis

^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 tBA_i ; $D = N_w/N_n$. Standard deviations were calculated from 3 measurements.

^b Characterized with DLS: l_b was calculated using the method of cumulants (eqns. 2-1 and 2-3) to quantify the polymer-grafted nanoparticle R_h , followed by subtraction of the silica nanoparticle radius r_0 . Standard deviations were calculated from 10 measurements on the same sample.

^c Characterized with TGA and EA.98

5.1. The Extent of pH-Response of l_b Depends on N_w and \oplus

For the low- N_w series ($N_w = 45$), l_b of the low-D PAA brush was independent of pH and was equal to $L_{c,w} = N_w l_0$, where $l_0 = 0.3$ nm (Figure 5.1a). In sharp contrast, l_b of the high-D PAA brush increased upon increasing pH and was markedly greater than both l_b of the low-D PAA brush and $L_{c,w}$. The greater value of l_b of the high-D PAA brush relative to that of the corresponding low-D PAA brush and to $L_{c,w}$ can be attributed to long chain effects.⁴⁹ 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-D brushes were less pronounced than for the low- N_w brushes and were statistically insignificant at some pH values (Figure 5-1b). Thus, D differently affected l_b of brushes at low and high N_w . This result is consistent with the behavior of neutral brushes observed in the Chapter 3, in which l_b increased with D at low N_w but was independent of D for high N_w .⁹⁸ To examine the extent of pH-response, l_b was normalized by $l_{b,max}$. At low N_w , the high-D brush exhibited a greater change in $l_b/l_{b,max}$ than the low-D brush as a function of pH. At high N_w , however, $l_b/l_{b,max}$ of both low- and high-D brushes collapsed with that of the low- N_w and high-D brush (Figure 5-1c). This comparison reveals that the extent of pHresponse in l_b can be enhanced by increasing either N_w or D (when N_w is low).



Figure 5-1. l_b as a function of pH of the (a) low- N_w PAA brush pair with $N_w = 45$, $\overline{D} = 1.09$ (light blue open triangle) and $N_w = 45$, $\overline{D} = 1.69$ (dark blue open square) and (b) high- N_w PAA brush pair with $N_w = 782$, $\overline{D} = 1.23$ (light blue closed triangle) and $N_w = 837$, $\overline{D} = 1.76$ (dark blue closed square). (c) l_b was normalized by $l_{b,max}$ 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- \overline{D} and high- \overline{D} PAA brushes, respectively.

Prior studies report the pH-responsive $l_b/l_{b,max}$ in polybasic PDMAEMA brushes $(N_w = 392 - 2541)^{49}$ and polyacid PAA brushes $(N_w = 250 - 1111)^{67}$. $l_b/l_{b,max}$ of PDMAEMA or PAA brushes as a function of pH collapsed onto a single curve for brushes of differing N_w ,⁴⁹ which is consistent with the behavior we observed in the high- N_w PAA brushes ($N_w = 782$ and 837) (Figure 5-2a). 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. ⁶⁷ ($N_w = 153$) was independent of pH, consistent with the behavior of our low- N_w , low-D brush ($N_w = 45$) (Figure 5-2b). 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 D. 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 , was sensitive to Dat low but not high N_w .



Figure 5-2. $l_b/l_{b,\text{max}}$, where $l_{b,\text{max}}$ 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 D = 1.23 (light blue closed triangles), $N_w = 837$ and D = 1.76 (dark blue closed squares), and PAA brushes from ref.⁶⁷ 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 D = 1.09 (light blue open triangles), $N_w = 45$ and D = 1.69 (dark blue open squares), and PAA brushes from ref.⁶⁷ with $N_w = 153$ (black closed diamonds).

5.2.PAA Brushes Dissociate Differently as a Function of N_w and \oplus

To test this idea, we determined α of the PAA brushes as a function of pH (Figure 5-3) as assessed via titration curves upon decreasing pH (Figure A1; procedures described in the Appendix). $^{100}\,\alpha$ monotonically increased with pH, in agreement with the previously reported behavior of annealed polyacid brushes.¹⁰¹⁻¹⁰⁴ 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 behavior, the data were fit with sigmoidal curves, and the average acid dissociation constant pK_a was obtained as the pH at $\alpha = 0.5$ for each of the brushes.¹⁰⁵ At low N_w , $pK_a = 6.14 \pm 0.06$ and 6.28 ± 0.06 for low- and high- \oplus brushes, respectively; at high N_w , $pK_a = 5.68 \pm 0.03$ and 5.96 ± 0.01 for low- and high- D 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 D slightly increased pK_a whereas increasing N_w decreased pK_a . The weak dependence of pK_a on D 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).⁸¹ By contrast, pK_a of the planar PAA brushes drastically increased with D when measured upon increasing pH.⁸¹



Figure 5-3. α as a function of pH of the (a) low- N_w PAA brush pair with $N_w = 45$, $\overline{D} = 1.09$ (light blue open triangle) and $N_w = 45$, $\overline{D} = 1.69$ (dark blue open square) and (b) high- N_w PAA brush pair with $N_w = 782$, $\overline{D} = 1.23$ (light blue closed triangle) and $N_w = 837$, $\overline{D} = 1.76$ (dark blue closed square). Light and dark blue solid lines are sigmoidal fits shown in Appendix (eqn. A19) of the low- \overline{D} and the high- \overline{D} PAA brushes, respectively.

We characterized ζ as a function of pH (Figure 5-4) to provide further insight into the dissociation behavior of PAA brushes. The PAA brushes were negatively charged at all pH values tested and ζ monotonically decreased with increasing pH. The decrease in ζ with increasing N_w arises from greater number of dissociated repeat units.¹⁰⁶ 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.^{33, 107} 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 \overline{P} brush (due to differences in l_b) (Figure 5-5, eqns. are shown in the Appendix).



Figure 5-4. ζ as a function of pH of the (a) low- N_w PAA brush pair with $N_w = 45$, $\overline{D} = 1.09$ (light blue open triangle) and $N_w = 45$, $\overline{D} = 1.69$ (dark blue open square) and (b) high- N_w PAA brush pair with $N_w = 782$, $\overline{D} = 1.23$ (light blue closed triangle) and $N_w = 837$, $\overline{D} = 1.76$ (dark blue closed square).



Figure 5-5. The concentration of condensed counterions C_i as a function of concentration of added ions I_s of low- N_w PAA brushes pair with N_w = 45 and D = 1.09 (light blue open triangle) and $N_w = 45$ and D = 1.69 (dark blue open square) and high- N_w PAA brush pair with N_w = 782 and D = 1.23 (light blue closed triangle) and $N_w = 837$ and D = 1.76 (dark blue closed square).

5.3. Polyelectrolyte Brush Regime Varies with N_w

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 Figure 5-1c) and α (in Figure 5-3, along with sigmoidal fits to the data). $l_b/l_{b,max}$ of the low- N_w PAA brushes scaled weakly with α : $l_b/l_{b,max} \sim \alpha^{0.027\pm0.005}$ for the low-D brush and $l_b/l_{b,max} \sim \alpha^{0.05\pm0.04}$ for the high- Dbrush (Figure 5-6). Although D did not affect the scaling exponent for low- N_w brushes, brushes with lower D had a greater degree of chain extension (e.g., greater $l_b/l_{b,max}$) at a given value of α (Figure 5-6). 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.^{46, 56} By contrast, $l_b/l_{b,max}$ for high- N_w brushes at both low- and high-D collapsed onto a single curve with that of PDMAEMA brushes (Figure 5-7),⁴⁹ which had a larger scaling exponent: $l_b/l_{b,max} \sim \alpha^{0.23\pm0.02}$ (Figure 5-6), consistent with the scaling of the SB regime from prior studies.^{47, 49} The transition from the q-NB to SB regimes upon increasing N_w is consistent with expectations from the star polyelectrolyte model.⁴⁶ Overall, $l_b/l_{b,max}$ collapsed as a function of α for the brushes with high but not low N_w (Figure 5-6), and $l_b/l_{b,max}$ for the high- N_w brushes and the low- N_w , high-D brush collapsed as a function of pH (Figure 5-1c).

Increasing D led to distinct behaviors for low- N_w brushes in the α - and pHresponses of $l_b/l_{b,max}$. Whereas the pH-dependence of $l_b/l_{b,max}$ showed a significant change as D increased (Figure 5-1c), the scaling of $l_b/l_{b,max}$ with α was unaffected by Đ (Figure 5-6). 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 (Figures. 5-1c and 5-6). These differences in relationships of $l_b/l_{b,max}$ with α and pH likely arise from subtle differences in dissociation behaviors among these brushes, quantified by the pK_a (Figure 5-3). We can identify different regimes of behavior in low- and high- N_w brushes using our data and that of a prior study. At high- N_w , the pH- and α -responses of $l_b/l_{b,max}$ each collapsed onto a single curve for PDMAEMA brushes ($N_w = 392 - 2541$; D = 1.31 - 2.10).⁴⁹ This behavior is consistent with our data on high- N_w PAA brushes ($N_w = 782$ and 837; D = 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 $l_b/l_{b,\text{max}}$ each collapsed to a curve independent of N_w and \mathbb{D} . 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 ($N_w = 45$; D = 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 $l_b/l_{b,\text{max}}$ were affected by subtle differences in pK_a (low- \mathbb{D} : $pK_a = 6.14 \pm 0.06$ and high-Đ : 6.28±0.06) (Figure 5-3).



Figure 5-6. $l_b/l_{b,max}$ as a function of α of the low- N_w PAA brush pair with $N_w = 45$, D = 1.09 (light blue open triangles) and $N_w = 45$, D = 1.69 (dark blue open squares) and the high- N_w PAA brush pair with $N_w = 782$, D = 1.23 (light blue closed triangles) and $N_w = 837$, D = 1.76 (dark blue closed squares). Solid lines indicate the fits for low- N_w brushes and the dashed line indicates the fit for the high- N_w brushes.



Figure 5-7. $l_b/l_{b,\text{max}}$ as a function of α for high- N_w PAA brush pair with $N_w = 782$ and D = 1.23 (light blue closed triangles) and $N_w = 837$ and D = 1.76 (dark blue closed squares); the PDMAEMA brushes with $N_w = 392 - 2541$ (black open symbols) from ref. ⁴⁹.

5.4. The Extent of pH-Response of Conformation Varies with N_w and D

We propose schematic representations for low- \tilde{D} (Figure 5-8a) and high- \tilde{D} (Figure 5-8b) annealed polyacid-grafted nanoparticles. Because l_b of the low- N_w , low- \tilde{D} 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 (Figure 5-8a).⁶⁷ The gradual increase of l_b to $L_{c,w}$ as pH increased for the high- N_w , low-D PAA brush indicates that the conformation transitioned from a relatively collapsed state to a near-fully extended state with increasing pH (Figure 5-8a). In the collapsed state, the brush was stretched near the particle surface arising from the proximity of neighboring chains. Further from the surface, the greater inter-chain distance allowed the brush to adopt an entropically favorable coiled conformation. In the extended state, the chain extension was induced by electrostatic excluded volume interactions.⁴⁶

The gradual increase of l_b to $L_{c,w}$ with increasing pH was also observed for the high-D PAA brushes, in which the conformation varied from collapsed to stretched with increasing pH (Figure 5-8b). In the collapsed state, the shorter chains of the high-D brush adopted a "crown and stem" conformation at short distances from the surface, although the conformation at the periphery remained coiled.²⁶ We propose that the conformation of the high-D brushes in the extended state was similar to that of the high- N_w , low-D brush (Figure 5-8b), evidenced by the collapse of $l_b/l_{b,max}$ on a single curve as a function of pH for these three brushes (Figure 5-1c)



Figure 5-8. Schematic representation of the conformation of annealed polyacidgrafted nanoparticles: (a) low \mathcal{P} and (b) high \mathcal{P} 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.

5.5.Conclusions

We investigated the dependence of l_b of annealed polyacid brushes and its pHresponse on N_w and \overline{D} . l_b increased with \overline{D} for the low- but not high- N_w PAA brushes. Increasing N_w or \overline{D} (in the case of low N_w brushes) enhanced the extent of pH-response of $l_b/l_{b,max}$, whereas the extent of α -response of $l_b/l_{b,max}$ increased with N_w but not \overline{D} . The scaling exponents of $l_b/l_{b,max}$ with α indicated the brush regime changed from q-NB to SB upon increasing N_w . Differences in pH- and α -responses of $l_b/l_{b,max}$ at low N_w were attributed to differences in the dissociation behaviors, quantified by pK_a . We propose that the low- N_w , low- \overline{D} 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 \overline{D} 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 \mathbb{D} (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.

Chapter 6. Summary and Future Work

6.1.Summary

We show that Đ is a tunable parameter to control conformation of neutral polymers and polyelectrolytes grafted on nanoparticles.

- We studied chain conformation by examining *l_b* of PtBA brushes with distinct Đ using DLS. *l_b* of the high-*N_w* PtBA brushes (in the SDPB regime) was independent of Đ, but that of the low-*N_w* PtBA brushes (in the CPB regime) increased with Đ. In the SDPB regime, *l_b* of different polymers from literature also collapsed onto the master curve with that of the PtBA brushes. In the CPB regime, *l_b* of these brushes collapsed onto a bifurcated curve. We hypothesized the coiled conformation at the periphery of polymer brushes in the SDPB regime was independent of Đ. In the CPB regime, the effects of Đ on conformation depended on the scaling variable, *N_wσ^{1/2}*. The, high-Đ brushes adopted a more extended conformation than the low-Đ brushes when *N_wσ^{1/2}* < 470 ± 30, but the difference in conformation between low- and high-Đ brushes at periphery was less significant at higher *N_wσ^{1/2}*.
- 2. We show the ρ profiles and l_b of the PtBA brushes with different N_w and \overline{P} characterized from SANS. A core-chain model which accounts for a binary system with a core and a polymer layer with different ρ profiles was selected to fit SANS data. The l_b of the high- \overline{P} brushes characterized from SANS was lower than that from DLS, indicating the long chains in disperse brushes was characterized by DLS but not SANS. The difference in l_b of the high- \overline{P} brushes was enhanced with increasing N_w . By contrast, variation of the ρ profiles among the low- and high- \overline{P} brushes were reduced with increasing N_w . At low N_w , ρ followed a linear and a power-law decay nearly throughout the whole polymer layer of low- and high- \overline{P}
brushes, respectively. At higher N_w , the ρ profiles were in the power-law region at the periphery regardless of \mathbb{D} , while at intermediate r, the ρ profile varied from power-law to linear with increasing \mathbb{D} . We proposed that these were related to variation in brush conformation as a function of \mathbb{D} .

3. We investigated the chain conformation of annealed PAA brushes as a function of pH, through quantifying *l_b* through DLS. We hydrolyzed two pairs of PtBA brushes to PAA brushes with the same *N_w* yet differing Đ: a low-*N_w* pair (*N_w* = 45 and Đ = 1.09 and 1.69) and a high-*N_w* pair (*N_w* ≈ 813 and Đ = 1.23 and 1.76). The extent of pH-response on *l_b/l_{b,max}* was enhanced with increasing *N_w* or Đ (when *N_w* is low). The scaling exponent of *l_b/l_{b,max}* with α, however, increased with *N_w* but not Đ. We suggested the difference between pH-response and α-response of the low-*N_w* PAA brushes arouse from the subtle difference in dissociation behaviors. We hypothesized the low-*N_w* and low-Đ PAA brush adopted a pH-independent and near-fully extended conformation due to the strong excluded volume interactions. By contrast, the PAA brushes with higher *N_w* or Đ adopted a collapse and an extended conformation at low and high pH, respectively.

We believe the emerging conformational behaviors obtained by increasing Đ can be leveraged to tune morphologies of polymer brushes dispersed in complex fluids and polymer matrices and utilized to guide future studies on control of brush conformation and improve efficacies of spherical polymer brushes in applications.

6.2.Future Work

Although we showed Đ affected conformation of neutral and pH-responsive polymer chains grafted on nanoparticles in dilute solutions, there are still questions needed to be answered to further understand how chain conformation varies with D and N_w .

- The deviation between fitted curves and SANS data of PtBA brushes can arise from the absence of structure factor in the fitting model. We hypothesize that the increase in molecular weight could induce interparticle attraction, leading to contributions of structure factor. The addition of structure factor to the model will be tested. In addition, the morphology and the average interparticle distance of PtBA brushes can be examined by using electron microscopies.
- 2. Chain conformation of spherical PAA brushes was examined by l_b of brushes with different N_w and D as a function of pH in the absence of added salts. However, the increase in C_s can greatly affect brush conformation by screening charges on polyelectrolyte chains. Therefore, the variation of pH-response on brush conformation with N_w and D in the presence of added salt will be an important topic to investigate.
- 3. We provided information that the extent of pH-response on conformation of the low- N_w and low-D PAA brushes was lower than that of the other brushes with higher N_w or D. However, we were not able to show the ρ profile of the PAA brushes to understand the brush conformation. Although studies from literature reported the ρ profiles of spherical PAA brushes from characterization of SANS, the effects of N_w and D on the monomer distribution were underexplored.^{28, 45} According to the results assessed from l_b of PAA brushes, PAA brushes at desire ranges of N_w and D can be select for SANS experiments.
- 4. We systematically studied spherical brush conformation in diluted solutions, which can be extended to brush conformation in polymer matrices due to great interests in

control of morphology of nanoparticles in polymer matrices. The parameters (e.g. σ of grafted polymer and difference in *N* between grafted polymer and polymer matrix) can affect morphology shown in experiments and simulations,^{19, 20, 30, 108} and the effects of \mathcal{D} on morphology of nanoparticles in polymer matrix were assessed by simulations in detail.¹⁰⁹ However, the effects of \mathcal{D} on conformation of spherical polymer brushes dispersed in polymer matrix remains unclear by experiments. From prior studies, we suggest the effects of \mathcal{D} on conformation and morphology of polymer brushes dispersed in polymer matrix can be reconciled by using SANS and electron microscopies.^{20, 110-112}

References

 Choi, J.; Hui, C. M.; Pietrasik, J.; Dong, H.; Matyjaszewski, K.; Bockstaller, M. R., Toughening Fragile Matter: Mechanical Properties of Particle Solids Assembled from Polymer-Grafted Hybrid Particles Synthesized by ATRP. *Soft Matter* 2012, 8 (15), 4072-4082.

2. Kubiak, J. M.; Yan, J.; Pietrasik, J.; Matyjaszewski, K., Toughening PMMA with Fillers Containing Polymer Brushes Synthesized via Atom Transfer Radical Polymerization (ATRP). *Polymer* **2017**, *117*, 48-53.

 Jiao, Y.; Tibbits, A.; Gillman, A.; Hsiao, M.-S.; Buskohl, P.; Drummy, L.
 F.; Vaia, R. A., Deformation Behavior of Polystyrene-Grafted Nanoparticle Assemblies with Low Grafting Density. *Macromolecules* 2018, *51* (18), 7257-7265.

4. Zorn, M.; Bae, W. K.; Kwak, J.; Lee, H.; Lee, C.; Zentel, R.; Char, K., Quantum Dot–Block Copolymer Hybrids with Improved Properties and Their Application to Quantum Dot Light-Emitting Devices. *ACS Nano* **2009**, *3* (5), 1063-1068.

5. Qiao, Y.; Yin, X.; Wang, L.; Islam, M. S.; Benicewicz, B. C.; Ploehn, H. J.; Tang, C., Bimodal Polymer Brush Core–Shell Barium Titanate Nanoparticles: A Strategy for High-Permittivity Polymer Nanocomposites. *Macromolecules* **2015**, *48* (24), 8998-9006.

6. Grabowski, C. r. A.; Fillery, S. P.; Koerner, H.; Tchoul, M.; Drummy, L.; Beier, C. W.; Brutchey, R. L.; Durstock, M. F.; Vaia, R. A., Dielectric Performance of High Permitivity Nanocomposites: Impact of Polystyrene Grafting on BaTiO₃ and TiO₂. *Nanocomposites* **2016**, *2* (3), 117-124.

7. Bell, M.; Krentz, T.; Nelson, J. K.; Schadler, L.; Wu, K.; Breneman, C.; Zhao, S.; Hillborg, H.; Benicewicz, B., Investigation of Dielectric Breakdown in Silica-Epoxy Nanocomposites Using Designed Interfaces. *J. Colloid Interface Sci.* **2017**, *495*, 130-139.

8. Khabibullin, A.; Fullwood, E.; Kolbay, P.; Zharov, I., Reversible Assembly of Tunable Nanoporous Materials from "Hairy" Silica Nanoparticles. *ACS Appl. Mater. Interfaces* **2014**, *6* (19), 17306-17312.

9. Wittemann, A.; Haupt, B.; Ballauff, M., Adsorption of Proteins on Spherical Polyelectrolyte Brushes in Aqueous Solution. *Phys. Chem. Chem. Phys.* **2003**, *5* (8), 1671-1677.

10. Yuan, L.; Tang, Q.; Yang, D.; Zhang, J. Z.; Zhang, F.; Hu, J., Preparation of pH-Responsive Mesoporous Silica Nanoparticles and Their Application in Controlled Drug Delivery. *J. Phys. Chem. C* **2011**, *115* (20), 9926-9932.

Zhi, S.-H.; Xu, J.; Deng, R.; Wan, L.-S.; Xu, Z.-K., Poly(Vinylidene Fluoride)
 Ultrafiltration Membranes Containing Hybrid Silica Nanoparticles: Preparation,
 Characterization and Performance. *Polymer* 2014, 55 (6), 1333-1340.

12. Qu, Z.; Xu, H.; Gu, H., Synthesis and Biomedical Applications of Poly((meth)acrylic acid) Brushes. *ACS Appl. Mater. Interfaces* **2015**, *7* (27), 14537-14551.

13. Paek, K.; Chung, S.; Cho, C.-H.; Kim, B. J., Fluorescent and pH-Responsive Diblock Copolymer-Coated Core–Shell CdSe/ZnS Particles for a Color-Displaying, Ratiometric pH Sensor. *Chem. Commun.* **2011**, *47* (37), 10272-10274.

14. Paek, K.; Yang, H.; Lee, J.; Park, J.; Kim, B. J., Efficient Colorimetric pH Sensor Based on Responsive Polymer–Quantum Dot Integrated Graphene Oxide. *ACS Nano* **2014**, *8* (3), 2848-2856.

15. Ma, Y.; Promthaveepong, K.; Li, N., CO₂-Responsive Polymer-Functionalized Au Nanoparticles for CO₂ Sensor. *Anal. Chem.* **2016**, 88 (16), 8289-8293.

16. Liu, G.; Cai, M.; Zhou, F.; Liu, W., Charged Polymer Brushes-Grafted Hollow Silica Nanoparticles as a Novel Promising Material for Simultaneous Joint Lubrication and Treatment. *J. Phys. Chem. B* **2014**, *118* (18), 4920-4931.

17. Giraud, L.; Bazin, G.; Giasson, S., Lubrication with Soft and Hard Two-Dimensional Colloidal Arrays. *Langmuir* **2017**, *33* (15), 3610-3623.

Seymour, B. T.; Wright, R. A. E.; Parrott, A. C.; Gao, H.; Martini, A.; Qu,
 J.; Dai, S.; Zhao, B., Poly(alkyl methacrylate) Brush-Grafted Silica Nanoparticles as
 Oil Lubricant Additives: Effects of Alkyl Pendant Groups on Oil Dispersibility,
 Stability, and Lubrication Property. *ACS Appl. Mater. Interfaces* 2017, *9* (29), 25038-25048.

 Asai, M.; Zhao, D.; Kumar, S. K., Role of Grafting Mechanism on the Polymer Coverage and Self-Assembly of Hairy Nanoparticles. *ACS Nano* 2017, *11* (7), 7028-7035.

Bachhar, N.; Jiao, Y.; Asai, M.; Akcora, P.; Bandyopadhyaya, R.; Kumar, S.
 K., Impact of the Distributions of Core Size and Grafting Density on the Self-Assembly of Polymer Grafted Nanoparticles. *Macromolecules* 2017, *50* (19), 7730-7738.

21. Bachhar, N.; Kumaraswamy, G.; Kumar, S. K., Core-Size Dispersity Dominates the Self-Assembly of Polymer-Grafted Nanoparticles in Solution. *Macromolecules* **2019**, *52* (13), 4888-4894.

22. Ma, S.; Zhang, X.; Yu, B.; Zhou, F., Brushing up Functional Materials. *NPG Asia Materials* **2019**, *11* (1), 24.

23. Ohno, K.; Morinaga, T.; Takeno, S.; Tsujii, Y.; Fukuda, T., Suspensions of Silica Particles Grafted with Concentrated Polymer Brush: Effects of Graft Chain

Length on Brush Layer Thickness and Colloidal Crystallization. *Macromolecules* **2007**, *40* (25), 9143-9150.

24. Dukes, D.; Li, Y.; Lewis, S.; Benicewicz, B.; Schadler, L.; Kumar, S. K., Conformational Transitions of Spherical Polymer Brushes: Synthesis, Characterization, and Theory. *Macromolecules* **2010**, *43* (3), 1564-1570.

25. de Vos, W. M.; Leermakers, F. A. M., Modeling the Structure of a Polydisperse Polymer Brush. *Polymer* **2009**, *50* (1), 305-316.

 Dodd, P. M.; Jayaraman, A., Monte Carlo Simulations of Polydisperse Polymers Grafted on Spherical Surfaces. J. Polym. Sci. Part B: Polym. Phys. 2012, 50 (10), 694-705.

27. Hore, M. J. A.; Ford, J.; Ohno, K.; Composto, R. J.; Hammouda, B., Direct Measurements of Polymer Brush Conformation Using Small-Angle Neutron Scattering (SANS) from Highly Grafted Iron Oxide Nanoparticles in Homopolymer Melts. *Macromolecules* **2013**, *46* (23), 9341-9348.

28. Joksimovic, R.; Prévost, S.; Schweins, R.; Appavou, M. S.; Gradzielski, M., Interactions of Silica Nanoparticles with Poly(ethylene oxide) and Poly(acrylic acid): Effect of the Polymer Molecular Weight and of the Surface Charge. *J. Colloid Interface Sci.* **2013**, *394*, 85-93.

29. Kim, C. J.; Kraska, M.; Mazurowski, M.; Sondergeld, K.; Gallei, M.; Rehahn, M.; Stühn, B., Polymer Chain Conformation on Deuterated Polystyrene Nanoparticles Investigated by SANS. *Soft Materials* **2014**, *12* (sup1), S41-S48.

30. Jiao, Y.; Akcora, P., Understanding the Role of Grafted Polystyrene Chain Conformation in Assembly of Magnetic Nanoparticles. *Physical Review E* **2014**, *90* (4), 042601. 31. Grünewald, T. A.; Lassenberger, A.; van Oostrum, P. D. J.; Rennhofer, H.; Zirbs, R.; Capone, B.; Vonderhaid, I.; Amenitsch, H.; Lichtenegger, H. C.; Reimhult, E., Core–Shell Structure of Monodisperse Poly(ethylene glycol)-Grafted Iron Oxide Nanoparticles Studied by Small-Angle X-ray Scattering. *Chemistry of Materials* **2015**, *27* (13), 4763-4771.

32. Wei, Y.; Xu, Y.; Faraone, A.; Hore, M. J. A., Local Structure and Relaxation Dynamics in the Brush of Polymer-Grafted Silica Nanoparticles. *ACS Macro Lett.* **2018**, *7* (6), 699-704.

33. Guo, X.; Ballauff, M., Spatial Dimensions of Colloidal Polyelectrolyte Brushes As Determined by Dynamic Light Scattering. *Langmuir* **2000**, *16* (23), 8719-8726.

34. Savin, D. A.; Pyun, J.; Patterson, G. D.; Kowalewski, T.; Matyjaszewski, K., Synthesis and Characterization of Silica-Graft-Polystyrene Hybrid Nanoparticles: Effect of Constraint on the Glass-Transition Temperature of Spherical Polymer Brushes. *J. Polym. Sci. Part B: Polym. Phys.* **2002**, *40* (23), 2667-2676.

35. Li, D.; He, Q.; Cui, Y.; Li, J., Fabrication of pH-Responsive Nanocomposites of Gold Nanoparticles/Poly(4-vinylpyridine). *Chem. of Mater.* **2007**, *19* (3), 412-417.

36. Zhou, L.; Yuan, J.; Yuan, W.; Sui, X.; Wu, S.; Li, Z.; Shen, D., Synthesis, Characterization, and Controllable Drug Release of pH-Sensitive Hybrid Magnetic Nanoparticles. *J. Magn. Magn. Mater.* **2009**, *321* (18), 2799-2804.

37. Bentz, K. C.; Savin, D. A., Chain Dispersity Effects on Brush Properties of Surface-Grafted Polycaprolactone-Modified Silica Nanoparticles: Unique Scaling Behavior in the Concentrated Polymer Brush Regime. *Macromolecules* **2017**, *50* (14), 5565-5573.

38. Tufani, A.; Ozaydin Ince, G., Smart Membranes with pH-Responsive Control of Macromolecule Permeability. *J. Membr. Sci.* **2017**, *537*, 255-262.

39. Kim, S.; Traore, Y. L.; Ho, E. A.; Shafiq, M.; Kim, S. H.; Liu, S., Design and Development of pH-Responsive Polyurethane Membranes for Intravaginal Release of Nanomedicines. *Acta Biomater.* **2018**, *82*, 12-23.

40. Guo, X.; Ballauff, M., Spherical Polyelectrolyte Brushes: Comparison between Annealed and Quenched Brushes. *Phys. Rev. E* **2001**, *64* (5), 051406.

41. Su, N.; Li, H.; Huang, Y.; Zhang, X., Synthesis of Salt Responsive Spherical Polymer Brushes. *J. Nanomater.* **2015**, *2015*, 956819.

42. Xie, J.; Nakai, K.; Ohno, S.; Butt, H.-J.; Koynov, K.; Yusa, S.-i., Fluorescence Correlation Spectroscopy Monitors the Hydrophobic Collapse of pH-Responsive Hairy Nanoparticles at the Individual Particle Level. *Macromolecules* **2015**, *48* (19), 7237-7244.

43. Sekar, S.; Giermanska, J.; Saadaoui, H.; Chapel, J.-P., Fine-Tuning the Assembly of Highly Stable Oppositely Charged Cerium Oxide Nanoparticles in Solution and at Interfaces. *Colloids Surf. A* **2016**, *500*, 98-104.

44. Conrad, J. C.; Robertson, M. L., Towards Mimicking Biological Function with Responsive Surface-Grafted Polymer Brushes. *Curr. Opin. Solid State and Mater. Sci.* **2019**, *23* (1), 1-12.

Li, H.; Wang, K.; Tuo, X.; Almásy, L.; Tian, Q.; Sun, G.; Henderson, M. J.;
Li, Q.; Wacha, A.; Courtois, J.; Yan, M., Thickness Determination of Ultrathin Poly(acrylic acid) Shell on γ-Fe2O3 Nanocore via Small-Angle Scattering. *Materials Chemistry and Physics* 2018, 204, 236-242.

46. Borisov, O. V.; Zhulina, E. B., Effects of Ionic Strength and Charge Annealing in Star-Branched Polyelectrolytes. *Eur. Phys. J. B* **1998**, *4* (2), 205-217.

47. Lee, A. S.; Bütün, V.; Vamvakaki, M.; Armes, S. P.; Pople, J. A.; Gast, A.
P., Structure of pH-Dependent Block Copolymer Micelles: Charge and Ionic Strength
Dependence. *Macromolecules* 2002, *35* (22), 8540-8551.

48. Riley, J. K.; Matyjaszewski, K.; Tilton, R. D., Electrostatically Controlled Swelling and Adsorption of Polyelectrolyte Brush-Grafted Nanoparticles to the Solid/Liquid Interface. *Langmuir* **2014**, *30* (14), 4056-4065.

49. Iqbal, D.; Yan, J.; Matyjaszewski, K.; Tilton, R. D., Swelling of Multi-Responsive Spherical Polyelectrolyte Brushes across a Wide Range of Grafting Densities. *Colloid Polym. Sci.* **2020**, *298* (1), 35-49.

50. Hariharan, R.; Biver, C.; Mays, J.; Russel, W. B., Ionic Strength and Curvature Effects in Flat and Highly Curved Polyelectrolyte Brushes. *Macromolecules* 1998, *31* (21), 7506-7513.

51. Wesley, R. D.; Cosgrove, T.; Thompson, L.; Armes, S. P.; Billingham, N. C.; Baines, F. L., Hydrodynamic Layer Thickness of a Polybase Brush in the Presence of Salt. *Langmuir* **2000**, *16* (10), 4467-4469.

52. Ueberschär, O.; Wagner, C.; Stangner, T.; Gutsche, C.; Kremer, F., The Effective Hydrodynamic Radius of Single DNA-Grafted Colloids as Measured by Fast Brownian Motion Analysis. *Polymer* **2011**, *52* (8), 1829-1836.

53. Li, G.; Xu, J.; Zhao, S.; Zhu, Y.; Li, L.; Guo, X., Spherical Polyelectrolyte Brushes on Colloidal Poly(butadiene) Particles. *Z. Phys. Chem.* **2012**, *226* (7-8), 613-623.

54. Zhulina, E. B.; Borisov, O. V., Self-Assembly in Solution of Block Copolymers with Annealing Polyelectrolyte Blocks. *Macromolecules* **2002**, *35* (24), 9191-9203.

55. Pincus, P., Colloid Stabilization with Grafted Polyelectrolytes. *Macromolecules***1991**, *24* (10), 2912-2919.

56. Zhulina, E. B.; Borisov, O. V., Polyelectrolytes Grafted to Curved Surfaces. *Macromolecules* **1996**, *29* (7), 2618-2626.

57. Ye, Z.; Li, L.; Zhao, F.; Tian, Y.; Wang, Y.; Yang, Q.; Dai, L.; Guo, X., Enrichment and Distribution of Counterions in Spherical Polyelectrolyte Brushes Probed by SAXS. *J. Polym. Sci. Part B: Polym. Phys.* **2019**, *57* (12), 738-747.

58. Kim, C. J.; Sondergeld, K.; Mazurowski, M.; Gallei, M.; Rehahn, M.; Spehr, T.; Frielinghaus, H.; Stühn, B., Synthesis and Characterization of Polystyrene Chains on the Surface of Silica Nanoparticles: Comparison of SANS, SAXS, and DLS Results. *Colloid Polym. Sci.* **2013**, *291* (9), 2087-2099.

59. Wei, Y.; Hore, M. J. A., Characterizing Polymer Structure with Small-Angle Neutron Scattering: A Tutorial. *J. Appl. Phys.* **2021**, *129* (17), 171101.

60. Zackrisson, M.; Stradner, A.; Schurtenberger, P.; Bergenholtz, J., Small-Angle Neutron Scattering on a Core–Shell Colloidal System: A Contrast-Variation Study. *Langmuir* **2005**, *21* (23), 10835-10845.

Karg, M.; Wellert, S.; Pastoriza-Santos, I.; Lapp, A.; Liz-Marzán, L. M.;
 Hellweg, T., Thermoresponsive Core–Shell Microgels with Silica Nanoparticle Cores:
 Size, Structure, and Volume Phase Transition of the Polymer Shell. *Phys. Chem. Chem. Phys.* 2008, *10* (44), 6708-6716.

62. Chevigny, C.; Gigmes, D.; Bertin, D.; Jestin, J.; Boué, F., Polystyrene Grafting from Silica Nanoparticles via Nitroxide-Mediated Polymerization (NMP): Synthesis and SANS Analysis with the Contrast Variation Method. *Soft Matter* **2009**, *5* (19), 3741-3753.

63. Hore, M. J. A., Polymers on Nanoparticles: Structure & Dynamics. *Soft Matter*2019, *15* (6), 1120-1134.

64. Daoud, M.; Cotton, J. P., Star Shaped Polymers : a Model for the Conformation and its Concentration Dependence. *J. Physique* **1982**, *43* (3), 531-538.

65. Reimhult, E.; Schroffenegger, M.; Lassenberger, A., Design Principles for Thermoresponsive Core–Shell Nanoparticles: Controlling Thermal Transitions by Brush Morphology. *Langmuir* **2019**, *35* (22), 7092-7104.

Yadav, V.; Hashmi, N.; Ding, W.; Li, T.-H.; Mahanthappa, M. K.; Conrad,
J. C.; Robertson, M. L., Dispersity Control in Atom Transfer Radical Polymerizations
Through Addition of Phenylhydrazine. *Polym. Chem.* 2018, *9* (33), 4332-4342.

67. Zhang, C.; Carlson, T.; Yang, S.; Akcora, P., Ordering pH-Responsive Polyelectrolyte-Grafted Nanoparticles in a Flow Coating Process. *Adv. Mater. Interfaces* **2018**, *5* (5), 1701318.

68. Matyjaszewski, K.; Patten, T. E.; Xia, J., Controlled/"Living" Radical Polymerization. Kinetics of the Homogeneous Atom Transfer Radical Polymerization of Styrene. *J. Am. Chem. Soc.* **1997**, *119* (4), 674-680.

69. Ponnapati, R.; Karazincir, O.; Dao, E.; Ng, R.; Mohanty, K. K.; Krishnamoorti, R., Polymer-Functionalized Nanoparticles for Improving Waterflood Sweep Efficiency: Characterization and Transport Properties. *Ind. Eng. Chem. Res.* **2011**, *50* (23), 13030-13036.

70. Jiang, F.; Meyer, W. G. H.; Zhang, J., Dense Poly(4-vinyl pyridine) Brushes Grafting from Silica Nanoparticles via Atom Transfer Radical Polymerization. *Colloids Surf. A* **2013**, *436*, 302-308.

71. Song, Y.; Yu, J.; Dai, D.; Song, L.; Jiang, N., Effect of Silica Particles Modified by In-Situ and Ex-Situ Methods on the Reinforcement of Silicone Rubber. *Mater. Des.* **2014**, *64*, 687-693.

72. Tanaka, H.; Watanabe, T.; Chikazawa, M.; Kandori, K.; Ishikawa, T., Surface Structure and Properties of Calcium Hydroxyapatite Modified by Hexamethyldisilazane. *J. of Colloid and Interface Sci.* **1998**, *206* (1), 205-211.

73. von Werne, T.; Patten, T. E., Atom Transfer Radical Polymerization from Nanoparticles: A Tool for the Preparation of Well-Defined Hybrid Nanostructures and for Understanding the Chemistry of Controlled/"Living" Radical Polymerizations from Surfaces. *J. Am. Chem. Soc.* **2001**, *123* (31), 7497-7505.

74. Fernandes, N. J.; Koerner, H.; Giannelis, E. P.; Vaia, R. A., Hairy Nanoparticle Assemblies as One-Component Functional Polymer Nanocomposites: Opportunities and Challenges. *MRS Commun.* **2013**, *3* (1), 13-29.

75. Li, D.; Sheng, X.; Zhao, B., Environmentally Responsive "Hairy" Nanoparticles: Mixed Homopolymer Brushes on Silica Nanoparticles Synthesized by Living Radical Polymerization Techniques. *J. Am. Chem. Soc.* **2005**, *127* (17), 6248-6256.

76. Frisken, B. J., Revisiting the Method of Cumulants for the Analysis of Dynamic Light-Scattering Data. *Appl. Opt.* **2001**, *40* (24), 4087-4091.

77. Critchfield, F. E.; Gibson, J. A.; Hall, J. L., Dielectric Constant and Refractive Index from 20 to 35° and Density at 25° for the System Tetrahydrofuran—Water. *J. Am. Chem. Soc.* **1953**, *75* (23), 6044-6045.

78. Ramkumar, D. H. S.; Kudchadker, A. P., Mixture Properties of the Water + γ -Butyrolactone + Tetrahydrofuran System. Part 2. Viscosities and Surface Tensions of γ -Butyrolactone + Water at 303.15-343.15 K and γ -Butyrolactone + Tetrahydrofuran at 278.15-298.15 K. *J. Chem. Eng. Data* **1989**, *34* (4), 463-465. 79. Kim, J. M.; Chang, S. M.; Kong, S. M.; Kim, K.-S.; Kim, J.; Kim, W.-S., Control of Hydroxyl Group Content in Silica Particle Synthesized by the Sol-Precipitation Process. *Ceramics International* **2009**, *35* (3), 1015-1019.

80. Fernández-García, M.; Fuente, J. L. d. l.; Cerrada, M. a. L.; Madruga, E. L., Preparation of Poly(*tert*-Butyl Acrylate-g-Styrene) as Precursors of Amphiphilic Graft Copolymers. 1. Kinetic Study and Thermal Properties. *Polymer* **2002**, *43* (11), 3173-3179.

 Yadav, V.; Harkin, A. V.; Robertson, M. L.; Conrad, J. C., Hysteretic Memory in pH-Response of Water Contact Angle on Poly(acrylic acid) Brushes. *Soft Matter* 2016, *12* (15), 3589-3599.

82. Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I., NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, *29* (9), 2176-2179.

83. Petroff, M. G.; Garcia, E. A.; Dengler, R. A.; Herrera-Alonso, M.; Bevan, M. A., kT-Scale Interactions and Stability of Colloids with Adsorbed Zwitterionic and Ethylene Oxide Copolymers. *Macromolecules* **2018**, *51* (22), 9156-9164.

84. Qi, S.; Klushin, L. I.; Skvortsov, A. M.; Schmid, F., Polydisperse Polymer Brushes: Internal Structure, Critical Behavior, and Interaction with Flow. *Macromolecules* **2016**, *49* (24), 9665-9683.

85. Aboudzadeh, M. A.; Iturrospe, A.; Arbe, A.; Grzelczak, M.; Barroso-Bujans,
F., Cyclic Polyethylene Glycol as Nanoparticle Surface Ligand. *ACS Macro Lett.* 2020, 1604-1610.

86. Baker, J. A.; Pearson, R. A.; Berg, J. C., Influence of Particle Curvature on Polymer Adsorption Layer Thickness. *Langmuir* **1989**, *5* (2), 339-342.

87. Ortiz, C.; Hadziioannou, G., Entropic Elasticity of Single Polymer Chains of Poly(methacrylic acid) Measured by Atomic Force Microscopy. *Macromolecules* **1999**, *32* (3), 780-787.

88. Yamamoto, S.; Ejaz, M.; Tsujii, Y.; Fukuda, T., Surface Interaction Forces of Well-Defined, High-Density Polymer Brushes Studied by Atomic Force Microscopy.
2. Effect of Graft Density. *Macromolecules* 2000, *33* (15), 5608-5612.

89. Rubinstein, M.; Colby, R. H., *Polymer Physics*. OUP Oxford: 2003.

90. Mendrek, B.; Trzebicka, B.; Wałach, W.; Dworak, A., Solution Behavior of 4-Arm Poly(*tert*-Butyl Acrylate) Star Polymers. *Eur. Polym. J.* **2010**, *46* (12), 2341-2351.

91. Jehser, M.; Zifferer, G.; Likos, C. N., Scaling and Interactions of Linear and Ring Polymer Brushes via DPD Simulations. *Polymers* **2019**, *11* (3).

92. Choi, J.; Hui, C. M.; Schmitt, M.; Pietrasik, J.; Margel, S.; Matyjazsewski,
K.; Bockstaller, M. R., Effect of Polymer-Graft Modification on the Order Formation
in Particle Assembly Structures. *Langmuir* 2013, 29 (21), 6452-6459.

93. Cole, D. H.; Shull, K. R.; Baldo, P.; Rehn, L., Dynamic Properties of a Model Polymer/Metal Nanocomposite: Gold Particles in Poly(tert-butyl acrylate). *Macromolecules* **1999**, *32* (3), 771-779.

94. Killgore, J. P.; Kocherlakota, L. S.; Overney, R. M., Enhanced mobility and increased gas sorption capacity in thin film and nanoconduit confined polymers. *J. Polym. Sci. B Polym. Phys.* **2010**, *48* (4), 434-441.

95. Herrera, D.; Zamora, J.-C.; Bello, A.; Grimau, M.; Laredo, E.; Müller, A. J.;
Lodge, T. P., Miscibility and Crystallization in Polycarbonate/Poly(ε-caprolactone)
Blends: Application of the Self-Concentration Model. *Macromolecules* 2005, *38* (12),
5109-5117.

96. Xiang, L.; Ryu, W.; Kim, H.; Ree, M., Precise Synthesis, Properties, and Structures of Cyclic Poly(ε-caprolactone)s. *Polymers* **2018**, *10* (6), 577.

97. Vogiatzis, G. G.; Theodorou, D. N., Structure of Polymer Layers Grafted to Nanoparticles in Silica–Polystyrene Nanocomposites. *Macromolecules* **2013**, *46* (11), 4670-4683.

98. Li, T.-H.; Yadav, V.; Conrad, J. C.; Robertson, M. L., Effect of Dispersity on the Conformation of Spherical Polymer Brushes. *ACS Macro Lett.* **2021**, *10* (5), 518-524.

99. Martin, J. R. S.; Bihannic, I.; Santos, C.; Farinha, J. P. S.; Demé, B.; Leermakers, F. A. M.; Pinheiro, J. P.; Rotureau, E.; Duval, J. F. L., Structure of Multiresponsive Brush-Decorated Nanoparticles: A Combined Electrokinetic, DLS, and SANS Study. *Langmuir* **2015**, *31* (16), 4779-4790.

100. Colombani, O.; Lejeune, E.; Charbonneau, C.; Chassenieux, C.; Nicolai, T.,
Ionization Of Amphiphilic Acidic Block Copolymers. *J. Phys. Chem. B* 2012, *116* (25),
7560-7565.

101. Uhlík, F.; Košovan, P.; Limpouchová, Z.; Procházka, K.; Borisov, O. V.; Leermakers, F. A. M., Modeling of Ionization and Conformations of Starlike Weak Polyelectrolytes. *Macromolecules* **2014**, *47* (12), 4004-4016.

102. Fresnais, J.; Yan, M.; Courtois, J.; Bostelmann, T.; Bée, A.; Berret, J. F., Poly(acrylic acid)-Coated Iron Oxide Nanoparticles: Quantitative Evaluation of the Coating Properties and Applications for the Removal of a Pollutant Dye. *J. Colloid Interface Sci.* **2013**, *395*, 24-30.

103. Plamper, F. A.; Becker, H.; Lanzendörfer, M.; Patel, M.; Wittemann, A.; Ballauff, M.; Müller, A. H. E., Synthesis, Characterization and Behavior in Aqueous

Solution of Star-Shaped Poly(acrylic acid). *Macromol. Chem. Phys.* 2005, 206 (18), 1813-1825.

104. Laguecir, A.; Ulrich, S.; Labille, J.; Fatin-Rouge, N.; Stoll, S.; Buffle, J., Size and pH Effect on Electrical and Conformational Behavior of Poly(acrylic acid): Simulation and Experiment. *Eur. Polym. J.* **2006**, *42* (5), 1135-1144.

105. Dolce, C.; Mériguet, G., Ionization of Short Weak Polyelectrolytes: When Size Matters. *Colloid Polym. Sci.* **2017**, *295* (2), 279-287.

106. Liufu, S.; Xiao, H.; Li, Y., Adsorption of Poly(acrylic acid) onto the Surface of Titanium Dioxide and the Colloidal Stability of Aqueous Suspension. *J. Colloid Interface Sci.* **2005**, *281* (1), 155-163.

107. Hariharan, R.; Biver, C.; Russel, W. B., Ionic Strength Effects in Polyelectrolyte Brushes: The Counterion Correction. *Macromolecules* **1998**, *31* (21), 7514-7518.

108. Green, P. F., The Structure of Chain End-Grafted Nanoparticle/Homopolymer Nanocomposites. *Soft Matter* **2011**, *7* (18), 7914-7926.

109. Martin, T. B.; Dodd, P. M.; Jayaraman, A., Polydispersity for Tuning the Potential of Mean Force between Polymer Grafted Nanoparticles in a Polymer Matrix. *Physical Review Letters* **2013**, *110* (1), 018301.

110. Jouault, N.; Crawford, M.; Chi, C.; Smalley, R.; Wood, B.; Jestin, J.; Melnichenko, Y.; He, L.; Guise, W.; Kumar, S., Polymer Chain Behavior in Polymer Nanocomposites with Attractive Interactions. *ACS Macro Lett.* **2016**, *5*, 523-527.

111. Midya, J.; Cang, Y.; Egorov, S. A.; Matyjaszewski, K.; Bockstaller, M. R.; Nikoubashman, A.; Fytas, G., Disentangling the Role of Chain Conformation on the Mechanics of Polymer Tethered Particle Materials. *Nano letters* **2019**, *19* (4), 2715-2722.

112. LaNasa, J. A.; Torres, V. M.; Hickey, R. J., In situ Polymerization and Polymer Grafting to Stabilize Polymer-Functionalized Nanoparticles in Polymer Matrices. *J. Appl. Phys.* **2020**, *127* (13), 134701.

113. Colombani, O.; Lejeune, E.; Charbonneau, C.; Chassenieux, C.; Nicolai, T., Ionization Of Amphiphilic Acidic Block Copolymers. *The Journal of Physical Chemistry B* **2012**, *116* (25), 7560-7565.

Appendices

Supporting Information for Chapter 3

Grafting Density of PtBA-Grafted Silica Nanoparticles as Assessed by EA and TGA

Weight percent of the capping agent. The bare silica nanoparticles were first functionalized with grafted initiator and then the capping agent prior to polymerization. Using bromine EA, the concentration of bromine (with atomic mass 79.9 g/mol) was quantified to be 0.85% in the initiator-functionalized nanoparticles, and bromine is found only in the grafted initiator (each grafted initiator molecule has one bromine). In 100 g of initiator-grafted silica nanoparticles (containing 0.85 g Br), the weight of the grafted initiator is calculated as:

$$\frac{0.85 \text{ g Br}}{79.9 \text{ g/mol}} = 0.011 \text{ mol Br} = 0.011 \text{ mol initiator}$$
(A1)

and
$$(0.011 \text{ mol initiator}) \times (238 \text{ g/mol}) = 2.53 \text{ g initiator}.$$
 (A2)

The weight loss of bare silica nanoparticles (MEK-ST) measured by TGA was 3.48%, attributed to the weight of silanols, indicating that the concentration of silica in the sample was 96.52% (Figure 2-1). The weight loss of initiator-grafted silica nanoparticles was 6.23%, representing the weights of the grafted initiator, the capping agent, and silanols (with the remaining 93.77% as silica) (Figure 2-1). Because the ratio of silanols to silica is constant (e.g. is the same in initiator-grafted nanoparticles as in the bare nanoparticles), the weight of silanols in 100 g of initiator-grafted nanoparticles is:

$$(3.48 \text{ g silanols} / 96.52 \text{ g silica}) \times 93.77 \text{ g silica} = 3.38 \text{ g silanols}.$$
 (A3)

In 100 g of the initiator-grafted silica nanoparticles, the weight of the capping agent is calculated by subtracting the weight of the grafted initiator (2.53 g) and that of the silanols (3.38 g) from the total weight of grafted initiator + silanols + capping agent (6.23 g), i.e.

$$6.23 \text{ g} - 2.53 - 3.38 \text{ g} = 0.32 \text{ g}. \tag{A4}$$

Initiator grafting density. The total surface area of the silica nanoparticles was calculated from the known specific surface area, which is $218 \text{ m}^2/\text{g}$ for MEK-ST.¹⁷ As determined previously, in 100 g of initiator-grafted silica nanoparticles, the weights of the grafted initiator and the capping agent are 2.53 g and 0.32 g, respectively. Note that silanols remain in the silica nanoparticles during measurements of specific surface area at low temperatures. Thus, the surface area of 100 g of silica nanoparticles is

$$(100 - 2.53 - 0.32)g \times 218m^2/g = 2.12 \times 10^4 m^2.$$
 (A5)

The grafting density of the initiator (with molecular weight 238 g/mol) is

$$\frac{2.53 \text{ g initiator} \times 6.02 \times 10^{23} \text{ molecule/mol}}{238 \text{ g/mol} \times 2.12 \times 10^4 \text{ m}^2 \times 10^{18} \text{ mm}^2 / \text{ m}^2} = 0.30 \text{ initiator molecules/nm}^2.$$
(A6)

Polymer grafting density. The weight loss of a representative sample of PtBAgrafted silica nanoparticles (L16) with polymer $M_n = 26.1$ kg/mol was measured to be 63.25% (Figure 2-1). This represents the sum of weight losses of grafted PtBA, grafted initiator, capping agent, and silanols, and the remaining 36.75% represents the weight of silica. In initiator-grafted silica nanoparticles, the mass ratios of grafted initiator : capping agent : silanols : silica were determined to be 0.027 : 0.0034: 0.036 : 1 (using the calculations described above). In 100 g of PtBA-grafted silica nanoparticles, containing 36.75 g of silica, the weights of the grafted initiator, the capping agent, and silanols are calculated to be 0.99 g, 0.13 g, and 1.32 g, respectively. The PtBA mass in 100 g of PtBA-grafted silica nanoparticles is therefore calculated by subtracting from the total weight (100 g) the weights of silica (36.75 g), grafted initiator (0.99 g), capping agent (0.13 g), and silanols (1.32 g)

$$100 \text{ g} - 36.75 \text{ g} - 0.99 \text{ g} - 0.13 \text{ g} - 1.32 \text{ g} = 60.81 \text{ g} PtBA.$$
 (A7)

In 100 g PtBA-grafted silica nanoparticles, the number of the grafted PtBA chains in sample L16 (with $M_n = 26.1$ kg/mol) is

$$\frac{60.81 \text{ g } PtBA}{2.61 \times 10^4 \text{ g/mol}} \times 6.02 \times 10^{23} \text{ chains/mol} = 1.40 \times 10^{21} \text{ chains.}$$
(A8)

The total weight of silica nanoparticles in 100 g of PGNPs is calculated by subtracting the weight of PtBA (60.81 g), grafted initiator (0.99 g), and the capping agent (0.13 g) from the total sample weight. The total surface area of silica nanoparticles is therefore

$$(100 - 60.81 - 0.99 - 0.13) \text{ g} \times 218 \text{ m}^2/\text{g} = 8.38 \times 10^3 \text{ m}^2.$$
 (A9)

Therefore, the PtBA grafting density is

$$\frac{1.40 \times 10^{21} \text{chains}}{8.38 \times 10^3 \times 10^{18} \text{nm}^2} = 0.17 \text{ chains/nm}^2.$$
(A10)

Initiator efficiency. The PtBA grafting density was divided by the initiator grafting density to calculate the initiator efficiency as

$$\frac{0.17 \text{ chains/nm}^2}{0.30 \text{ molecules/nm}^2} \times 100\% = 57\%.$$
 (A11)

Characteristics of PtBA-Grafted Silica Nanoparticles

Table A1. Low-Đ PtBA-grafted silica nanoparticles

ID	N_n^{a}	N_w^{a}	Ða	$R_h (\text{nm})^{\text{b}}$	$l_b (nm)^b$	σ	$v^{ m d}$	$r_c (nm)^e$
						(chains/n		
						m ²) ^c		
L1	30±1	32.5±0.3	1.09	10.7±0.2	5.0±0.3	0.42	_	_
L2	43±3	44 <u>+</u> 4	1.05	12.23±0.0	6.6±0.2	0.39	_	_
				4				
L3	58±3	67.2±0.3	1.15	15.2±0.1	9.6±0.2	0.44	_	_
L4	82±4	105.9±0.8	1.29	19.54±0.0	13.9±0.2	0.35	_	_
				8				
L5	85±4	90±2	1.06	16.62±0.0	11.0±0.2	0.38	_	_
				3				
L6	93±5	100±5	1.08	19.5±0.1	13.9±0.2	0.38	_	_
L7	93±5	109±6	1.16	21.3±0.1	15.7±0.2	0.45 ± 0.03	_	_
L8	110±6	141±9	1.24	27.3±0.2	21.7±0.2	0.39	_	_
L9	124+6	143+6	1.15	22.17+0.0	16.5 ± 0.2	0.34	_	_
				9				
L10	127±6	160±10	1.28	26.7±0.1	21.1±0.2	0.38	_	_
L11	129+6	170+30	1.11	24.14+0.0	18.5 ± 0.2	0.26	_	_
211	12/20	1,0200		8	10102012	0.20		
L12	140±30	160±30	1.19	29.0±0.1	23.4±0.2	0.35	_	_
L13	137+7	141+7	1.03	23.3+0.1	17.6 ± 0.2	0.30	_	_
L14	143+9	160+10	1.09	23.79+0.0	18.1+0.2	0.33	_	_
211	1.0	100_10	1107	7	1011_012	0.000		
L15	177±9	190±30	1.06	32.0±0.2	26.4±0.3	0.27	_	_
L16	200±10	224±3	1.11	24.0±0.2	18.7±0.3	0.17	_	_
L17	210 + 10	250+10	1.16	30.4+0.2	24.8 ± 0.3	0.27	_	_
L18	290+40	340+50	1.16	39.3+0.2	33.7+0.3	0.32	0.29+0.05	30 + 10
L19	290+20	350+30	1.21	39.7+0.3	34.0+0.3	0.37	0.22 ± 0.05	39+9
L20	310+20	310+20	1.03	36.6+0.1	30.9+0.2	0.29	0.26+0.04	29+5
L21	330+20	390+30	1.19	39.2+0.1	33.5+0.3	0.28	0.21 ± 0.04	36+7
L22	330+20	400+10	1 19	40.2 ± 0.2	34 6+0 3	0.43	0.15+0.02	62+7
L23	350 ± 20 350+20	394+8	1.13	42.1+0.2	36 4+0 3	0.15	0.10 ± 0.02 0.50+0.04	11+1
L24	350 ± 20 350+20	394 6+0 9	1.13	40.0+0.1	34 3+0 2	0.48	0.20 ± 0.01	77+5
221	550_20	571.0_0.7	1.10	10.0_0.1	51.520.2	0.10	06	11_0
L25	360±30	470±30	1.30	42.8±0.2	37.1±0.2	0.32	0.17 ± 0.04	50±10
L26	370+20	430+5	1.17	44.5+0.3	38.8+0.3	0.19	0.43+0.03	14+1
L27	370 + 20	464+4	1.24	44.0+0.2	38.3+0.3	0.30	0.20 ± 0.01	38+3
L28	470+20	560+50	1.18	50.28+0.0	44.6+0.2	0.23+0.02	0.31+0.08	22+6
220		000200	1110	7		0.20_0.02	010120100	
L29	570±30	680±20	1.19	57.1±0.4	51.5±0.4	0.17	0.44 ± 0.04	13±1
L30	620±30	750±20	1.20	62.8±0.4	57.2±0.5	0.40	0.24 ± 0.02	38±4
L31	650±30	780±50	1.23	62.8±0.2	57.2±0.3	0.32	0.26 ± 0.05	31±6
L32	680±30	810±20	1.19	68.3±0.4	62.6±0.4	0.37 ± 0.01	0.31±0.03	28±3
L33	830±40	1020±30	1.22	76.0±0.5	70.3±0.5	0.38	0.26±0.03	34±4
L34	840±40	1050 ± 70	1.25	78.4±0.4	72.7±0.5	0.40	0.26±0.06	34±8
Chamastan	and with C	DC: N and N		loulated using	M _n and M _w	magnastival	w where M	100

^a Characterized with GPC: N_n and N_w were calculated using $\frac{M_n}{M_0}$ and $\frac{M_w}{M_0}$, respectively, where $M_0 = 128$ g/mol is the molecular weight of *t*BA, and $\overline{P} = \frac{N_w}{N_n}$. Errors were calculated from 3 measurements.

^b Characterized with DLS: R_h was calculated from the cumulant fit (eqns. 2-1 and 2-3), $l_b = R_h - r_0$, and errors were calculated from 10 measurements.

^c Characterized with TGA and EA: error was analyzed on selected samples from 3 TGA measurements.

^d Calculated from the MWC-Z model: error was propagated from errors of l_b , N_w , r_0 , and σ .

^e Calculated from $r_c = r_0 \sigma^{*0.5} v^{*-1}$: error was propagated from errors of r_0 , v, and σ .

Table A2. High-Đ PtBA-grafted silica nanoparticles

ID	N _n ^a	N ^a	$\tilde{\mathbf{D}}^{\mathrm{a}}$	$R_{\rm h} \ ({\rm nm})^{\rm b}$	$l_{\rm h} (\rm nm)^{\rm b}$	σ (chains/nm ²) ^c
	11	- · W	-	// ()	• 0 ()	• (••••••• •••••)

H1	16±1	27±2	1.58	15.3±0.7	9.7±0.8	0.54
H2	35±1	69±2	1.98	29.6±0.1	24.0±0.2	0.77
H3	50±6	90±10	1.58	33.3±0.6	27.6±0.6	0.62
H4	26±2	42±2	1.58	20.3±0.1	14.6±0.2	0.66
H5	27±4	40±5	1.50	19.6±0.1	14.0 ± 0.2	0.55
H6	34±2	52±3	1.49	21.21±0.06	15.6±0.2	0.54
H7	36±2	57±2	1.54	20.70±0.08	15.1±0.2	0.39
H8	37±7	59±3	1.59	24.6±0.2	18.9±0.3	0.51
H9	49±2	74 <u>+</u> 4	1.50	23.6±0.1	17.9±0.2	0.39
H10	60±10	98±6	1.63	33.4±0.2	27.8±0.3	0.72
H11	166±8	300±10	1.79	39.8±0.4	34.1±0.5	0.46
H12	210±10	290±20	1.51	46.9±0.2	41.3±0.3	0.34
H13	220±10	360±20	1.60	42.1±0.2	36.4±0.3	0.56 ± 0.07
H14	220±40	440±30	1.96	55.5±0.4	49.8±0.4	1.35
H15	370±20	610±30	1.65	58.8 ± 0.4	53.2±0.4	0.39±0.03
H16	440±20	720±40	1.63	63.0±0.4	57.3±0.4	0.35
H17	510±30	860±40	1.69	68.1±0.5	62.5±0.5	0.56
H18	560±30	1040 ± 50	1.85	90.0±0.5	84.3±0.6	0.74±0.03
H19	600±30	1120±60	1.87	70.4±0.7	64.7±0.7	0.67
H20	670±30	1140 ± 60	1.70	73.7±0.6	68.0±0.6	0.60
H21	750±40	1400 ± 70	1.85	86.9±0.8	81.3±0.8	1.15
H22	1080 ± 50	2000±100	1.82	123.2±0.8	117.5±0.8	0.58
H23	1090 ± 50	2000±100	1.81	115.0±0.6	109.4±0.6	0.47

a Characterized with GPC: N_n and N_w were calculated using $\frac{M_n}{M_0}$ and $\frac{M_w}{M_0}$, respectively, where $M_0 = 128$ g/mol is the molecular weight of tBA, and $D = \frac{N_w}{N_n}$. Errors were calculated from 3 measurements.

b Characterized with DLS: R_h was calculated from the cumulant fit (eqns. 2.1 and 2.3), $l_b = R_h - r_0$, and errors were calculated from 10 measurements.

c Characterized with TGA and EA: error was analyzed on selected samples from 3 TGA measurements.

Supporting Information for Chapter 5

Potentiometric titration.

Four PAA brushes as hydrolyzed from 4 PtBA brushes in Table 5-1 were titrated

by 0.5 M HCl_(aq) from pH 12 until the curves reached plateaus (Figure A1).



Figure A1. Titration curves of low- N_w PAA brush pair with (a) $N_w = 45$ and $\overline{D} = 1.09$ (light blue open triangle) and 1.69 (dark blue open square) and high- N_w PAA brush pair with (b) $N_w = 782$ and $\overline{D} = 1.23$ (light blue closed triangle) and $N_w = 837$ and $\overline{D} = 1.76$ (dark blue closed square).

During the titration, the titrant HCl can react in 3 different ways:¹¹³

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

$$HCl + NaOH \rightarrow H2O + NaCl.$$
 (A12)

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

$$\mathrm{HCl} + \mathrm{AA}^{-} \to \mathrm{AAH} + \mathrm{Cl}^{-} \tag{A13}$$

3. HCl dissociation: when the base and acrylic acid were consumed by HCl, HCl started to dissociate by itself:

$$\mathrm{HCl} \to \mathrm{H}^{+} + \mathrm{Cl}^{-}. \tag{A14}$$

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

$$n_{\text{NaCl}} = V_{\text{start}} \times 10^{-14 + \text{pH}_{\text{start}}} - (V_{\text{start}} + V_{\text{HCl}}) 10^{-14 + \text{pH}}.$$
 (A15)

The mole number of dissociated HCl was calculated as:

$$n_{\rm HCl\,dissociated} = (V_{\rm start} + V_{\rm HCl}) \times 10^{-\rm pH} - V_{\rm start} 10^{-\rm pH}_{\rm start}.$$
 (A16)

Because HCl is a strong acid and fully reacted through the three mechanisms,

the mole number of the associated acrylic acid n_{AAH} was calculated as:

$$n_{\text{AAH}} = 0.5 \ M \times V_{\text{HCl}} - n_{\text{NaCl}} - n_{\text{HCl dissociated}} \ . \tag{A17}$$

The degree of dissociation of PAA α was calculated as:

$$\alpha = 1 - \frac{n_{\text{AAH}}}{n_{\text{AAH,max}}},\tag{A18}$$

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 $n_{\text{AAH,max}}$ is the maximum value of n_{AAH} .

From eqn. A15 to A17, mole numbers of individual substance formed due to consumption of HCl during titration of 4 PAA brushes are shown as a function of volume of added HCl_(aq) (Figure A2). Nonmonotonic behavior for n_{AAH} indicates degradation of PAA at pH lower than 2.



Figure A2. The mole numbers of NaCl (green open circle), HCl dissociation (red open inverse triangle), and AAH (blue open triangle), for the PAA

brushes with (a) $N_w = 45$ and $\overline{D} = 1.09$, (b) $N_w = 45$ and $\overline{D} = 1.69$, (c) $N_w = 782$ and $\overline{D} = 1.23$, and (d) $N_w = 837$ and $\overline{D} = 1.76$.

The titration curves of α as a function of pH (Figure 5-2) were fit by

$$\alpha = A_2 + \frac{(A_1 - A_2)}{\frac{(pH - x_0)}{d_x}},$$
(A19)

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 of the PAA brushes are shown in Table A3.

Table A3. The fitting parameters for the titration curves of the PAA brushes

PtBA brushes	x_0	d_x
Low N_w , Low $\overline{\mathbb{P}}$	6.14±0.04	0.88 ± 0.04
Low N_w , High Đ	6.28±0.04	0.83 ± 0.04
High N_w , Low Đ	5.68±0.02	0.85 ± 0.02
High N_w , High Đ	5.96±0.01	0.82±0.01

Calculation of C_i

 C_i of the PAA brushes was calculated at ionic strengths I_s 10⁻⁴ M (pH 10). The average charge density ρ_f in the brush layer is^{33, 107}

$$\rho_f = \frac{3er_0^2 \sigma L_c}{l_B[(r_0 + l_b)^3 - r_0^3]},\tag{A20}$$

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^{33, 107}

$$C_i = I_s \left[1 + \left(\frac{z \rho_f}{2e N_A I_s} \right)^2 \right]^{1/2},$$
 (A21)

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

Scaling of l_b with α



Figure A3. 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). Solid lines indicate the fits for low- N_w brushes, and the dashed line indicates the fit for high- N_w brushes.