Controlled Polymer Monolayer Synthesis by Radical Transfer to Surface Immobilized Transfer Agents

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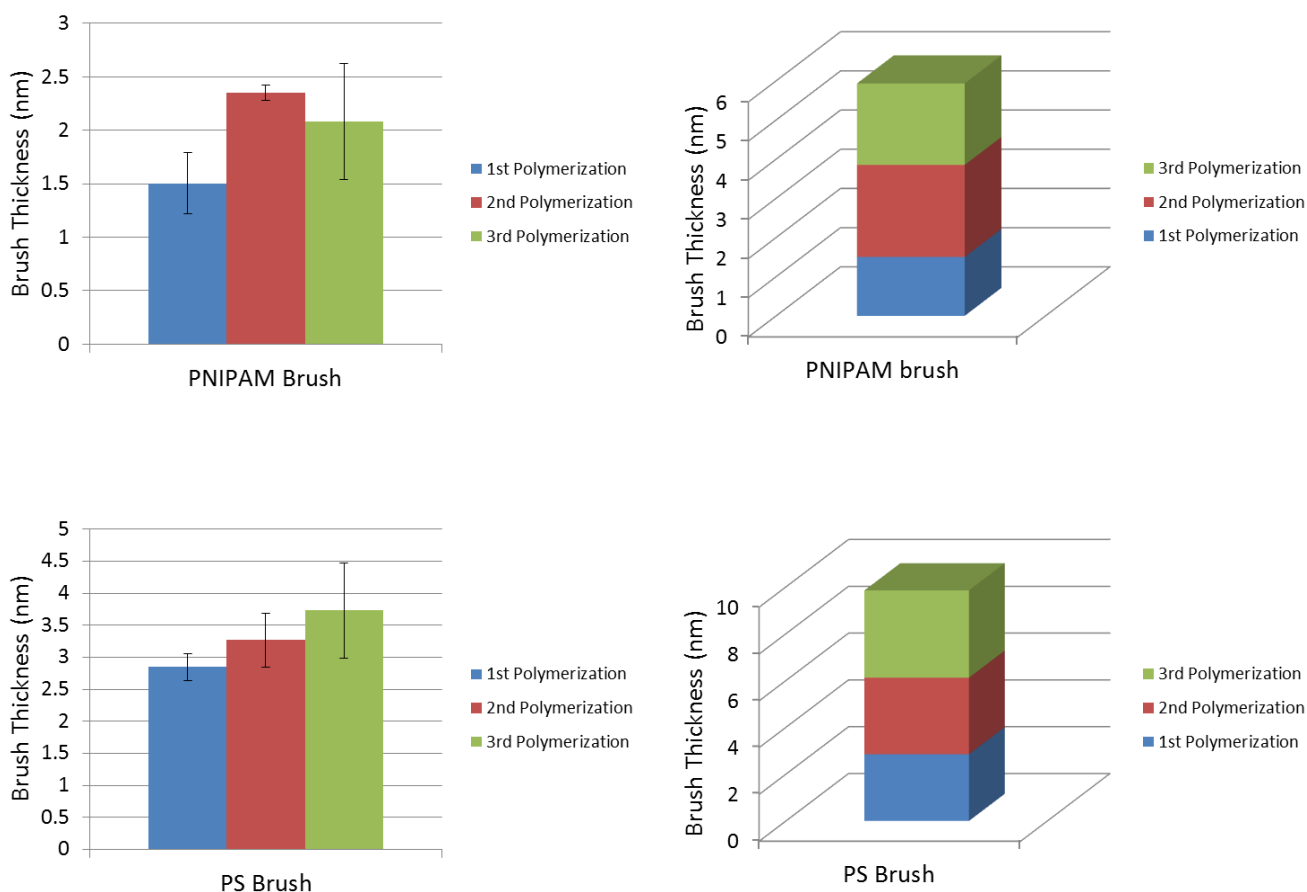
Supporting Information

Figure S1. Brush thickness may be sequentially increased by activating additional surface thiols by washing away physically adsorbed polymer and subjecting to another polymerization. The top images show PNIPAM growth for three sequential polymerizations, the bottom images show PS growth. The left images show brush growth for each polymerization and the right images show the average cumulative brush thickness following each polymerization and removal of physically adsorbed polymer by Soxhlet extraction in chloroform. For PNIPAM brushes: [NIPAM] = 1000 mM, [AIBN] = 6.09×10^{-3} M, Temperature = 60 $^{\circ}$C, and t = 6 h in 1,4-Dioxane. For PS brushes: [styrene] = 1000 mM, [AIBN] = 6.09×10^{-3} M, Temperature = 60 $^{\circ}$C, and t = 6 h in 1,4-Dioxane.

Radius of Gyration Calculations

According to Brittain and Minko[1], "As the size of grafted polymer chains approaches the distance between grafting points, the grafted chains overlap. This point is a transition point between a single grafted chain (mushroom) regime and brush regime." The size they refer to is the radius of gyration, R_g, and the transition is often quantified by the reduced tethered density, Σ, where:

$$\Sigma = D\pi R_g^2$$

with D being the grafting density. For $\Sigma < 1$, the grafted polymer layer is typically in the mushroom regime, transitioning at $\Sigma \approx 1$, and in the brush regime for $\Sigma > 1$. In real systems, the transition between mushroom and brush is not sharp due to polydispersity of the grafter polymers.

Clearly R_g is critical to the determination of the transition point. Under specific conditions R_g can be determined experimentally by light scattering, small-angle x-ray scattering, or viscosity measurements.[2] In practice R_g is frequently inferred from published measurements of the root mean-square end-to-end distances of a polymer, r_o.[2] This distance takes into accounts "short-range interactions" such as bond angle restrictions and steric hindrances as well as osmotic swelling by the solvent. The measured values for R_g is dependent on the solvent and temperature of the system, however differences between r_o when good solvents are used are typically less than 10%.[2] Therefore, one must bear in mind that the mushroom to brush transition will vary somewhat when the solvent or temperature of the system is changed.

1. W.J. Brittain and S. Minko, *J. Polym. Sci. Part A: Polym. Chem.*, 2007, 45, 3505-3512.

2. J. Brandrup, E. H. Immergut and E. A. Grulke, *Polymer Handbook, 4th ed.*, John Wiley & Sons, New York, 1999.