Supporting Information

Chain Dispersity Effects on Brush Properties of Surface Grafted Polycaprolactone-Modified Silica Nanoparticles: Unique Scaling Behavior in the Concentrated Polymer Brush Regime

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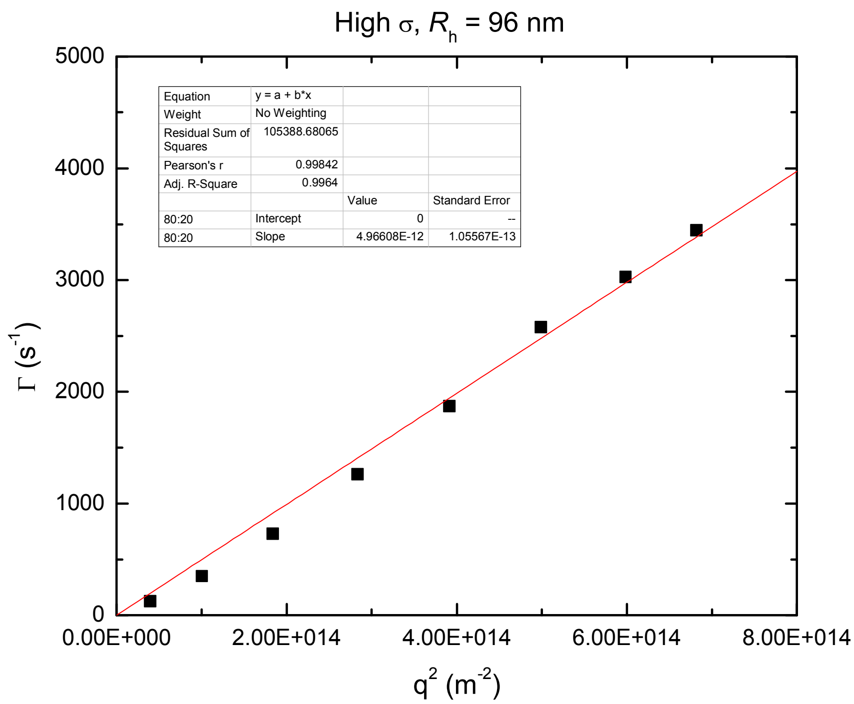


Figure S1. Γ vs q^2 plot for high σ, 26 nm brush particles

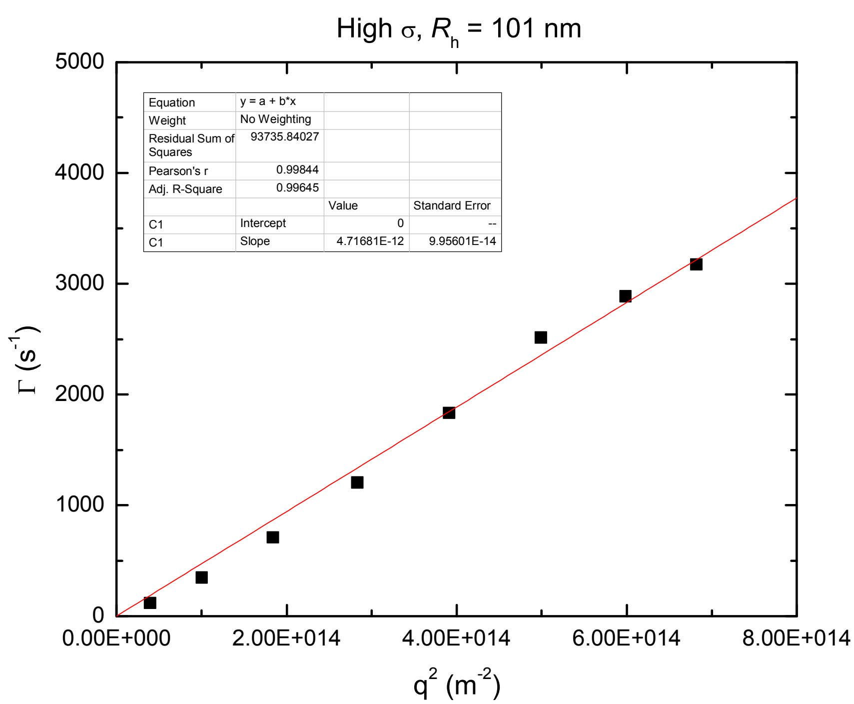


Figure S2. Γ vs q^2 plot for high σ, 31 nm brush particles

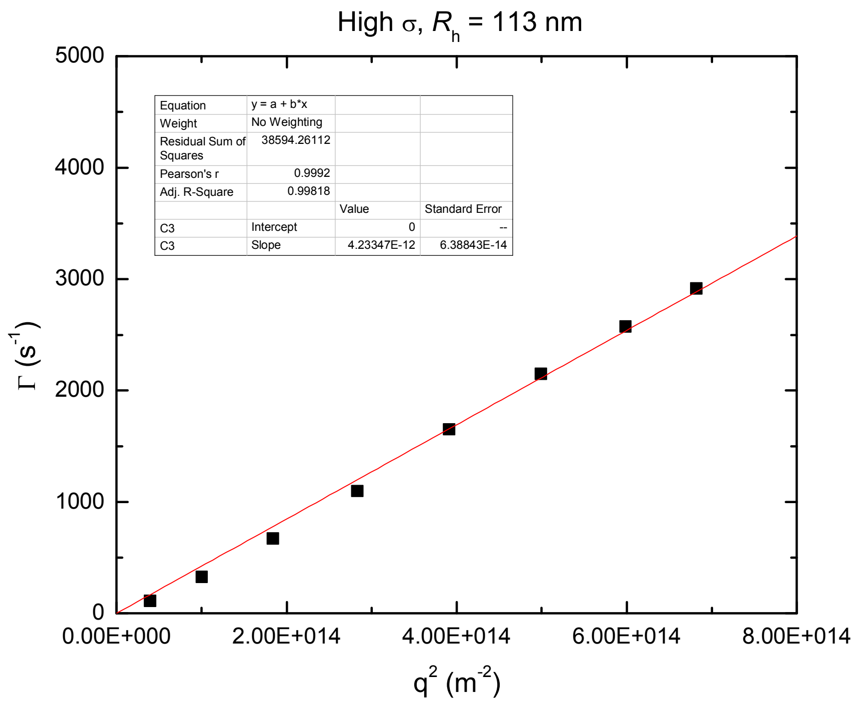


Figure S3. Γ vs q^2 plot for high σ, 43 nm brush particles

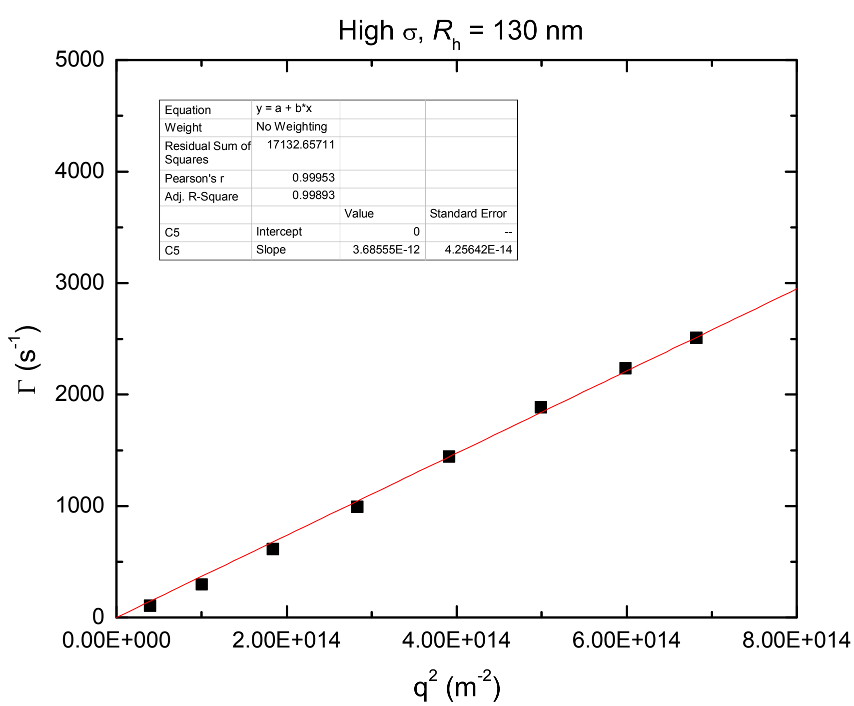


Figure S4. Γ vs q^2 plot for high σ, 60 nm brush particles

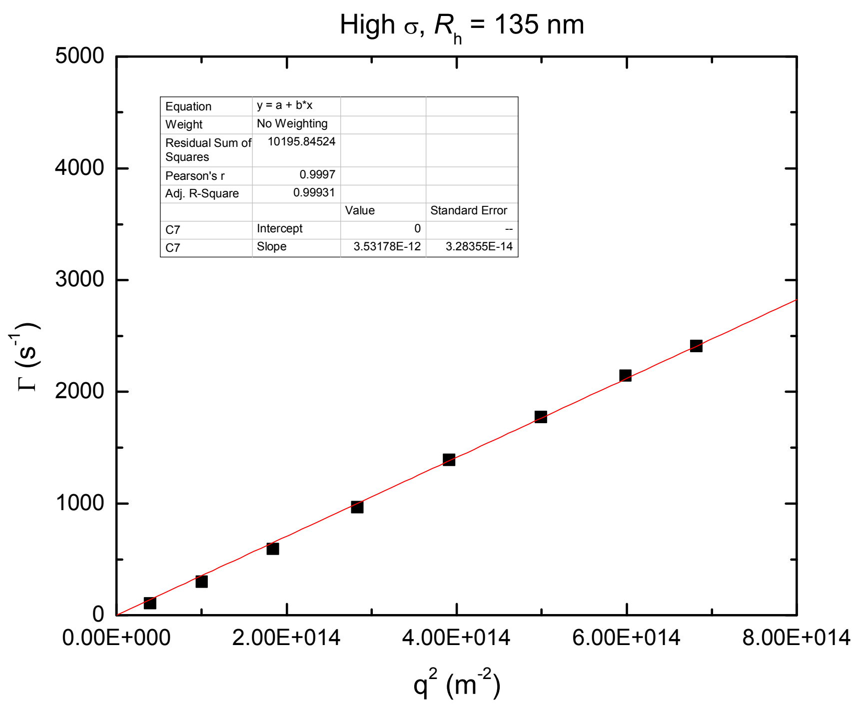


Figure S5. Γ vs q^2 plot for high σ, 65 nm brush particles

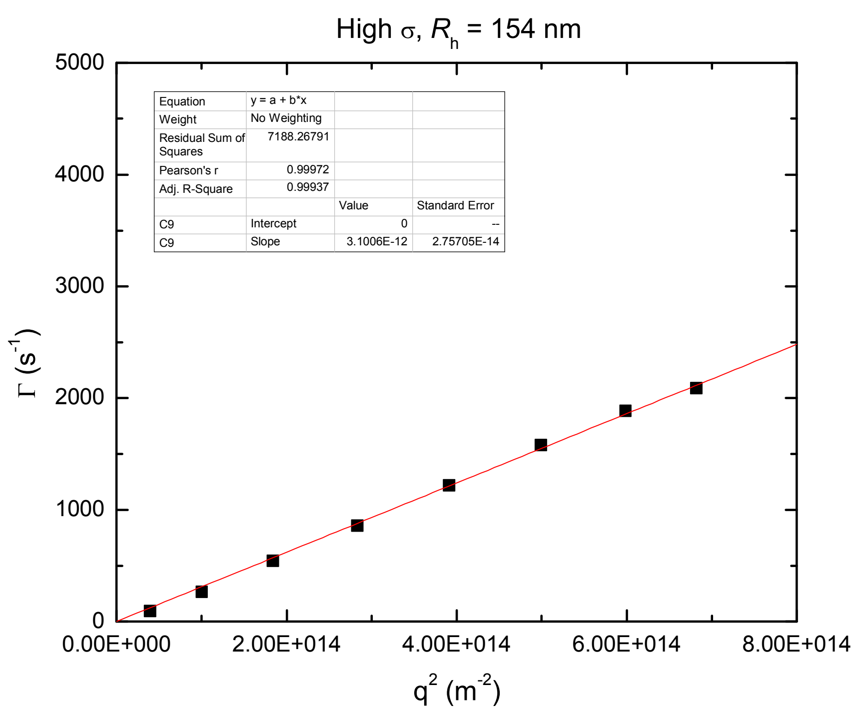


Figure S6. Γ vs q^2 plot for high σ, 84 nm brush particles

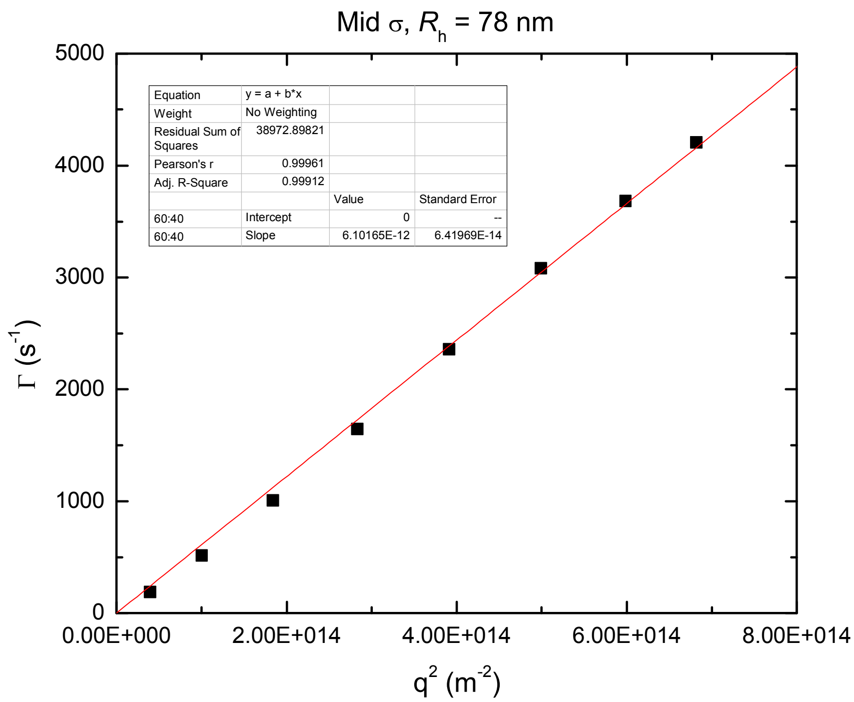


Figure S7. Γ vs q^2 plot for mid σ, 8 nm brush particles

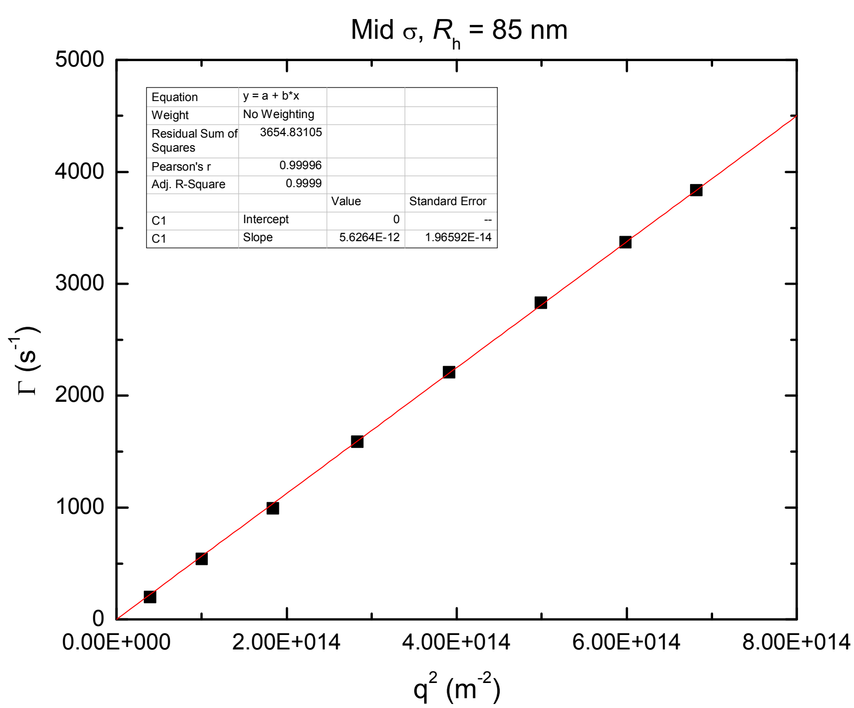


Figure S8. Γ vs q^2 plot for mid σ, 15 nm brush particles

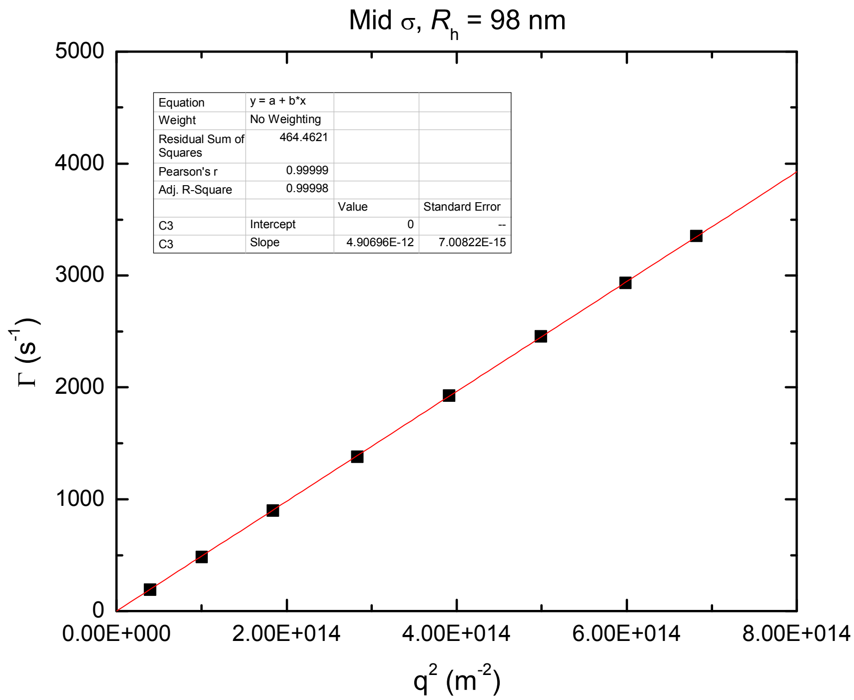


Figure S9. Γ vs q^2 plot for mid σ, 28 nm brush particles

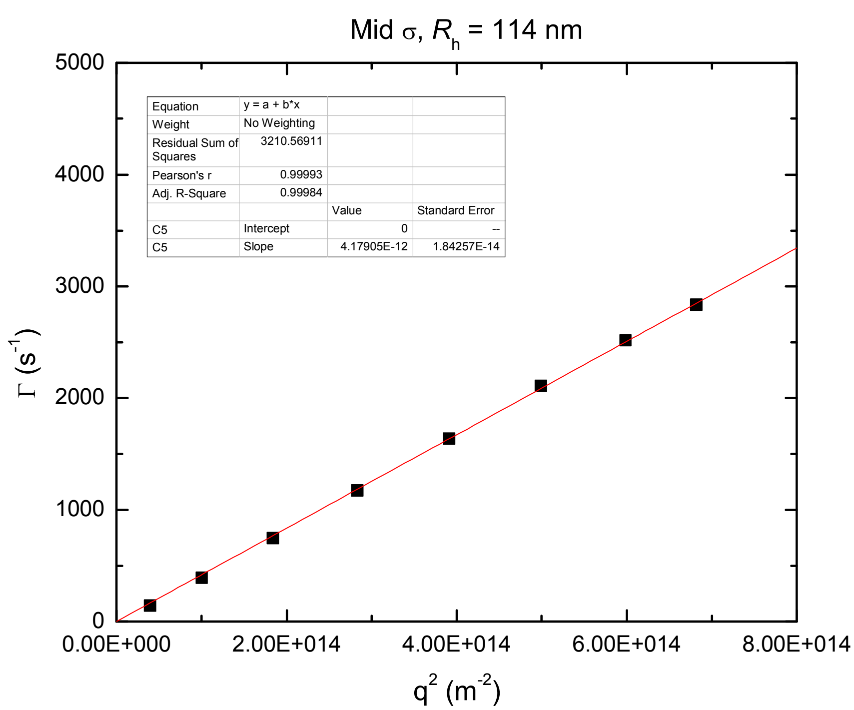


Figure S10. Γ vs q^2 plot for mid σ, 44 nm brush particles

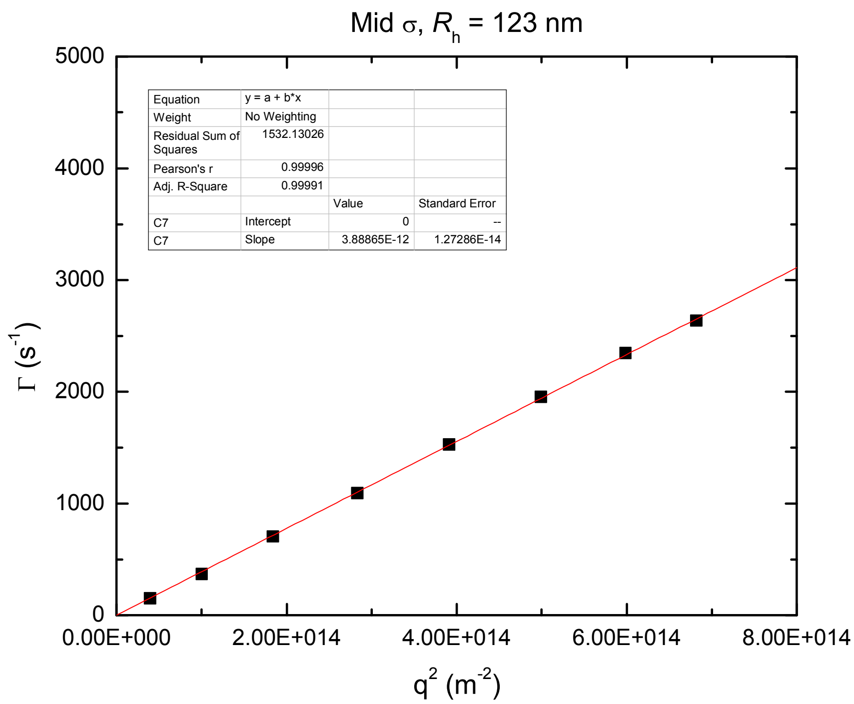


Figure S11. Γ vs q^2 plot for mid σ, 53 nm brush particles

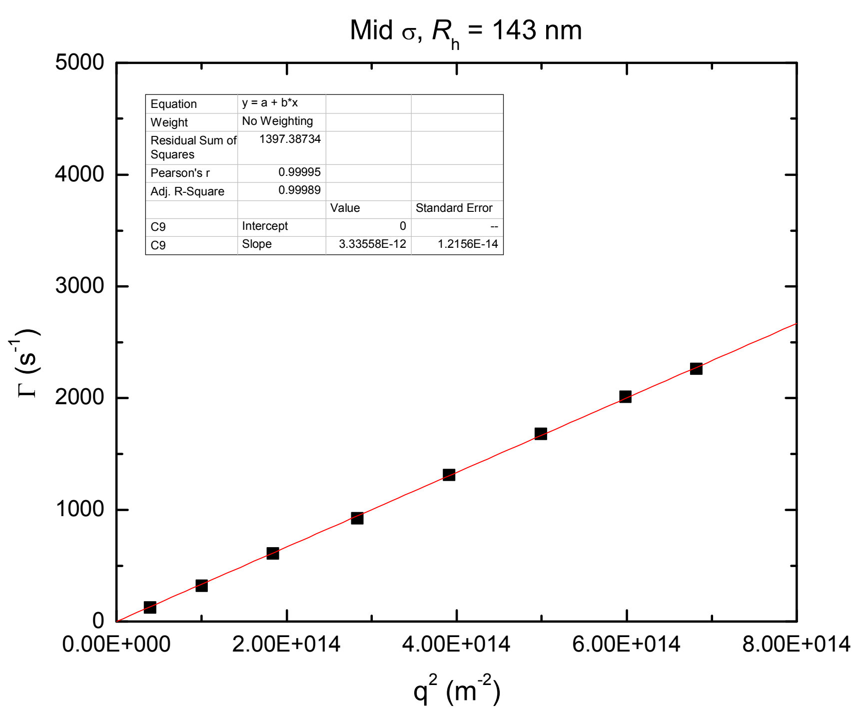


Figure S12. Γ vs q^2 plot for mid σ, 73 nm brush particles

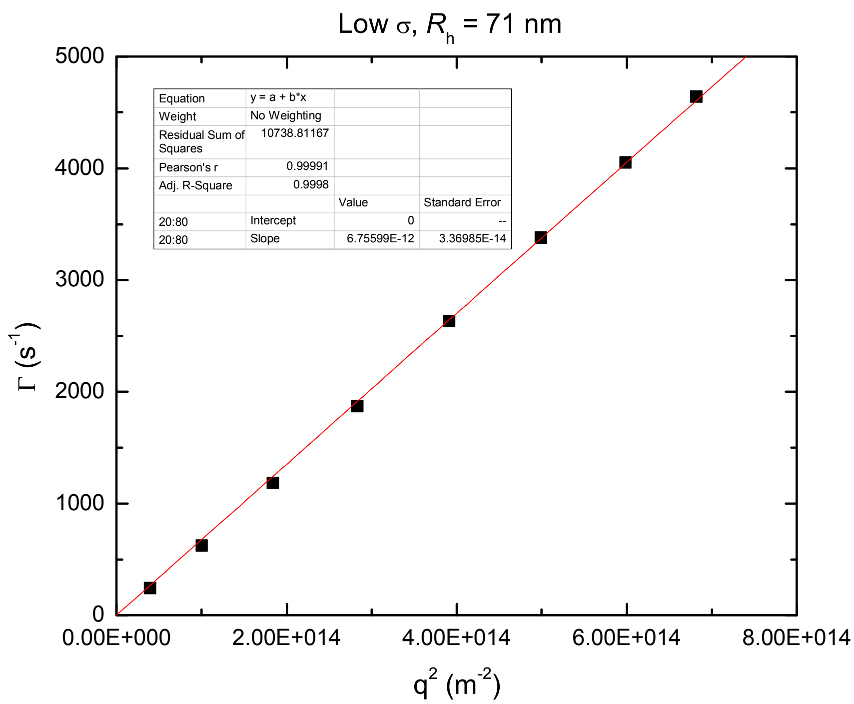


Figure S13. Γ vs q^2 plot for low σ, 1 nm brush particles

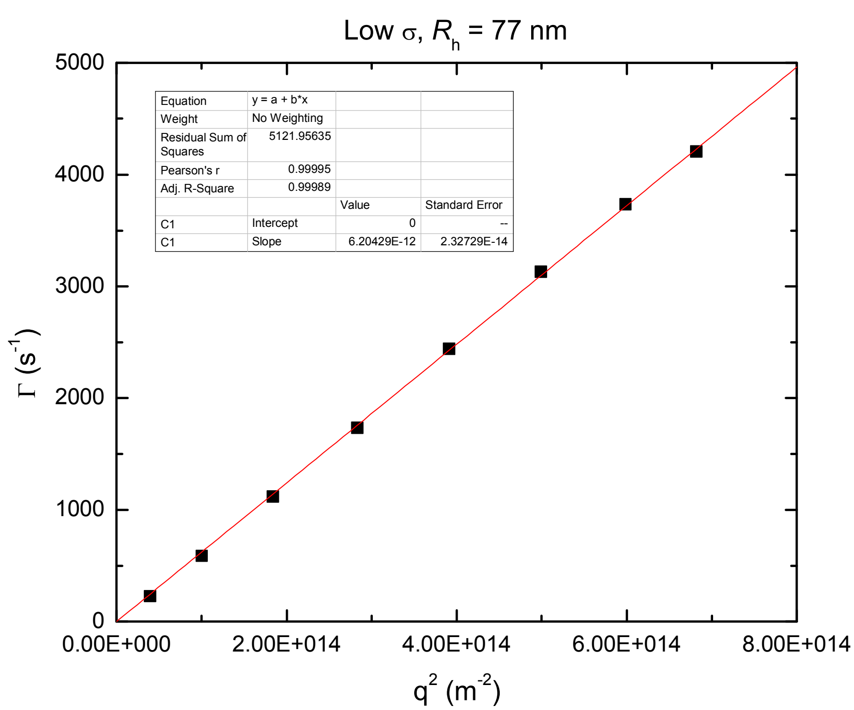


Figure S14. Γ vs q^2 plot for low σ, 7 nm brush particles

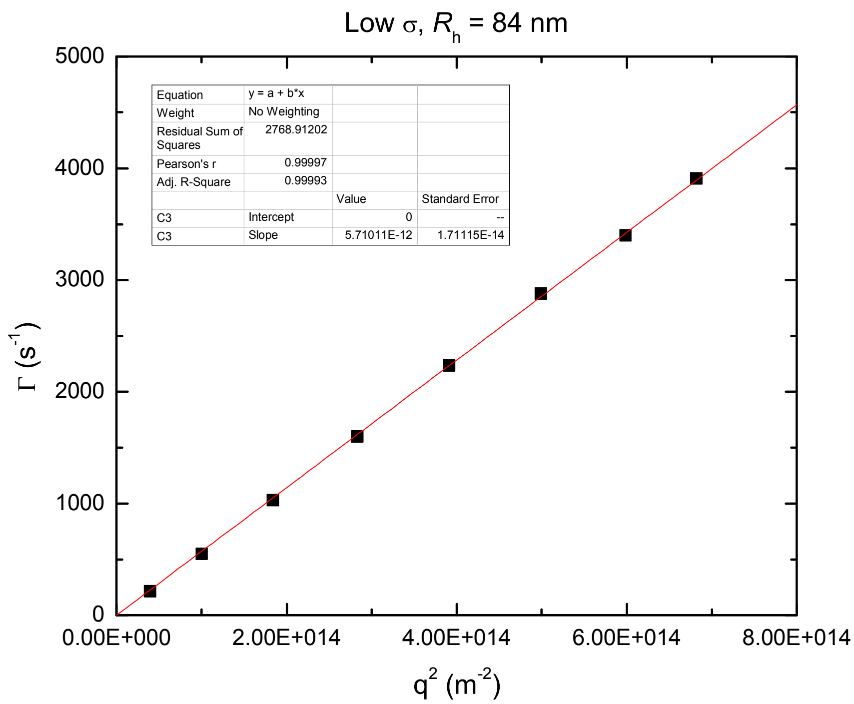


Figure S15. Γ vs q^2 plot for low σ, 14 nm brush particles

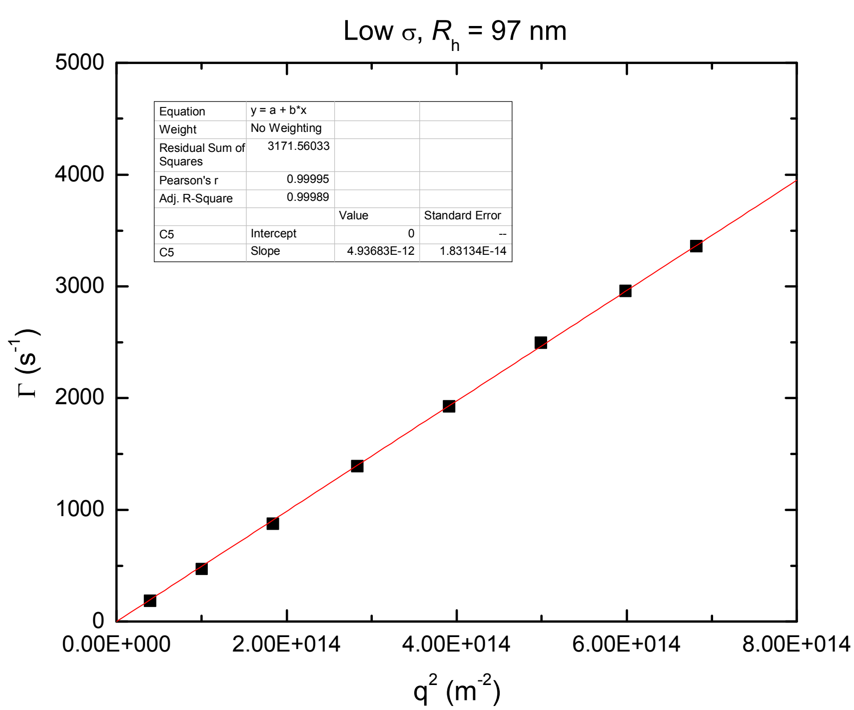


Figure S16. Γ vs q^2 plot for low σ, 27 nm brush particles

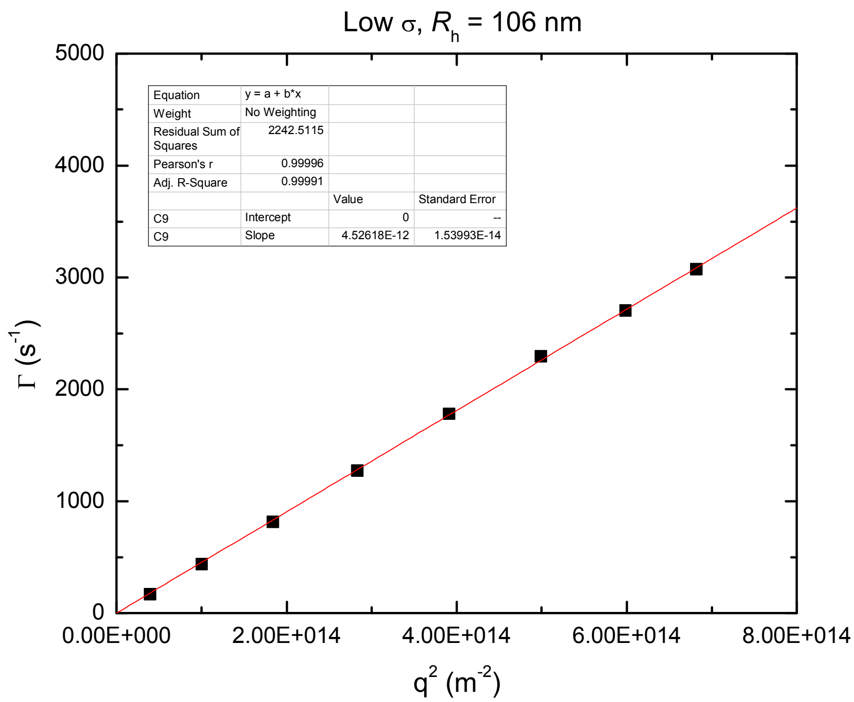


Figure S17. Γ vs q^2 plot for low σ, 36 nm brush particles

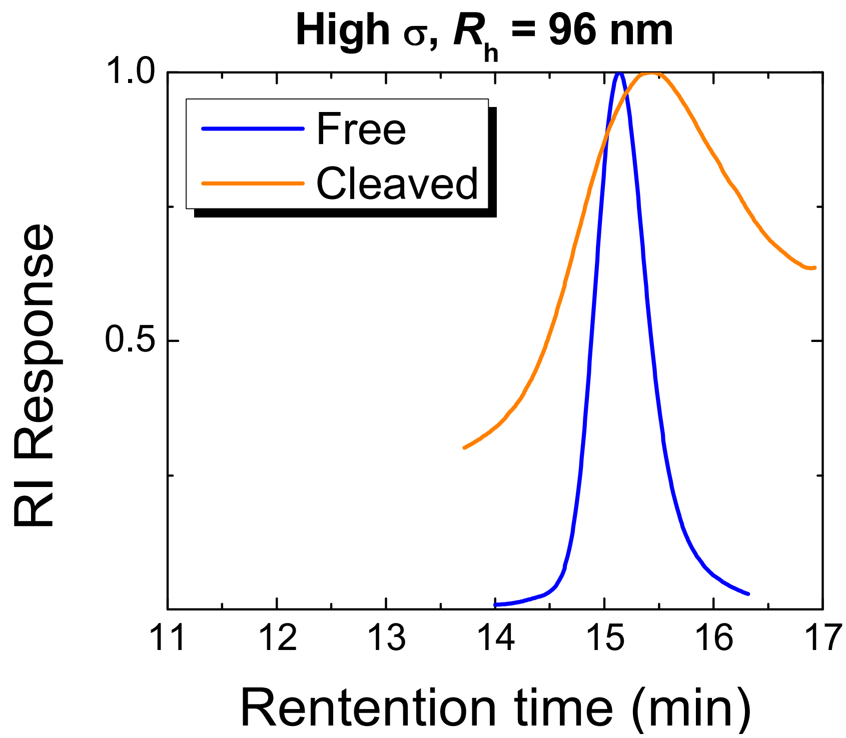


Figure S18. GPC chromatograms for high σ, 26 nm brush particles. Blue trace, free polymer in solution; orange trace, cleaved brush polymer.

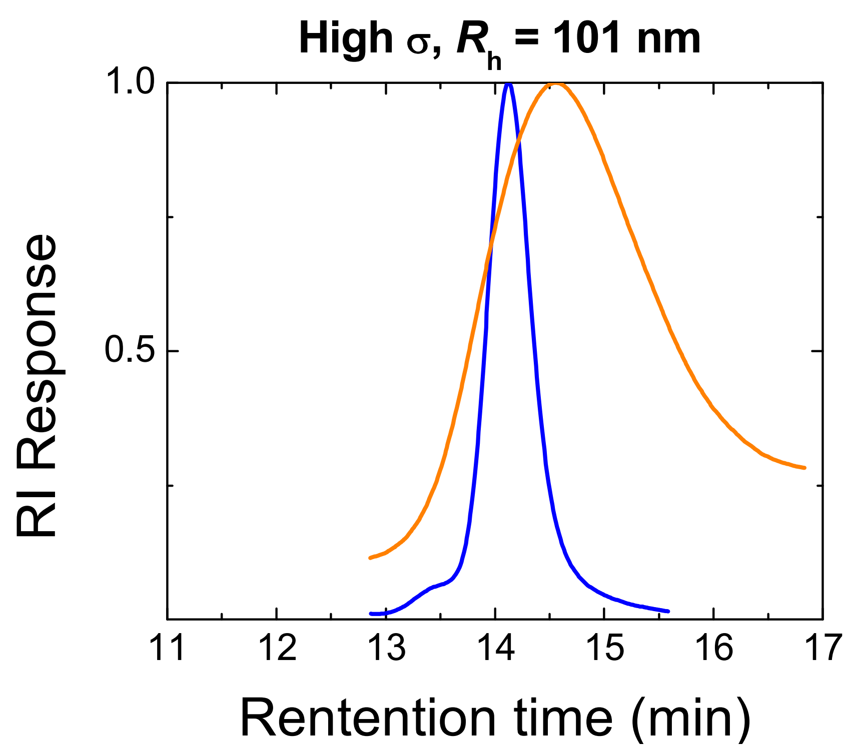


Figure S19. GPC chromatograms for high σ, 31 nm brush particles. Blue trace, free polymer in solution; orange trace, cleaved brush polymer.

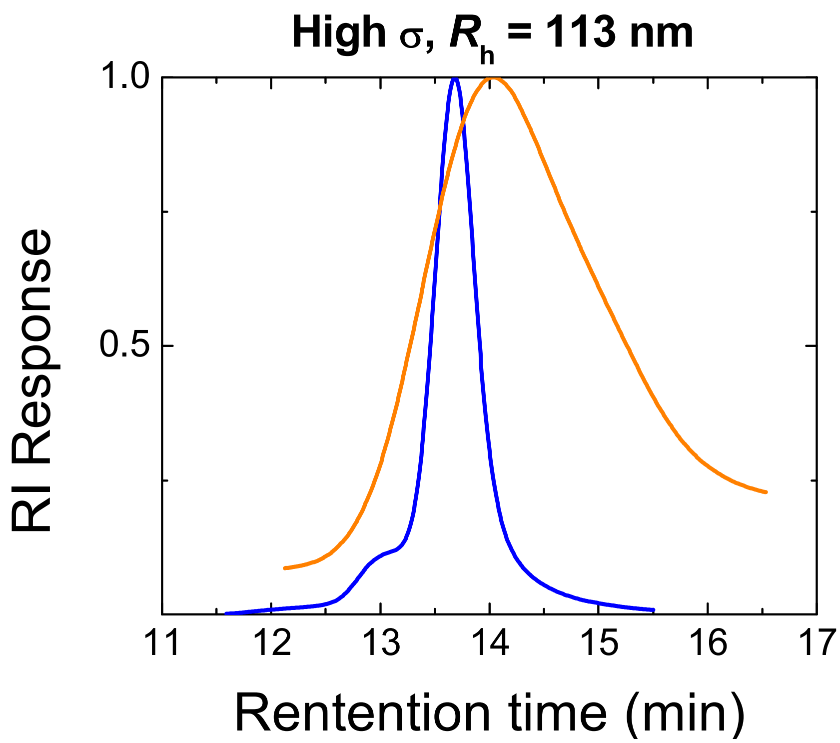


Figure S20. GPC chromatograms for high σ, 43 nm brush particles. Blue trace, free polymer in solution; orange trace, cleaved brush polymer.

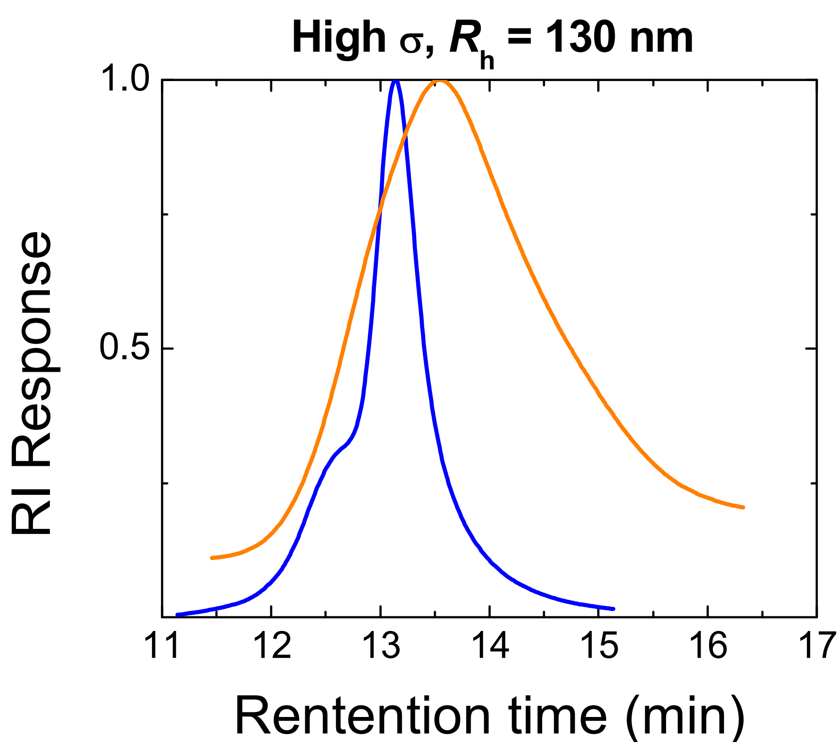


Figure S21. GPC chromatograms for high σ, 60 nm brush particles. Blue trace, free polymer in solution; orange trace, cleaved brush polymer.

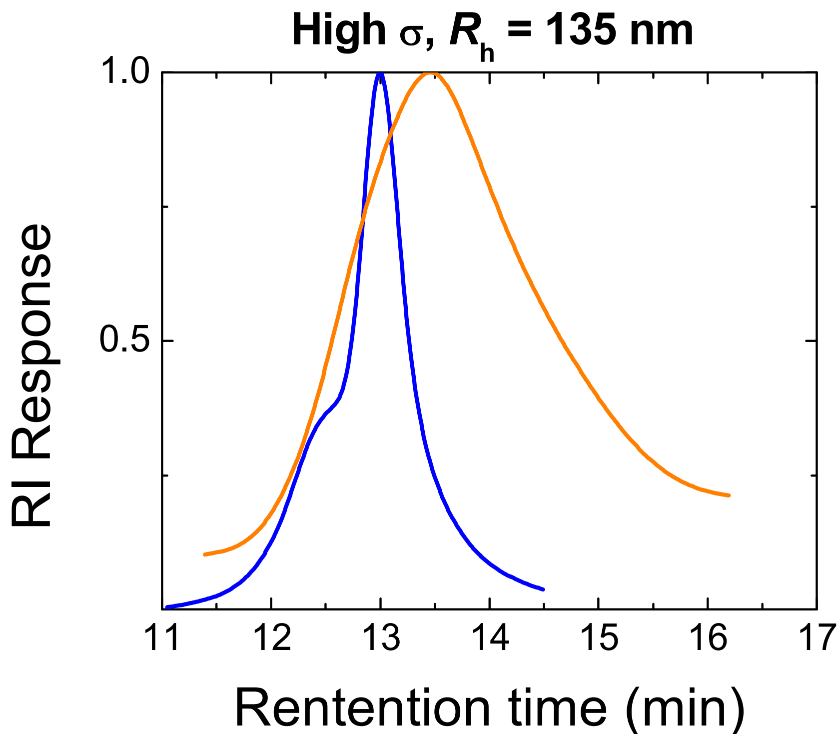


Figure S22. GPC chromatograms for high σ, 65 nm brush particles. Blue trace, free polymer in solution; orange trace, cleaved brush polymer.

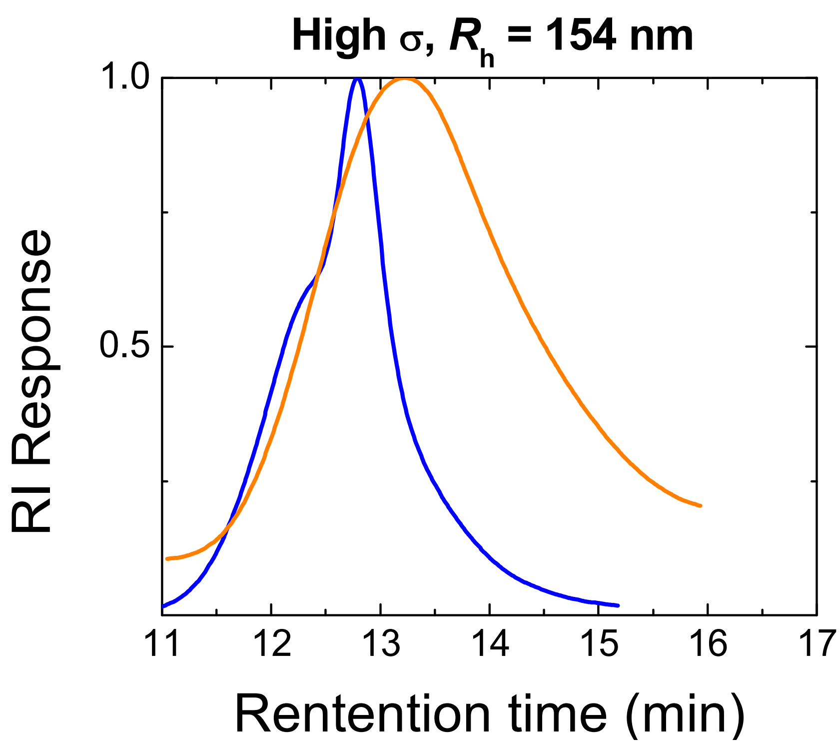


Figure S23. GPC chromatograms for high σ, 84 nm brush particles. Blue trace, free polymer in solution; orange trace, cleaved brush polymer.

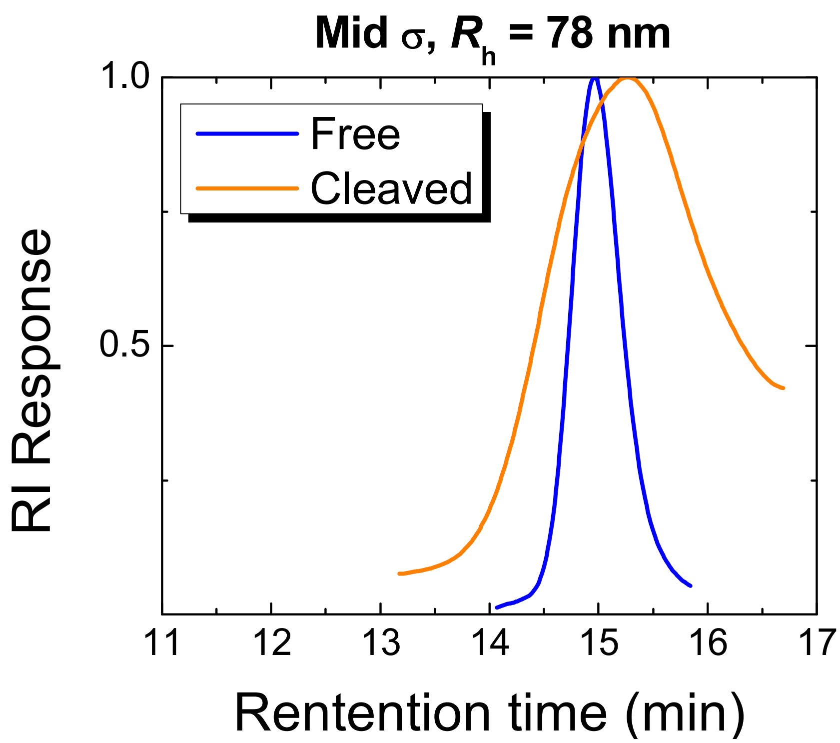


Figure S24. GPC chromatograms for mid σ, 8 nm brush particles. Blue trace, free polymer in solution; orange trace, cleaved brush polymer.

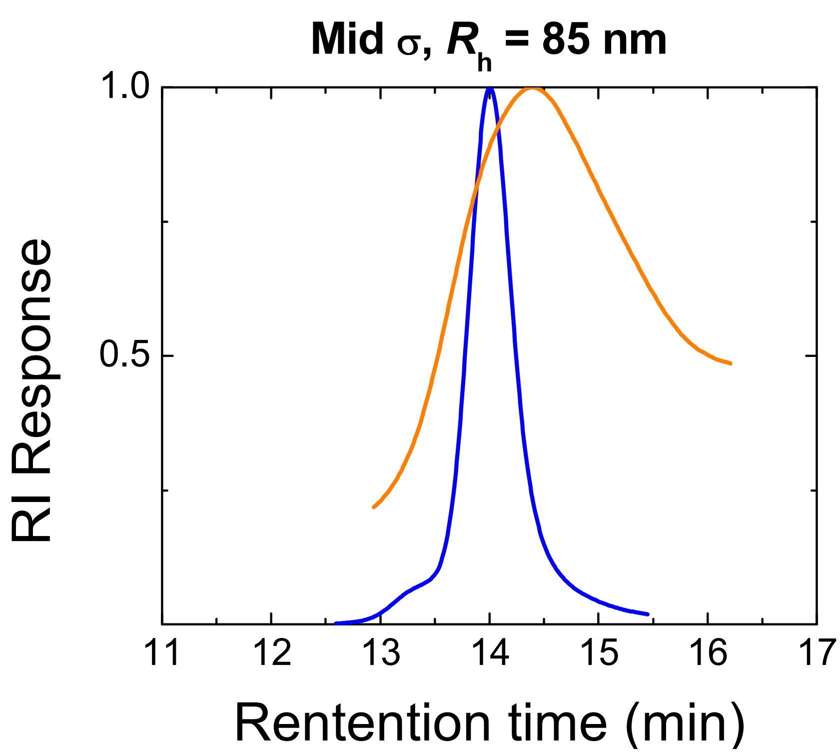


Figure S25. GPC chromatograms for high σ, 15 nm brush particles. Blue trace, free polymer in solution; orange trace, cleaved brush polymer.

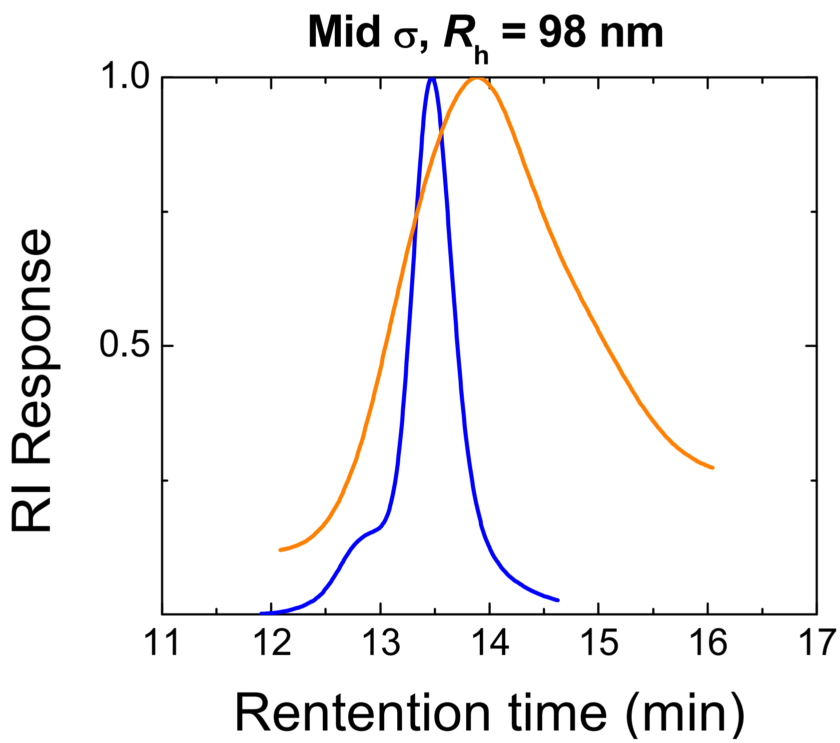


Figure S26. GPC chromatograms for mid σ, 28 nm brush particles. Blue trace, free polymer in solution; orange trace, cleaved brush polymer.

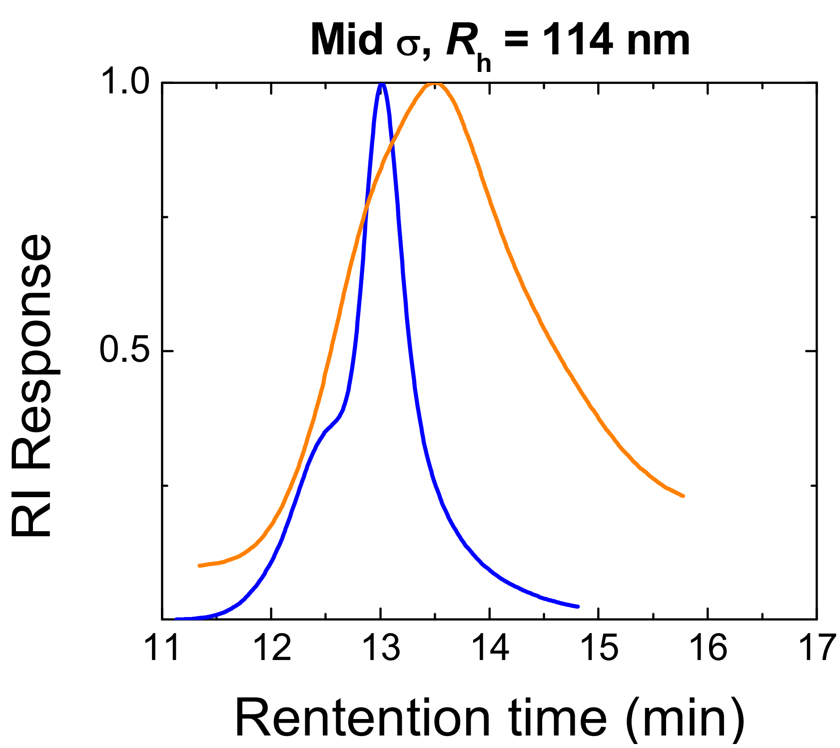


Figure S27. GPC chromatograms for mid σ, 44 nm brush particles. Blue trace, free polymer in solution; orange trace, cleaved brush polymer.

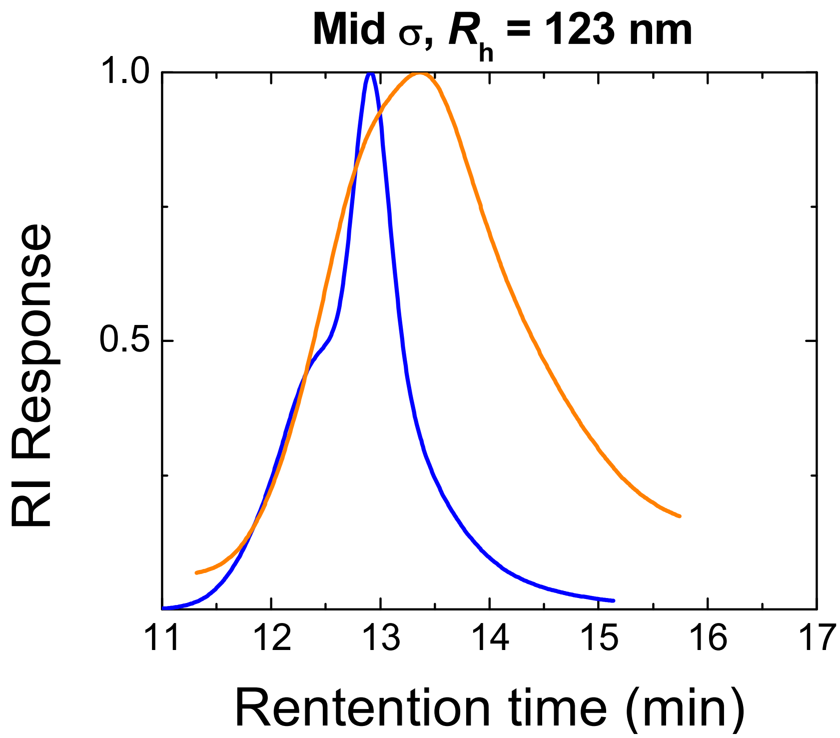


Figure S28. GPC chromatograms for mid σ, 73 nm brush particles. Blue trace, free polymer in solution; orange trace, cleaved brush polymer.

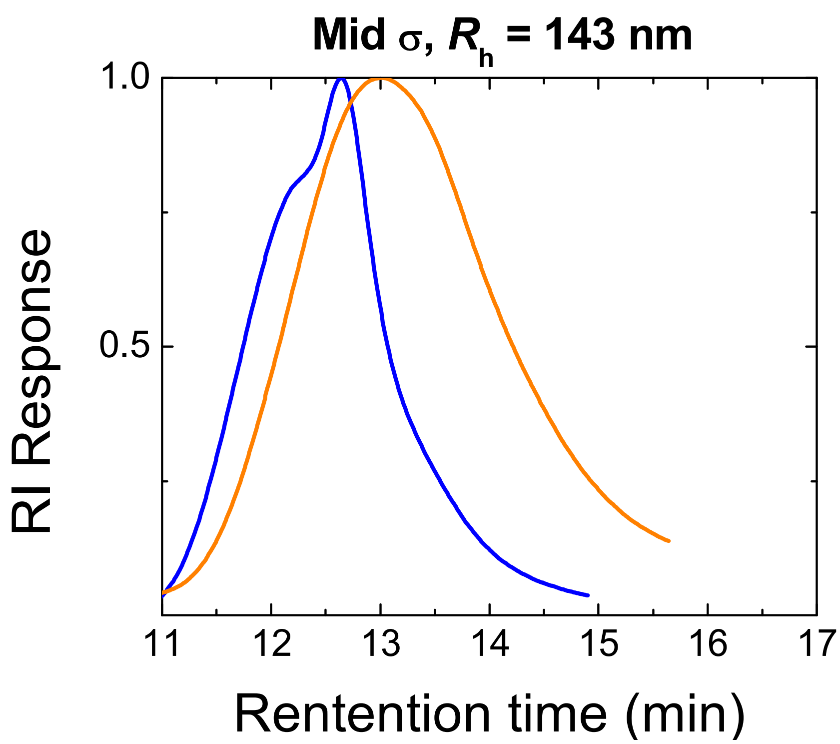


Figure S29. GPC chromatograms for mid σ, 73 nm brush particles. Blue trace, free polymer in solution; orange trace, cleaved brush polymer.

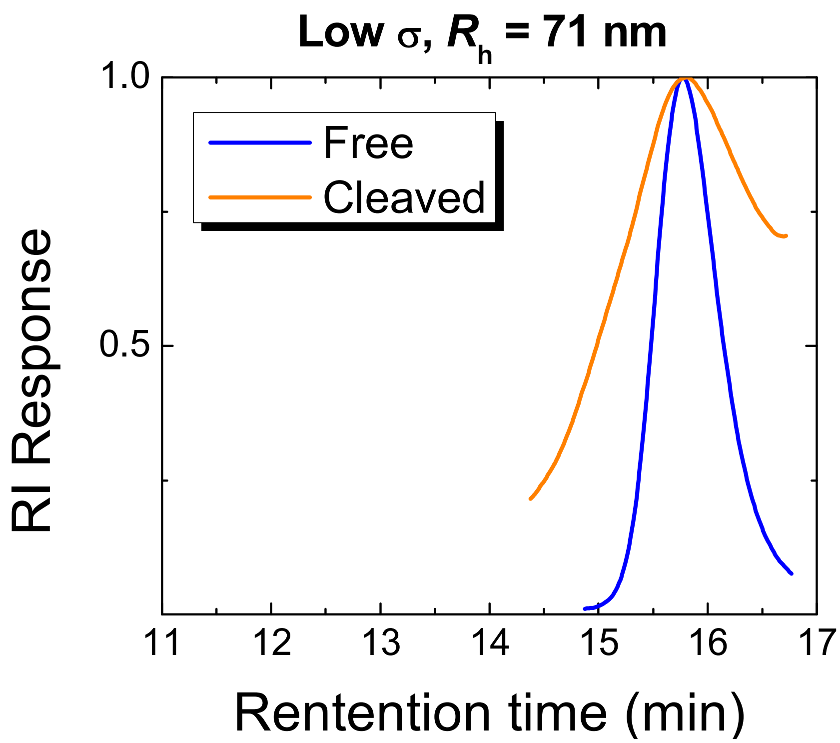


Figure S30. GPC chromatograms for low σ, 1 nm brush particles. Blue trace, free polymer in solution; orange trace, cleaved brush polymer.

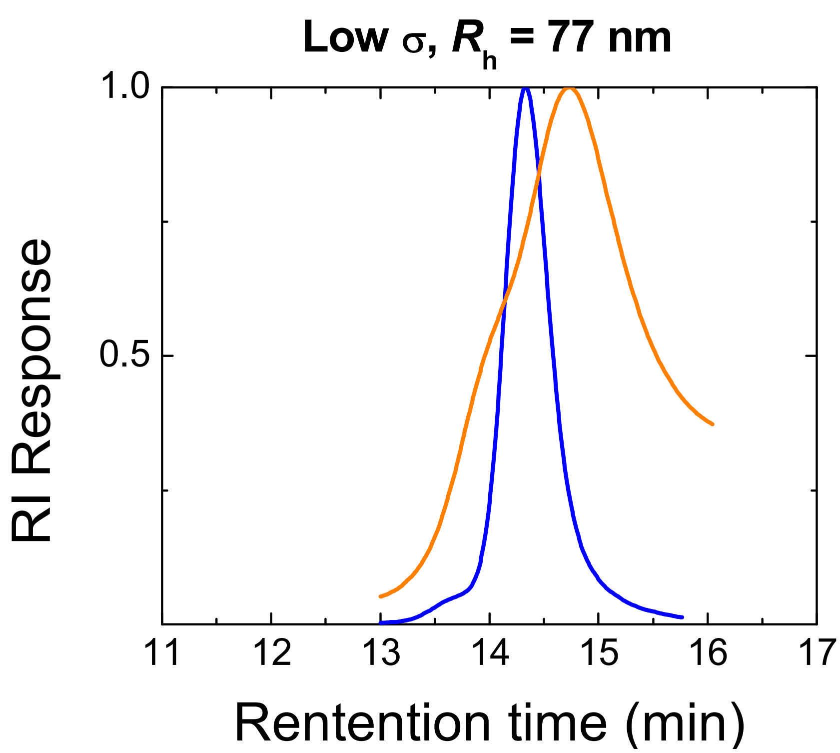


Figure S31. GPC chromatograms for low σ, 7 nm brush particles. Blue trace, free polymer in solution; orange trace, cleaved brush polymer.

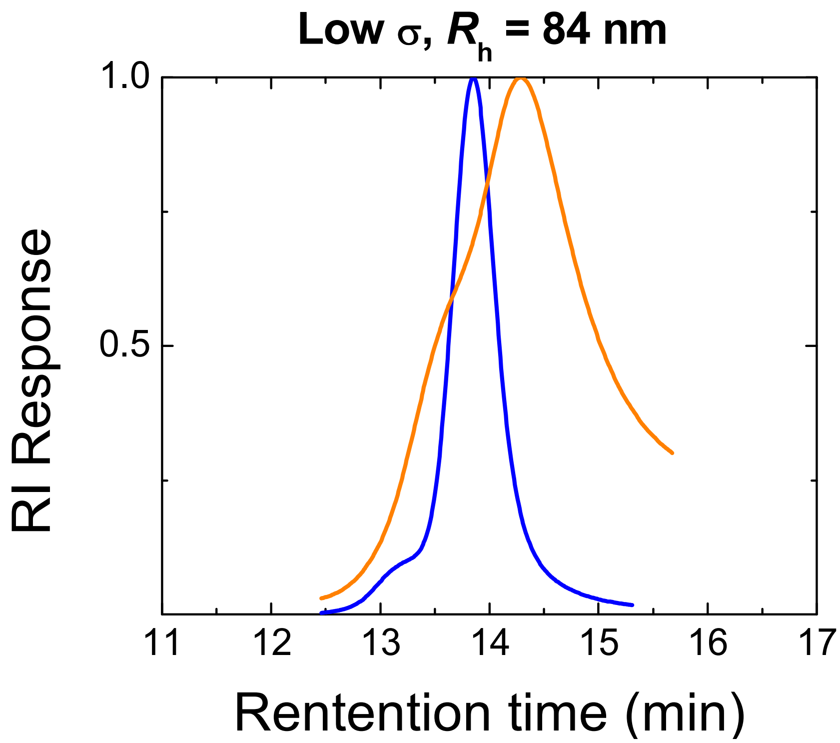


Figure S32. GPC chromatograms for low σ, 14 nm brush particles. Blue trace, free polymer in solution; orange trace, cleaved brush polymer.

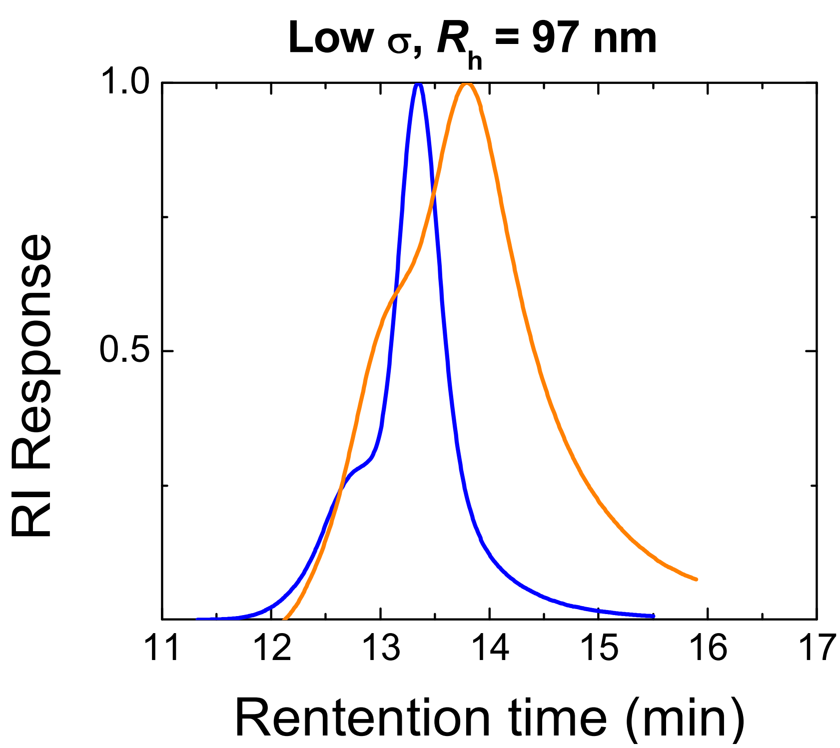


Figure S33. GPC chromatograms for low σ, 27 nm brush particles. Blue trace, free polymer in solution; orange trace, cleaved brush polymer.

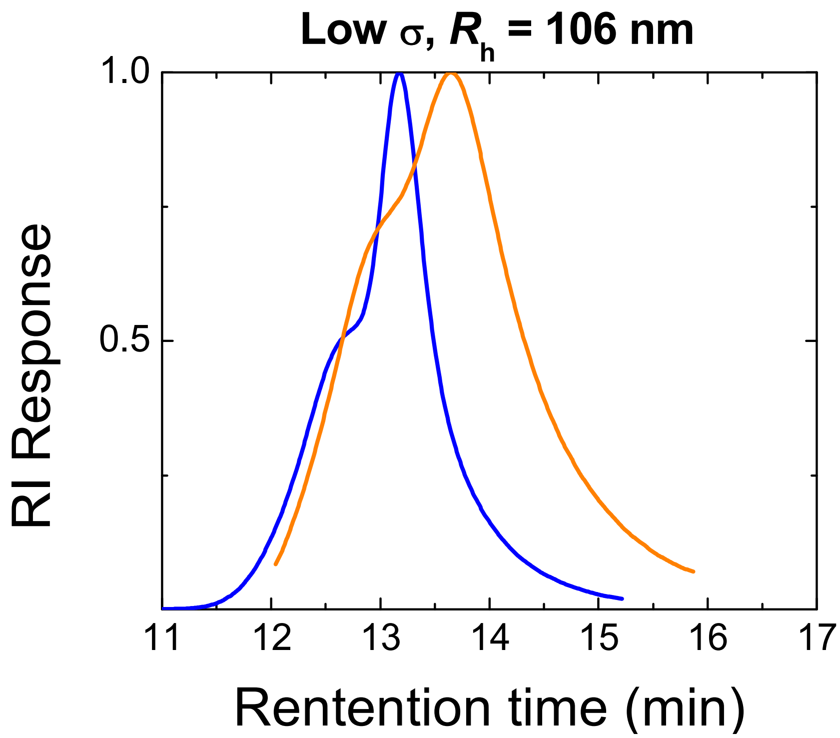


Figure S34. GPC chromatograms for low σ, 36 nm brush particles. Blue trace, free polymer in solution; orange trace, cleaved brush polymer.

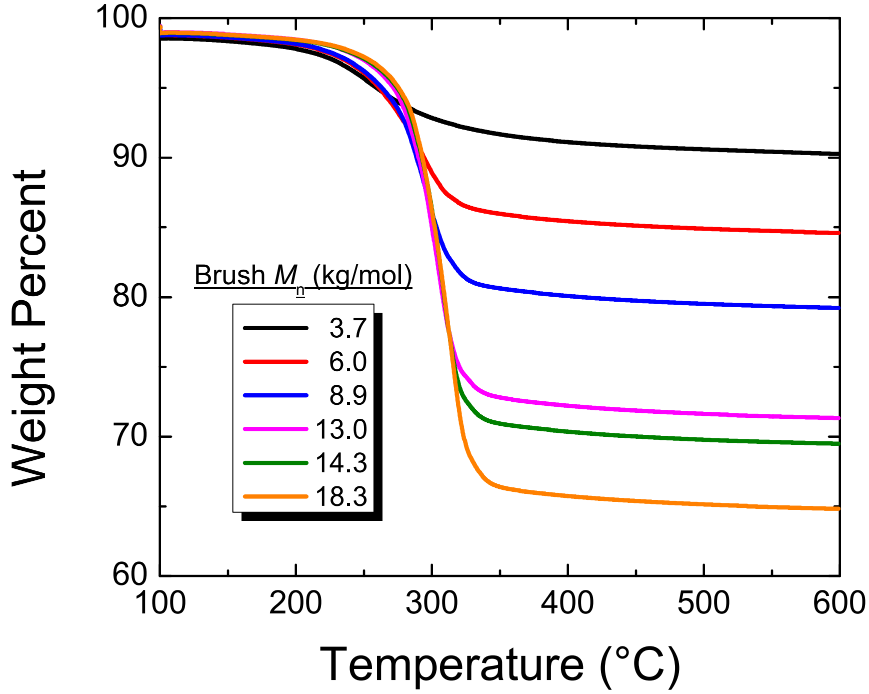


Figure S35. TGA mass loss profiles for high σ particle set.

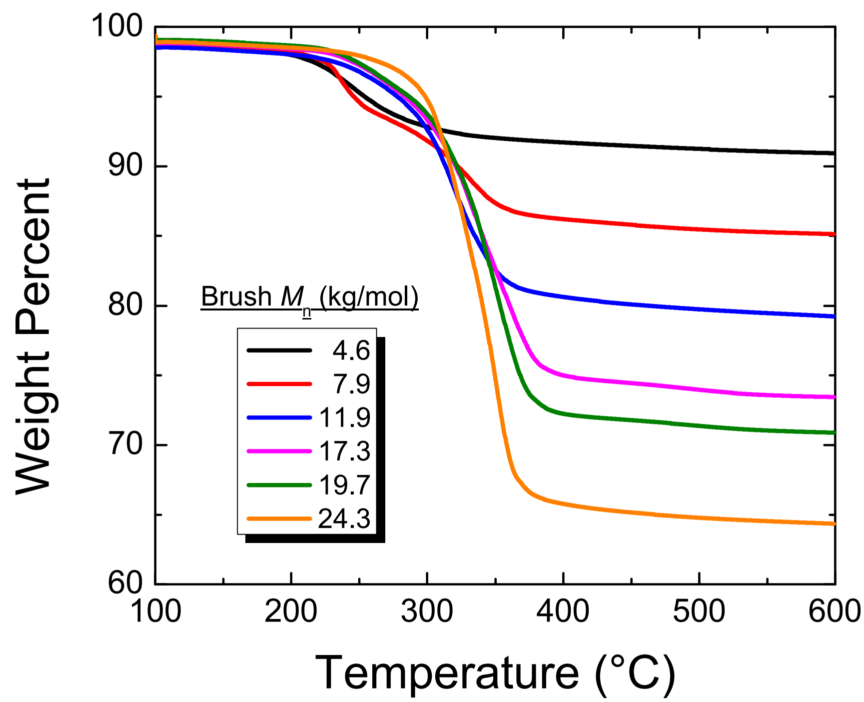


Figure S36. TGA mass loss profiles for mid σ particle set.

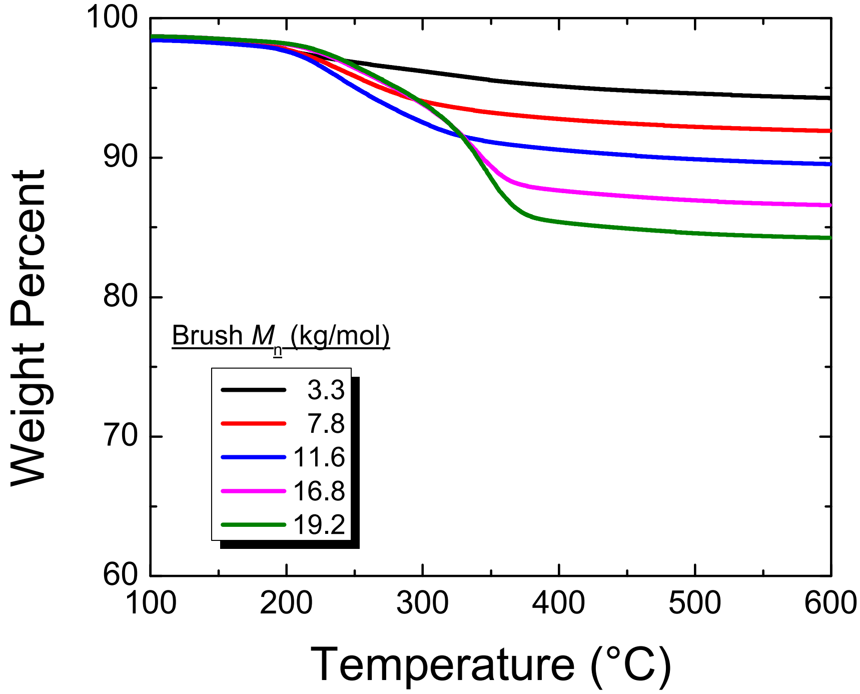


Figure S37. TGA mass loss profiles for low σ particle set.

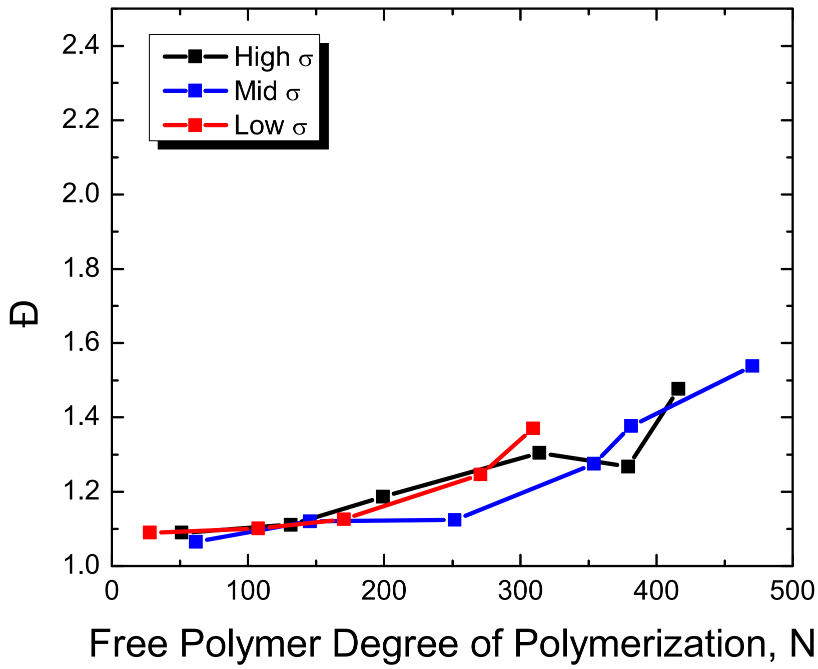
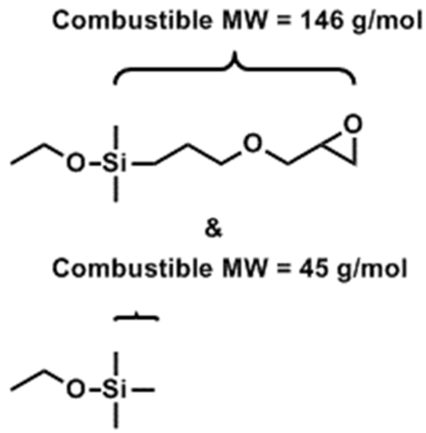


Figure S38. Plot of dispersity as a function of degree of polymerization for free solution chains. Dispersity of free chains is independent of grafting density.

Determination of initiator surface density

Example calculation for high σ:



Taking into account the combustible portion of each silane, an adjusted molecular weight is calculated for each molecule. The percentage of organic material attached to the silica nanoparticle surface is calculated by taking the difference in weight percent at T = 300 °C and T = 250 °C.

Therefore, for the high σ particles the combustible portion is given by:

$$99.19\% - 98.09\% = 1.10\%\ Combustible\ portion$$

An effective molecular weight is then calculated to account for the mole percent of each silane used

$$0.8\left(146\ \frac{g}{mol}\right) + 0.2\left(45\ \frac{g}{mol}\right) = 126\ g/mol$$

In an arbitrary 100 g of initiator functional silica nanoparticles, the number of silanes grafted to the surface can be calculated by

$$\frac{1.1g\ combustible\ material}{126\ g/mol} = 5.26\ x\ 10^{21}\ silane\ molecules$$

The number of nanoparticles in the same arbitrary 100 g of material can be found by

$$\frac{98.9\ g\ silica}{1.4418\ x\ 10^{-15}\ g\ per\ silica\ nanoparticle} = 6.86\ x\ 10^{16}\ particles$$

The number of silane molecules on each nanoparticle can be found by

$$\frac{5.26\ x\ 10^{21}\ silane\ molecules}{6.86\ x\ 10^{16}\ particles} = 76{,}600\ silane\ molecules/particle$$

Dividing by the surface area of a silica nanoparticle gives the surface density of silanes

$$\frac{76{,}600\ silane\ molecules/particle}{39{,}400\ nm^2/particle} = 1.95\ silanes/nm^2$$

Finally, multiplying by the percentage of initiator functional silanes gives the surface density of initiating species

$$0.8\left(1.95\frac{silanes}{nm^2}\right) = \mathbf{1.55\ \boldsymbol{initiators/nm^2}}$$

Determination of brush surface density

Example calculation for high σ, 26 nm brush particles with an M_n of 3,654 g/mol:

Mass loss at 600 °C is 8.29%. In an arbitrary 100 g of particles, the number of polymer chains is given by

$$\left(\frac{8.29\ g\ polymer}{3{,}654\ g/mol}\right)(6.022\ x\ 10^{23}\ mol^{-1}) = 1.37\ x\ 10^{21}\ polymer\ chains$$

In the same arbitrary 100 g of particles, the number of particles is given by

$$\frac{91.71\ g\ silica}{1.4418\ x\ 10^{-15}\ g\ per\ silica\ nanoparticle}\ 6.36\ x\ 10^{16}\ particles$$

Dividing the number of chains by the number of nanoparticles gives the number of chains per particle

$$\frac{1.37\ x\ 10^{21}\ polymer\ chains}{6.36\ x\ 10^{16}\ silica\ nanoparticles} = 21{,}477\ chains\ per\ particle$$

Dividing the number of chains per particle by the surface area of the nanoparticle gives the grafting density of polymer chains

$$\frac{21{,}477\ chains\ per\ particle}{39{,}400\ nm^2\ per\ particle} = 0.54\ nm^{-2}$$

This calculation is done for each different brush length particle and the numbers are averaged to give a final grafting density for the set.

Table S1. Properties of high σ nanoparticles.

High Grafting Density						
Polymerization time (min)	Brush length (nm)	M_n Brush (g/mol)	Đ Brush	M_n Free (g/mol)	Đ Free	Mass loss (%, as % at 100 °C - % at 600 °C)
40	26	3,700	1.69	5,800	1.09	8.3
80	31	6,000	1.88	14,900	1.11	14.2
120	43	8,900	2.02	22,700	1.19	19.6
160	60	13,000	2.39	35,800	1.30	27.6
200	65	14,300	2.35	43,200	1.27	29.5
240	84	18,300	2.39	47,400	1.48	34.1

Table S2. Properties of mid σ nanoparticles.

Mid Grafting Density						
Polymerization time (min)	Brush length (nm)	M_n Brush (g/mol)	Đ Brush	M_n Free (g/mol)	Đ Free	Mass loss (%, as % at 100 °C - % at 600 °C)
40	8	4,600	1.56	7,000	1.06	7.7
80	15	7,900	1.68	16,600	1.12	13.7
120	28	11,900	1.86	28,700	1.12	18.4
160	44	17,300	2.06	40,400	1.28	25.4
200	53	19,700	1.98	43,500	1.38	28.2
240	73	24,300	2.06	53,600	1.54	34.2

Table S3. Properties of low σ nanoparticles.

Low Grafting Density						
Polymerization time (min)	Brush length (nm)	M_n Brush (g/mol)	Đ Brush	M_n Free (g/mol)	Đ Free	Mass loss (%, as % at 100 °C - % at 600 °C)
40	1	3,300	1.32	3,200	1.09	4.2
80	7	7,800	1.42	12,300	1.10	6.6
120	14	11,600	1.43	19,400	1.13	8.9
160	27	16,800	1.55	30,900	1.25	12.1
200	36	19,200	1.64	35,300	1.37	14.5