Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Factors affecting bottlebrush polymer synthesis by the transfer-to method using reversible addition–fragmentation chain transfer (RAFT) polymerization

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Table S1: PCTA characterization data.

PCTA DP	NMR Conv.	Theo. M_n[a]	M_n (GPC)	Đ (GPC)
50	>99	16,500	17,000	1.09
100	>99	32,900	35,600	1.15
250	>99	82,300	-[b]	-[b]
500	>99	165,000	-[b]	-[b]
750	>99	247,000	-[b]	-[b]
1000	>99	329,000	-[b]	-[b]

[a]Based on M_n = (NMR Conv.)/100 * MW CTA*targeted DP [b]Polymer was not soluble in THF.

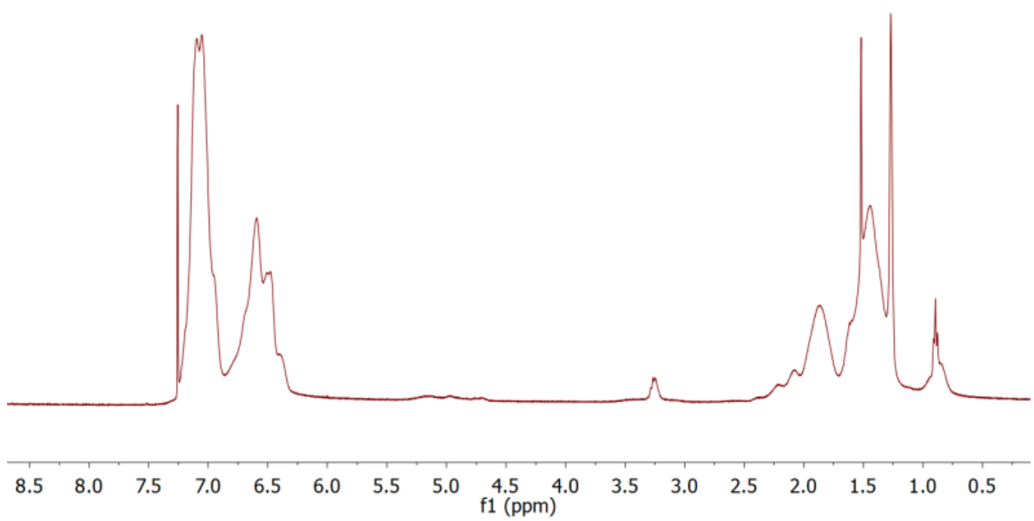

Figure S1: Representative ^{1}H NMR spectrum of bottlebrush polymer prepared using styrene as the monomer (Table 1, entry 2).

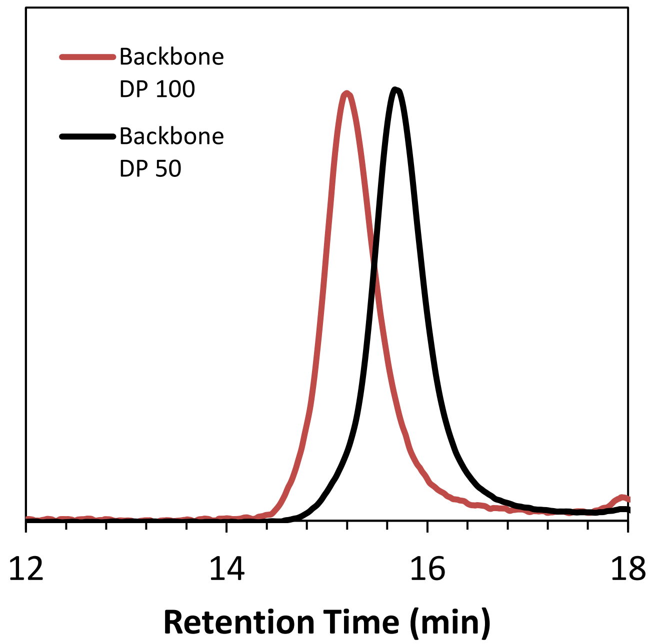

Figure S2: SEC traces of backbone PCTA with DP of 50 and 100.

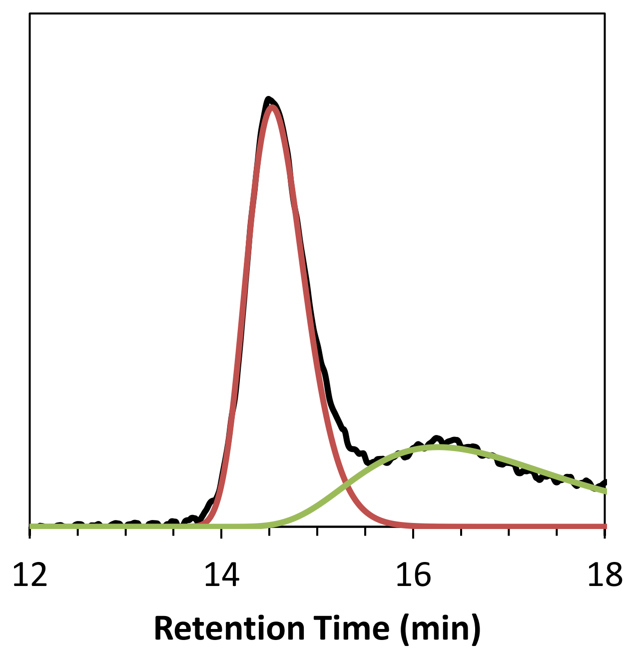

Figure S3: SEC trace and peak fit of bottlebrush polymer from Table 1, entry 1. The black trace is the raw RI signal obtained via SEC. Red and green traces represent fits of bottlebrush and linear polymer populations, respectively.

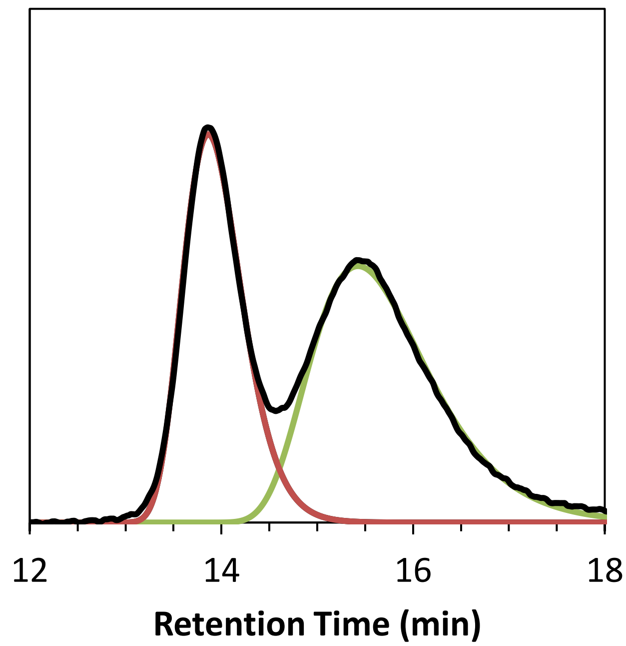

Figure S4: SEC trace and peak fit of bottlebrush polymer from Table 1, entry 2. The black trace is the raw RI signal obtained via SEC. Red and green traces represent fits of bottlebrush and linear polymer populations, respectively.

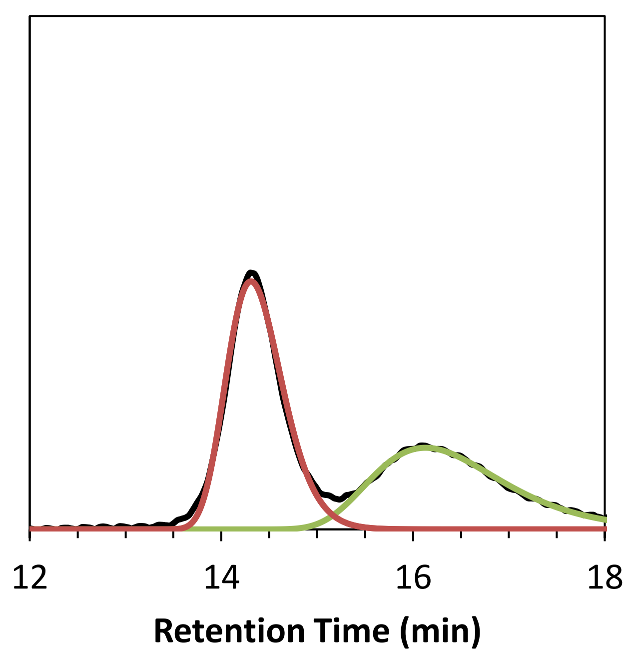

Figure S5: SEC trace and peak fit of bottlebrush polymer from Table 1, entry 3. The black trace is the raw RI signal obtained via SEC. Red and green traces represent fits of bottlebrush and linear polymer populations, respectively.

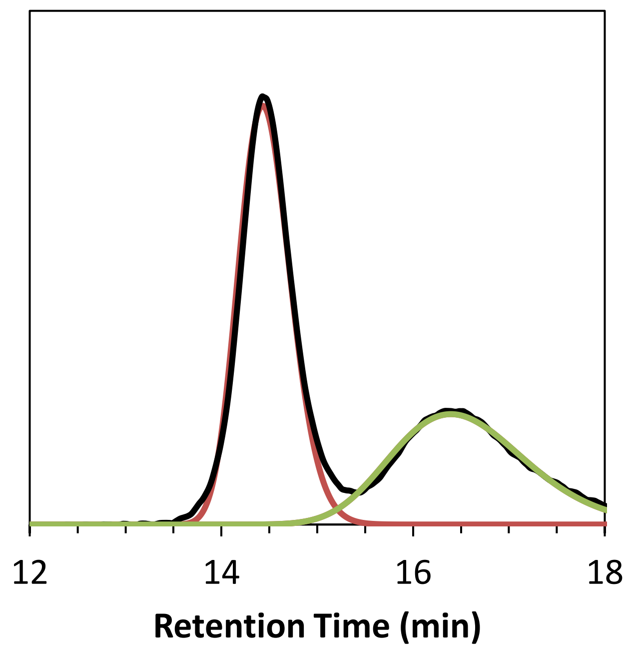

Figure S6: SEC trace and peak fit of bottlebrush polymer from Table 1, entry 4. The black trace is the raw RI signal obtained via SEC. Red and green traces represent fits of bottlebrush and linear polymer populations, respectively.

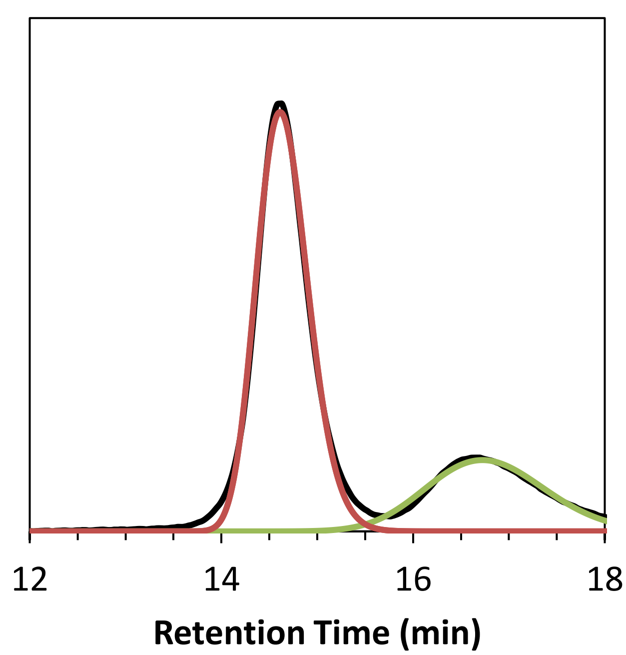

Figure S7: SEC trace and peak fit of bottlebrush polymer from Table 1, entry 5. The black trace is the raw RI signal obtained via SEC. Red and green traces represent fits of bottlebrush and linear polymer populations, respectively.

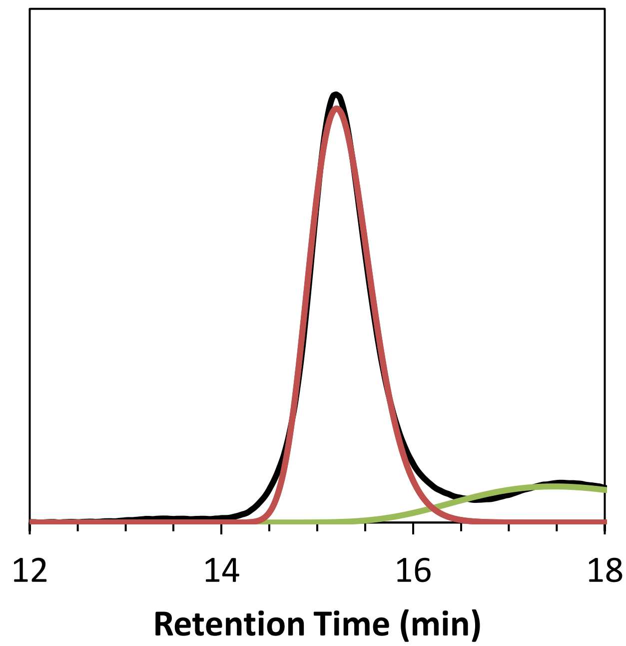

Figure S8: SEC trace and peak fit of bottlebrush polymer from Table 1, entry 6. The black trace is the raw RI signal obtained via SEC. Red and green traces represent fits of bottlebrush and linear polymer populations, respectively.

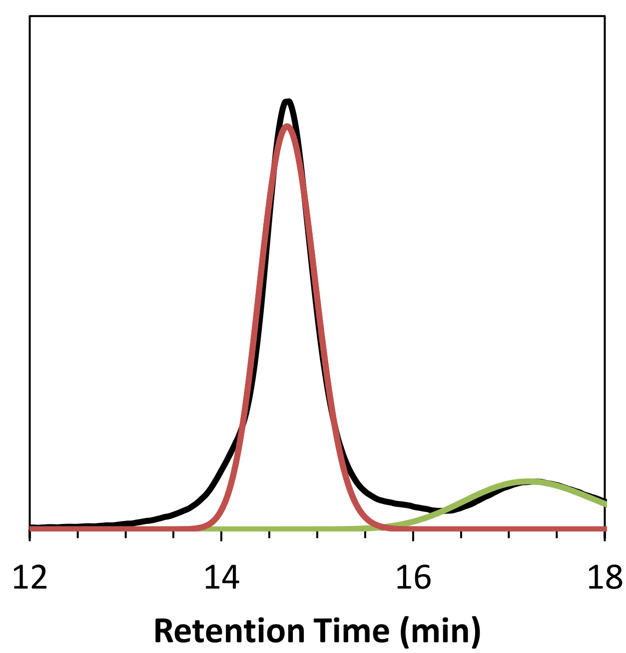

Figure S9: SEC trace and peak fit of bottlebrush polymer from Table 1, entry 7. The black trace is the raw RI signal obtained via SEC. Red and green traces represent fits of bottlebrush and linear polymer populations, respectively.

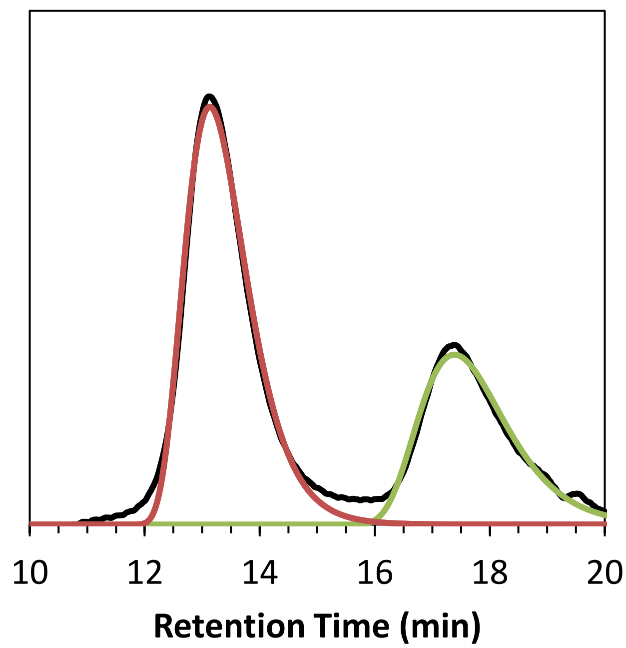

Figure S10: SEC trace and peak fit of bottlebrush polymer from Table 1, entry 8. The black trace is the raw RI signal obtained via SEC. Red and green traces represent fits of bottlebrush and linear polymer populations, respectively.

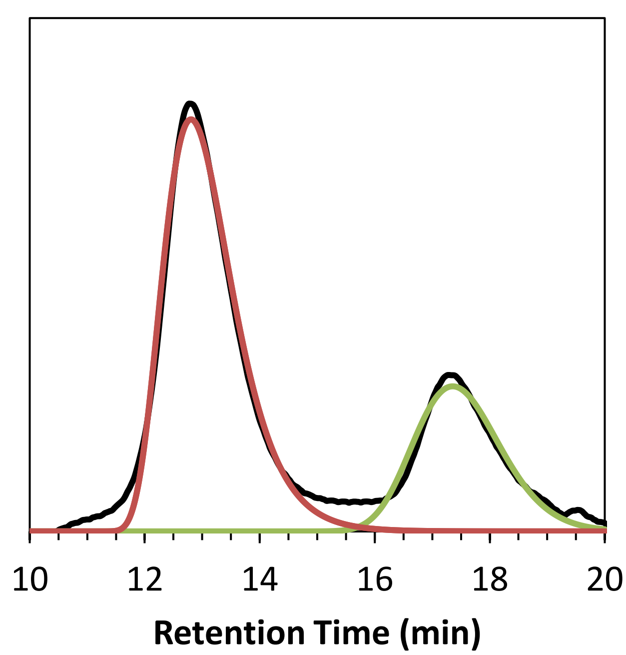

Figure S11: SEC trace and peak fit of bottlebrush polymer from Table 1, entry 9. The black trace is the raw RI signal obtained via SEC. Red and green traces represent fits of bottlebrush and linear polymer populations, respectively.

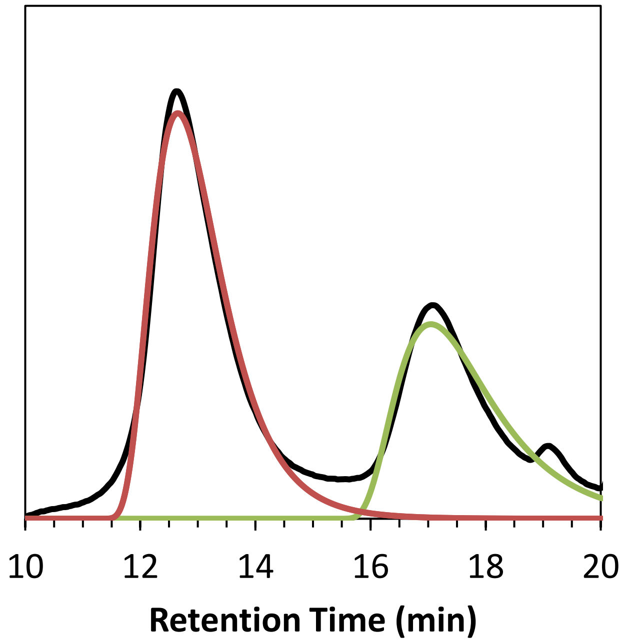

Figure S12: SEC trace and peak fit of bottlebrush polymer from Table 1, entry 10. The black trace is the raw RI signal obtained via SEC. Red and green traces represent fits of bottlebrush and linear polymer populations, respectively.

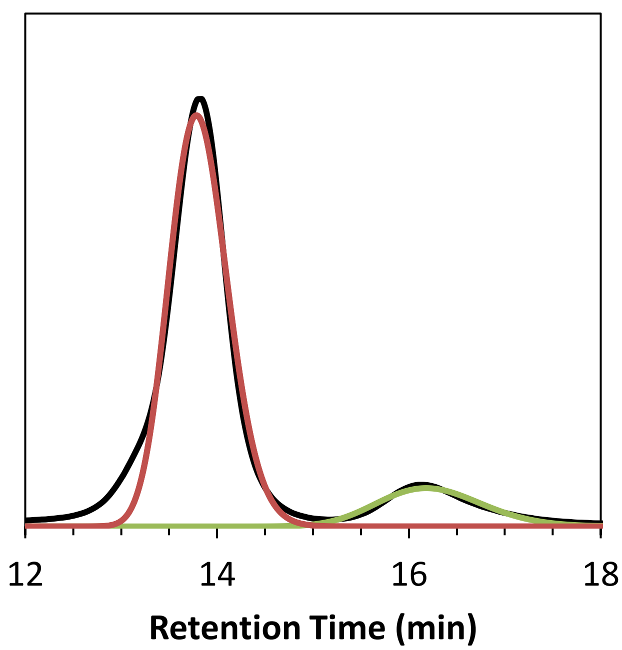

Figure S13: SEC trace and peak fit of bottlebrush polymer from Table 1, entry 11. The black trace is the raw RI signal obtained via SEC. Red and green traces represent fits of bottlebrush and linear polymer populations, respectively.

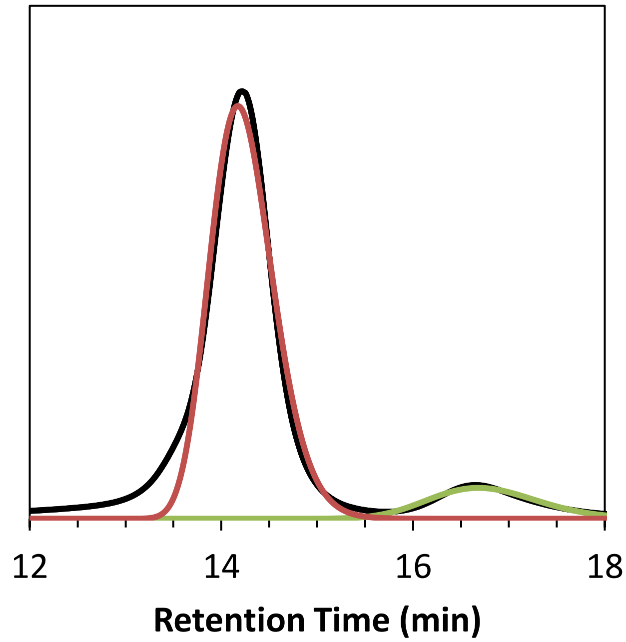

Figure S14: SEC trace and peak fit of bottlebrush polymer from Table 1, entry 12. The black trace is the raw RI signal obtained via SEC. Red and green traces represent fits of bottlebrush and linear polymer populations, respectively.

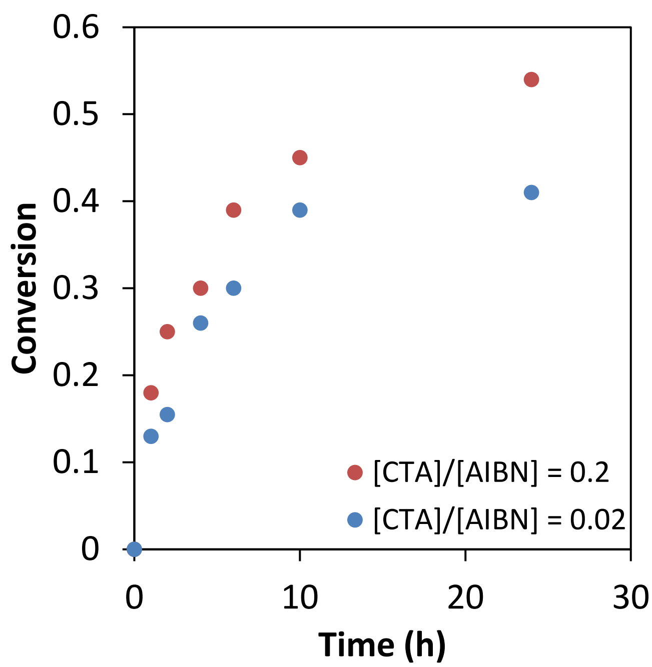

Figure S15. Kinetics of RAFT transfer-to polymerization of styrene with different amounts of radical initiator. Polymerizations were conducted at [M]/[CTA] = 1000 with different equivalents of AIBN relative to CTA.

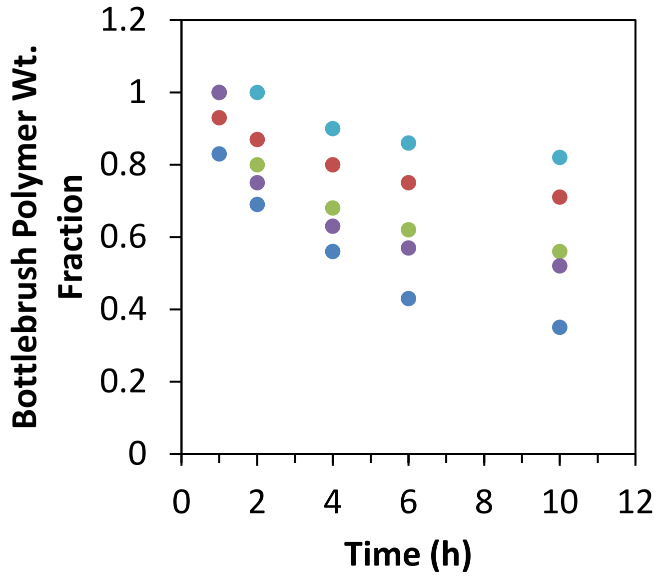

Figure S16. Change in bottlebrush weight fraction over time for polymerizations conducted with [M]/[CTA] = 1000 (dark blue circles), 750 (purple circles), 500 (green circles), 100 (red circles), and 50 (light blue circles).

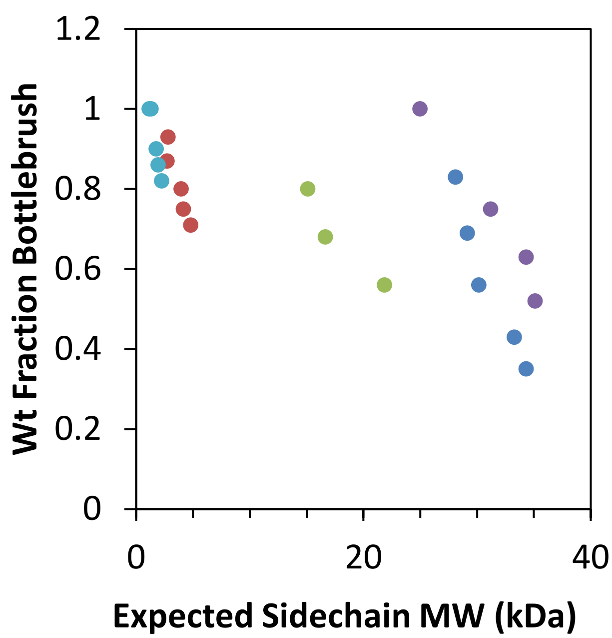

Figure S17. Relationship between expected sidechain molecular weight, calculated using the equation $MW_{sidechains} = conv * \frac{[M]}{[CTA]} * MW_{styrene}$, and the bottlebrush polymer sample composition based on area under the curves of the SEC traces at each time point for polymerizations conducted with [M]/[CTA] = 1000 (dark blue circles), 750 (purple circles), 500 (green circles), 100 (red circles), and 50 (light blue circles).

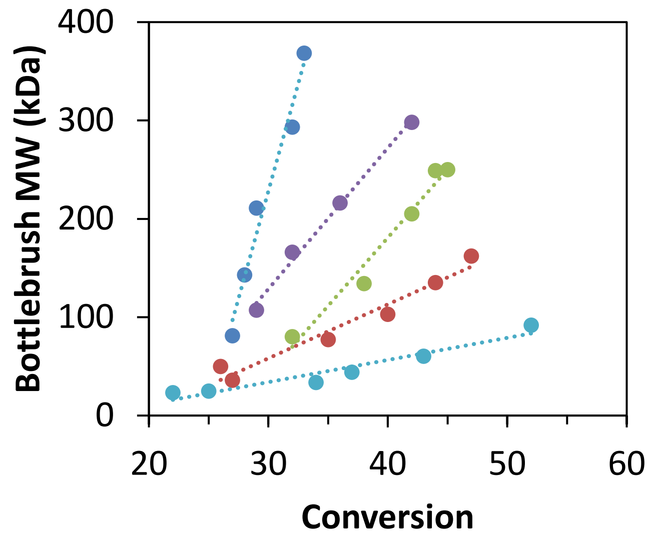

Figure S18. MW vs conversion for polymerizations conducted with conducted with [M]/[CTA] = 1000 (dark blue circles), 750 (purple circles), 500 (green circles), 100 (red circles), and 50 (light blue circles). Linear fit lines have been provided as a visual aid.

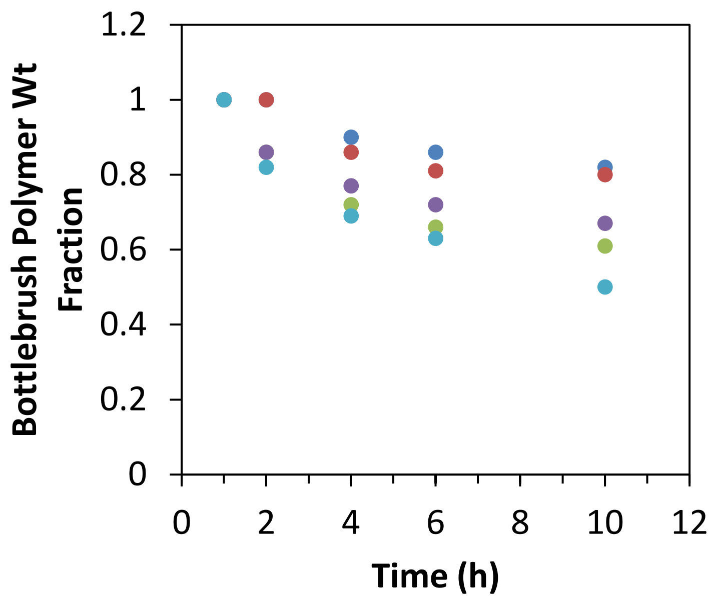

Figure S19. Change in bottlebrush polymer weight fraction over time for polymerizations conducted with PCTA DP = 50 (dark blue circles), 100 (purple circles), 500 (green circles), 750 (red circles), and 1000 (light blue circles).

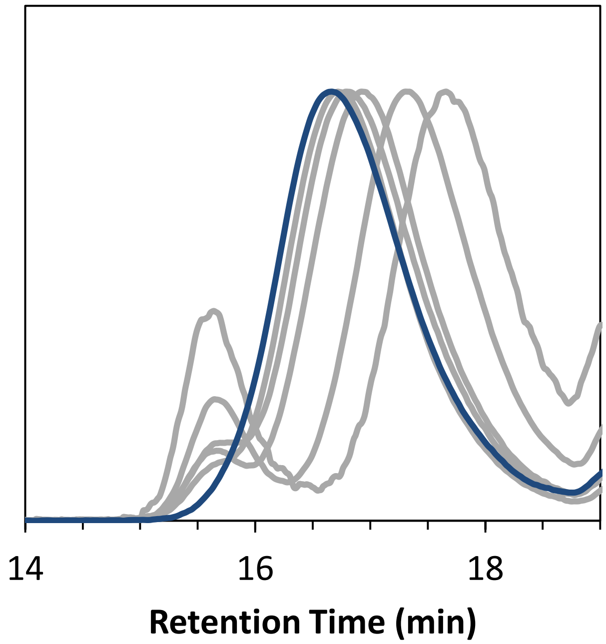

Figure S20. SEC traces of aminolyzied bottlebrush polymers from the polymerization denoted as Table 1, entry 6 at various time points. The final time point for each run (blue lines) was taken after 24 h. Aminolysis experiments were conducted by adding 0.5 mL of a 40 v/v% solution of methylene in H_2O to a solution of ~100 mg of bottlebrush polymer in 1 mL of THF for each time point. These mixtures were stirred for a minimum of 48 h under air to ensure complete oxidation of the ω-chain end thiols before the samples were analyzed by SEC.

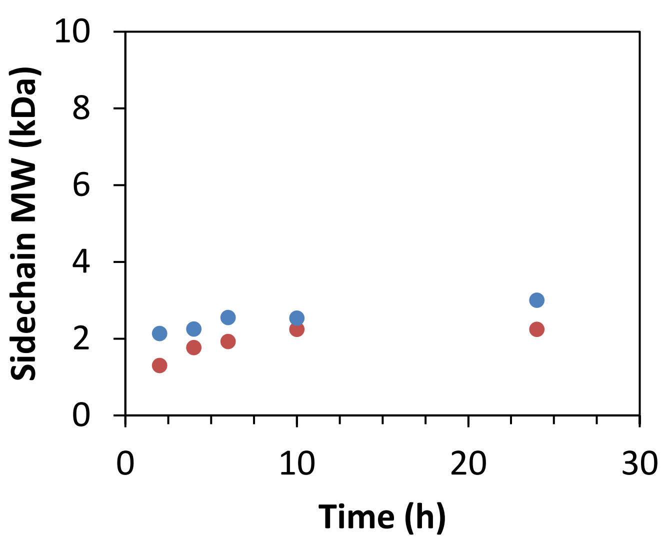

Figure S21. Comparison of bottlebrush polymer sidechain MWs calculated from monomer conversions obtained via ^{1}H NMR spectroscopy (red circles) and measured for cleaved sidechains (blue circles) for the polymerization with [M]/[CTA] = 50 and a backbone DP of 50. Sidechains MWs were calculated using the equation $MW_{sidechains} = conv * \frac{[M]}{[CTA]} * MW_{styrene}$.

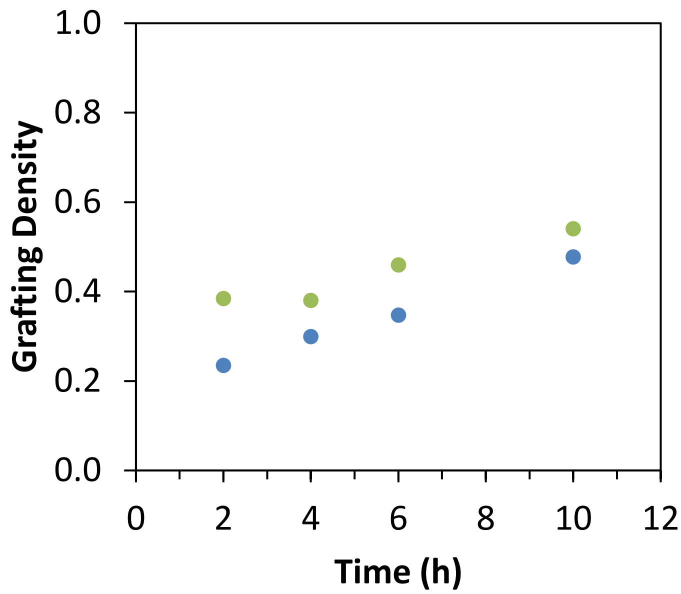

Figure S22. Comparison of bottlebrush polymer grafting density calculated by diving the observed MW of the bottlebrush polymer by sidechain MWs calculated from monomer conversions obtained via ^{1}H NMR spectroscopy (green circles) and measured for cleaved sidechains (blue circles) for the polymerization with [M]/[CTA] = 50 and a backbone DP of 50.