

In the past project year, we studied the conformation of disperse polymer brushes grafted on spherical nanoparticles in collaboration with our co-advised PRF-supported PhD student, Tzu-Han Li, who received advanced training in polymer synthesis and characterization. Such polymer-grafted nanoparticles (PGNPs) are used as viscosity modifiers and interfacial agents in oil and gas exploration and production, and more broadly find application in mechanical reinforcement and lubrication. Furthermore, they are appealing candidates as functional additives for polymer-based coatings and composites. Although the conformation of the grafted polymer chains affects the function of PGNPs, it remains poorly understood how the breadth of the polymer molecular-weight distribution alters spherical brush conformation.

Poly(*tert*-butyl acrylate) brushes were grown from silica nanoparticles *via* surface-initiated atom transfer radical polymerization, and their dispersity was varied between 1.1 and 1.7 through addition of phenylhydrazine to selected syntheses. The molecular weight and dispersity of the grafted polymer, cleaved from the nanoparticle using HF_(aq), were characterized *via* gel permeation chromatography (GPC), and the grafting density σ was determined using thermogravimetric analysis. The brush length was calculated by subtracting the particle radius from the hydrodynamic radius of the PGNPs, characterized using dynamic light scattering (DLS).

Figure 1 shows that the effect of brush dispersity on the average brush length depends on the brush molecular weight. For weight-average degree of polymerization $N_w = 47$, the characteristic time scale extracted from the intensity-intensity correlation functions increases with dispersity (**Figure 1a**), indicating that the hydrodynamic radius of the PGNP and hence the average thickness of the brush layer are greater. At higher $N_w = 845$, however, the intensity-intensity correlation functions obtained for brushes of two different dispersities are identical (**Figure 1b**), indicating that the hydrodynamic radius does not change with the increase in dispersity. This surprising result suggests that dispersity markedly alters brush conformation only in a particular range of N_w .

Figure 2 shows that brush dispersity affects the average thickness of the brush layer. The average brush length increases with dispersity for constant number-average degree of polymerization N_n (**Figure 2a**). Surprisingly, at lower values of N_n , the length of high-dispersity brushes is greater than the weight-average contour length $L_{c,w}$, determined as the full length of the all-trans conformation of PtBA with $\mathcal{D} = 1.7$. This intriguing result confirms that long brushes contribute substantially to brush length when the molecular weight distribution is broad. To account for long brushes in a broad molecular weight distribution, we examined the dependence of brush length on N_w , which represents the molecular weight with weight fraction at approximately 60% in the distribution. For $N_w > 80$, brush lengths with varying dispersities collapse onto a master curve. At lower N_w , however, brushes of higher dispersity are up to twice as thick as low-dispersity brushes and approach the weight-average contour length (**Figure 2b**). Notably, scaling by N_w more reasonably describes brush length at high dispersity.

Figure 3 shows that brushes collapse onto different master curves in the esemidilute polymer brush (SDPB) or concentrated polymer brush (CPB) regimes. The length of low-dispersity PtBA brushes collapse onto a master curve as a function of $N_w \sigma^{1/3}$ with an exponent of 0.62 ± 0.04 , in agreement with theoretical predictions (**Figure 3a**). Moreover, low-dispersity polystyrene (PS; Dukes *et al.*, *Macromolecules* (2010)) and poly(methyl methacrylate) (PMMA; Ohno *et al.*, *Macromolecules* (2007)) brushes also collapse onto this universal scaling curve. The lengths of

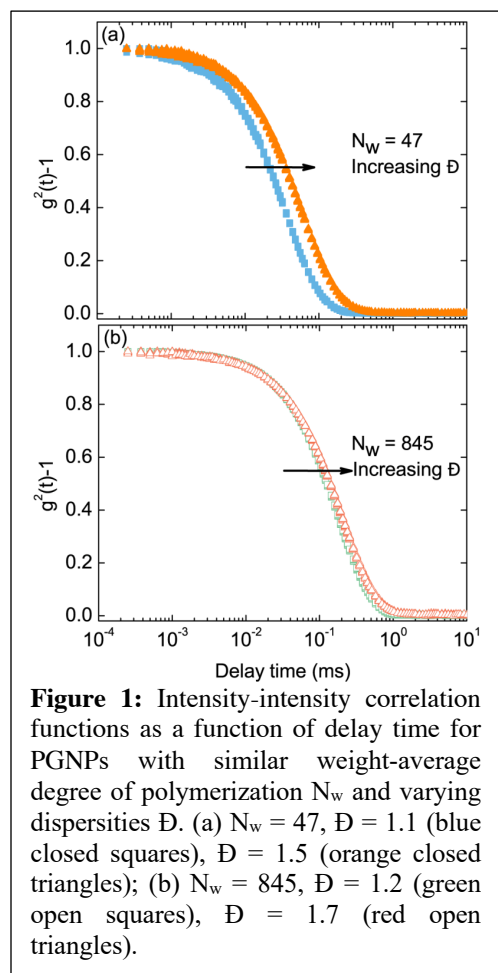
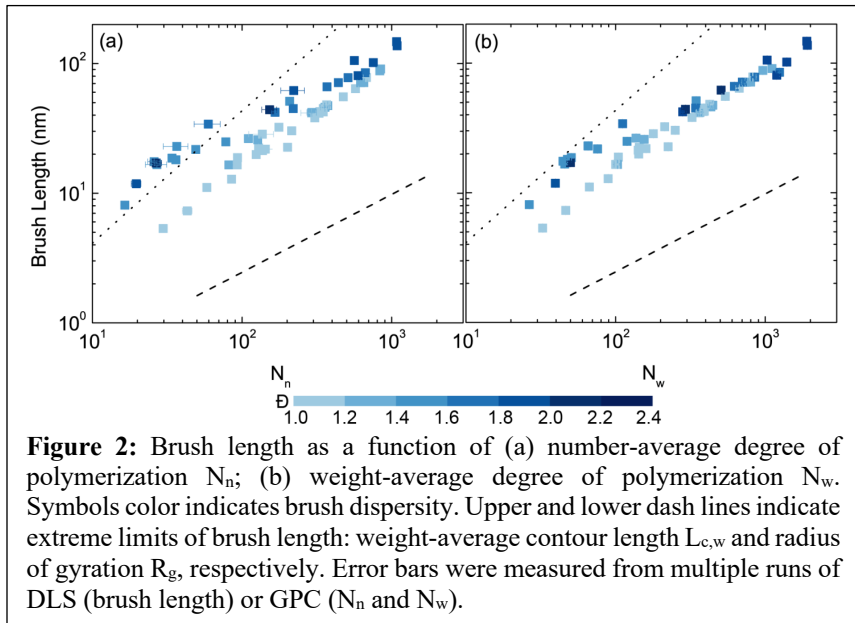
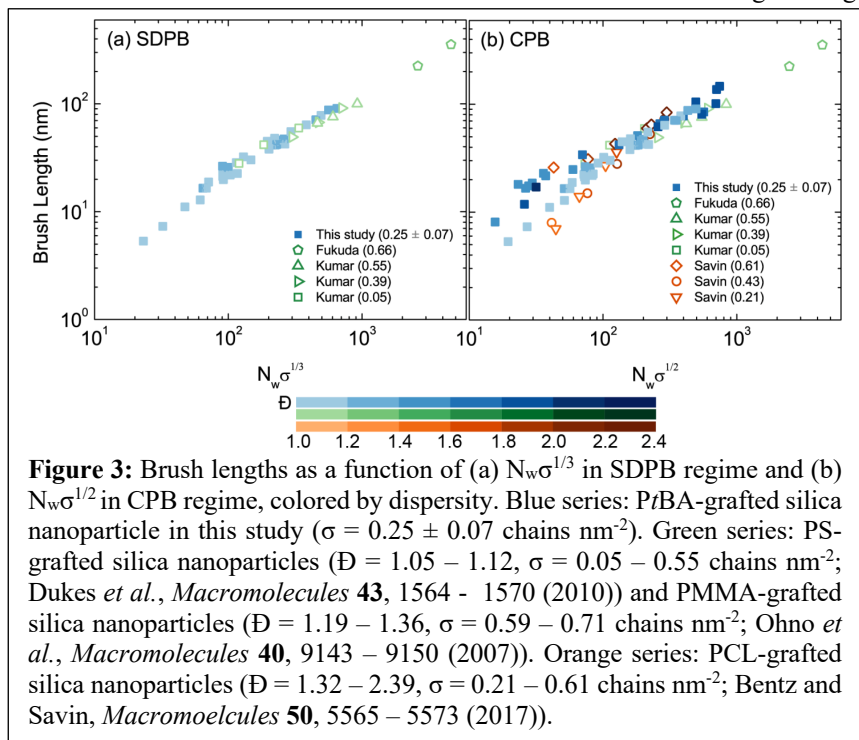


Figure 1: Intensity-intensity correlation functions as a function of delay time for PGNPs with similar weight-average degree of polymerization N_w and varying dispersities \mathcal{D} . (a) $N_w = 47$, $\mathcal{D} = 1.1$ (blue closed squares), $\mathcal{D} = 1.5$ (orange closed triangles); (b) $N_w = 845$, $\mathcal{D} = 1.2$ (green open squares), $\mathcal{D} = 1.7$ (red open triangles).



Figures 1 – 3 indicate that dispersity drives a transition in brush conformation from SDPB to CPB, as indicated by the change in the scaling exponents. In the SDPB regime, our results suggest that brushes stretch when their length exceeds a critical thickness r_c , approaching the conformation of semidilute polymer solution when N_w is further increased. In the CPB regime, we posit that densely grafted brushes at low-dispersity experience higher-order interactions, such that brush length below r_c increases dramatically with N_w . For high dispersity, short brushes are compressed toward the surface and slightly stretch intermediate brushes, so that long brushes are strongly extended by neighboring short and intermediate brushes as a stem. The greater brush length at low N_w and high \bar{D} observed experimentally is driven by the stem conformation. At higher N_w , the free ends of long brushes adopt a more entropically favorable coiled “crown” conformation. This crown formation reduces the overall brush length at high dispersity.

In the next project year we will examine how dispersity-driven changes in brush conformation affect the pH-response of poly(acrylic acid) (PAA) brushes grafted to silica nanoparticles, which we will generate through hydrolysis of PtBA. PAA is fully deprotonated and swollen at high pH, but protonated and collapsed at low pH. We hypothesize that the brush dispersity will affect the dependence of PAA brush length and conformation on the pH response. The anticipated results will provide the necessary fundamental understanding for our ongoing initiative to design fouling-release, nanoparticle-based additives for coatings. This thrust is a central focus of our collaborative work.



high-dispersity PtBA brushes collapse onto a bifurcated curve as a function of $N_w \sigma^{1/2}$ with an exponent of 0.78 ± 0.08 , indicating that they are in the CPB regime (**Figure 3b**). The bifurcation, however, indicates that the polymer conformation in CPB varies with dispersity. Polycaprolactone (PCL) brushes (Bentz and Savin, *Macromolecules* (2017)) also collapse onto the bifurcated master curve, with high- and low-dispersity brushes collapsing onto the upper (longer) and lower (shorter) branches, respectively. PMMA and PS brushes in this regime also collapsed onto the upper branch.

Together, the results in