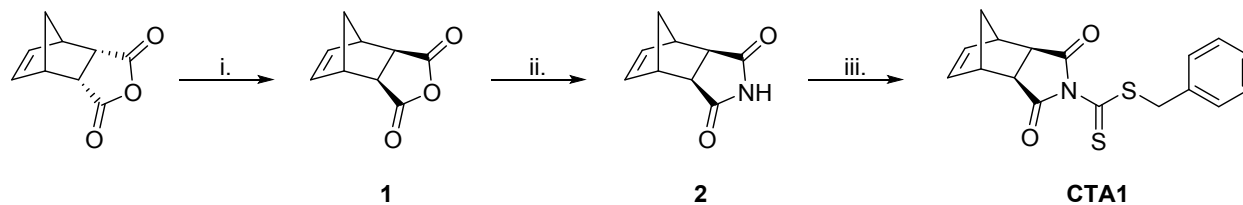


**Synthesis of Bottlebrush Polymers via Transfer-To and Grafting-Through Approaches
Using a RAFT Chain Transfer Agent with a ROMP-Active Z-Group**

Scott C. Radzinski, Jeffrey C. Foster, John B. Matson.*

Department of Chemistry and Macromolecules and Interfaces Institute, Virginia Tech,
Blacksburg, Virginia 24061, United States.

Email: jbmatson@vt.edu



Scheme S1: Synthesis of **CTA1**. Experimental conditions: i. 1,2-dichlorobenzene at reflux; ii. urea, 135 °C; iii. KOH, CS₂, benzyl bromide, rt.

Synthesis of *cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride (1). A round-bottom flask was charged with *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride (200 g). 200 mL 1,2-dichlorobenzene was added, a condenser was attached, and the reaction apparatus was immersed in an oil bath at 185 °C for 2.5 h. Once cool, the flask was further cooled to 0 °C, and the precipitate was recovered by filtration and washed with hexanes. This crude product was recrystallized from benzene three times to yield 50.0 g pure *exo* product (25% yield). ¹H NMR (CDCl₃): δ 1.46 (d, 1H, *J* = 8 Hz), 1.66 (d, 1H, *J* = 8 Hz), 3.00 (s, 2H), 3.45 (s, 2H), 6.33 (s, 2H). ¹³C NMR (CDCl₃): δ 171.69, 138.09, 48.90, 47.02, 44.26. HRMS: calculated 165.0552, found 165.0536 [M+H]⁺.

Synthesis of *exo*-norbornene imide (2). A 100 mL round bottom flask was charged with (1) (4.02 g, 24.5 mmol) and urea (1.61 g, 26.8 mmol). The flask was fitted with a condenser. The reaction was conducted in the melt at 140 °C for 30 min. The reaction mixture was allowed to cool to rt. The crude product was purified by recrystallization from H₂O. The resulting white crystals were recovered via vacuum filtration and were dried under vacuum overnight to yield 2.84 g of pure product (71% yield). ¹H NMR (CDCl₃): δ 1.43 (d, 1H, *J* = 8 Hz), 1.51 (d, 1H, *J* = 8 Hz), 2.69 (s, 2H), 3.24 (s, 2H), 6.24 (s, 2H), 9.20 (bs, 1H). ¹³C NMR (CDCl₃): δ 178.98, 137.80, 49.26, 45.16, 42.95. HRMS: calculated 162.0555, found 162.0546 [M-H]⁻.

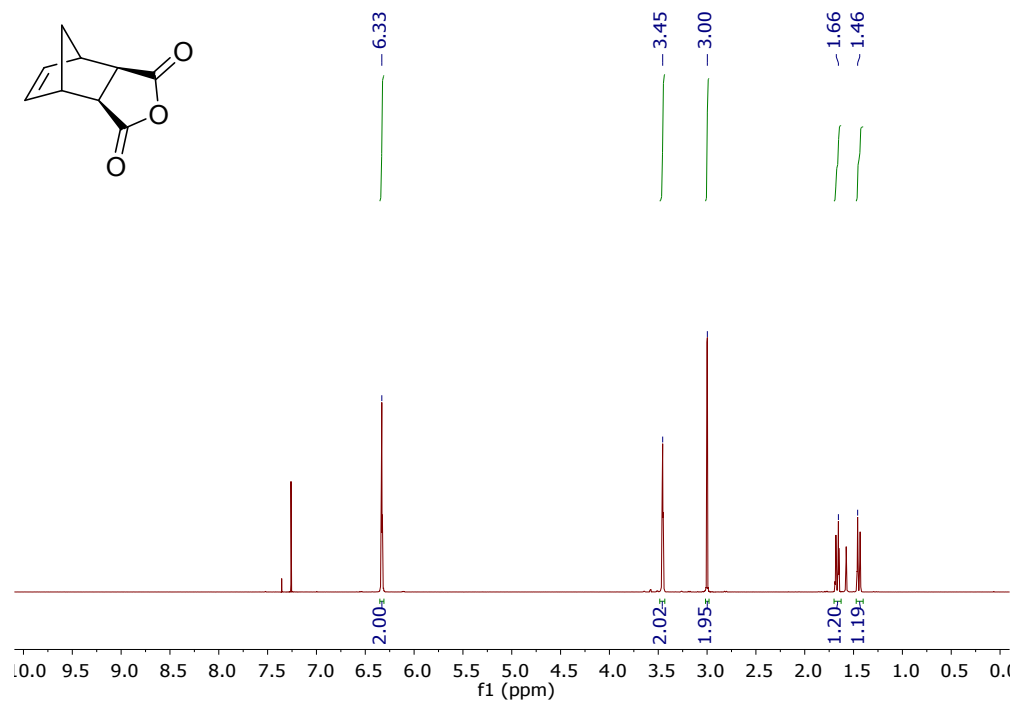


Figure S1: ¹H NMR of (1)

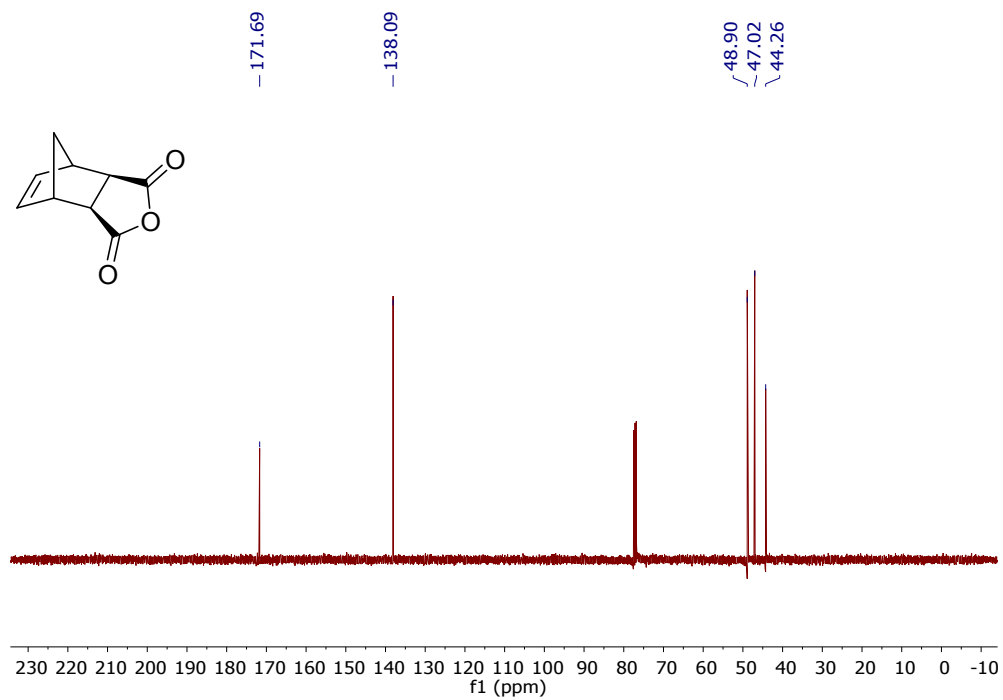


Figure S2: ¹³C NMR of (1)

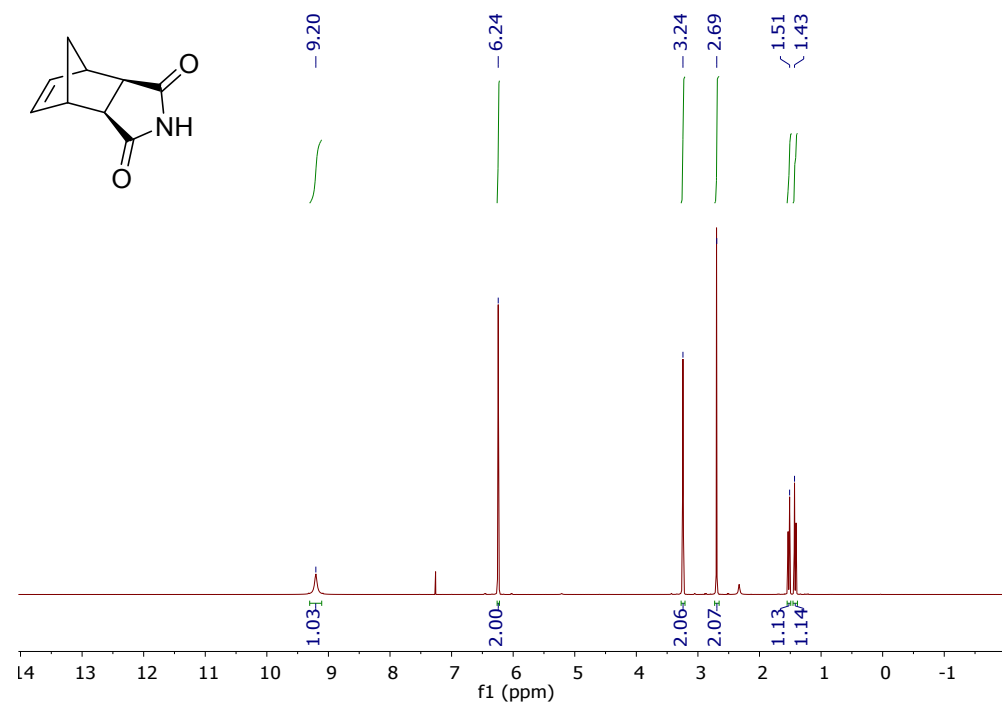


Figure S3: ¹H NMR of (2)

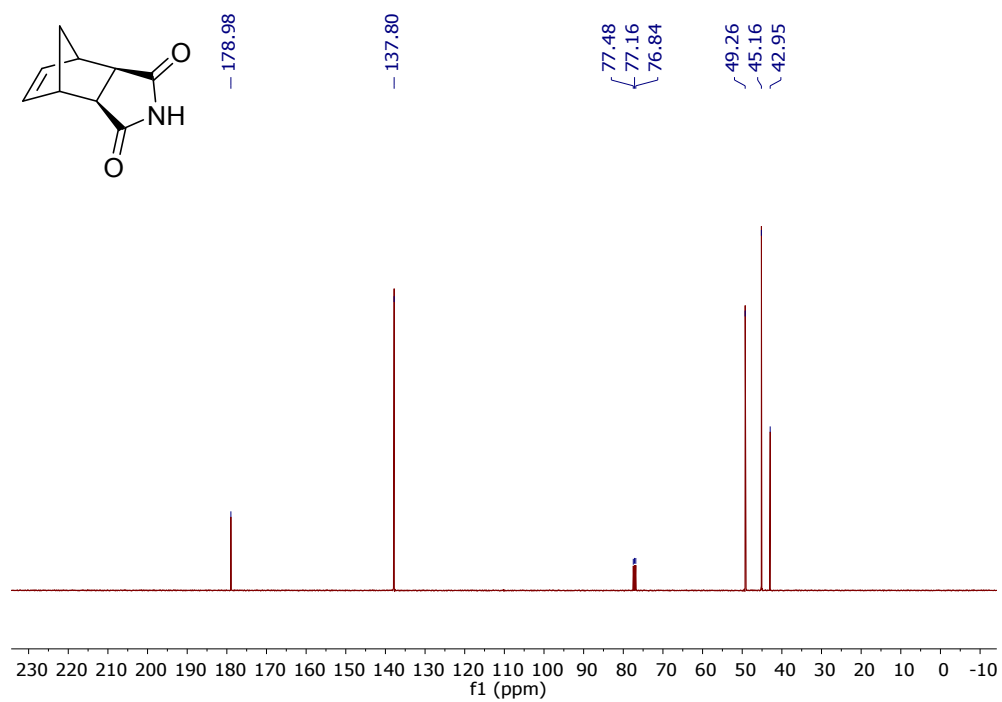


Figure S4: ¹³C NMR of (2)

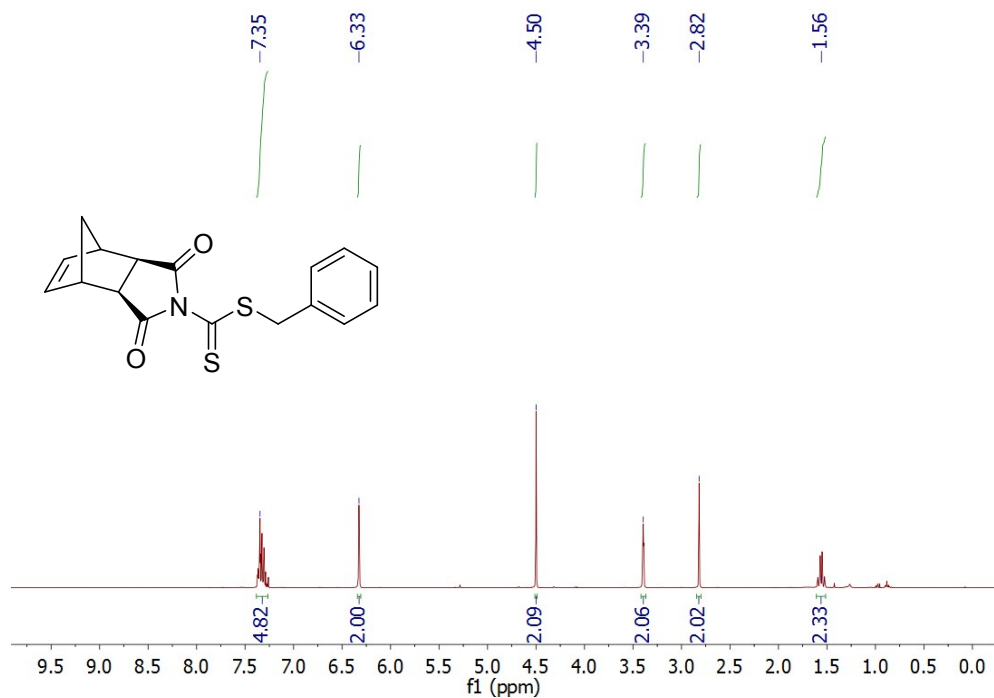


Figure S5: ^1H NMR of CTA1

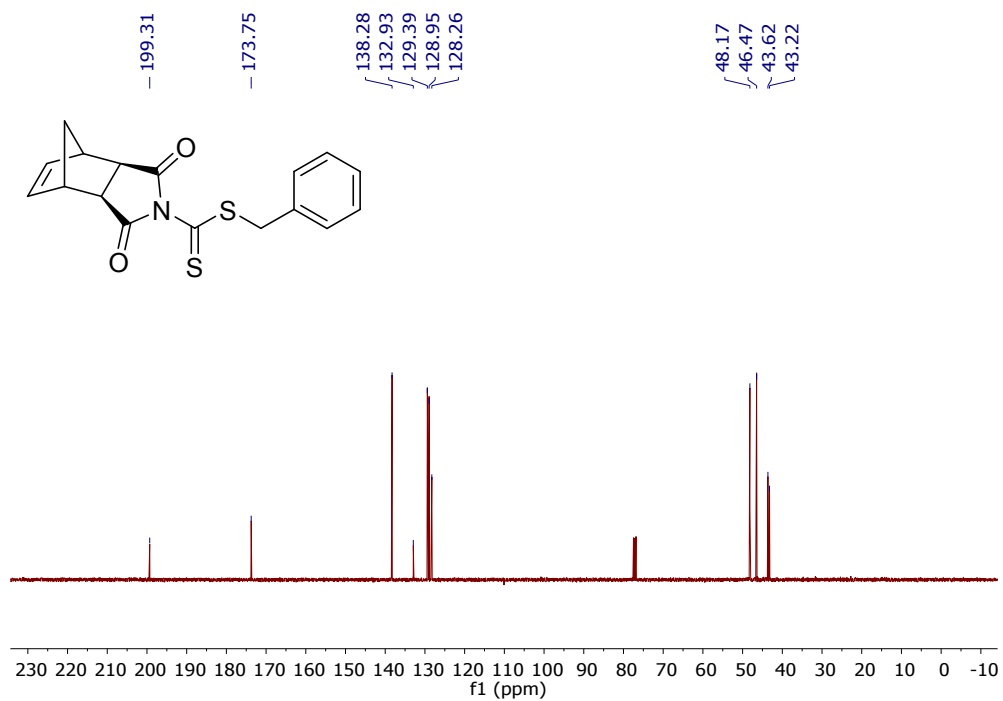


Figure S6: ^{13}C NMR of CTA1

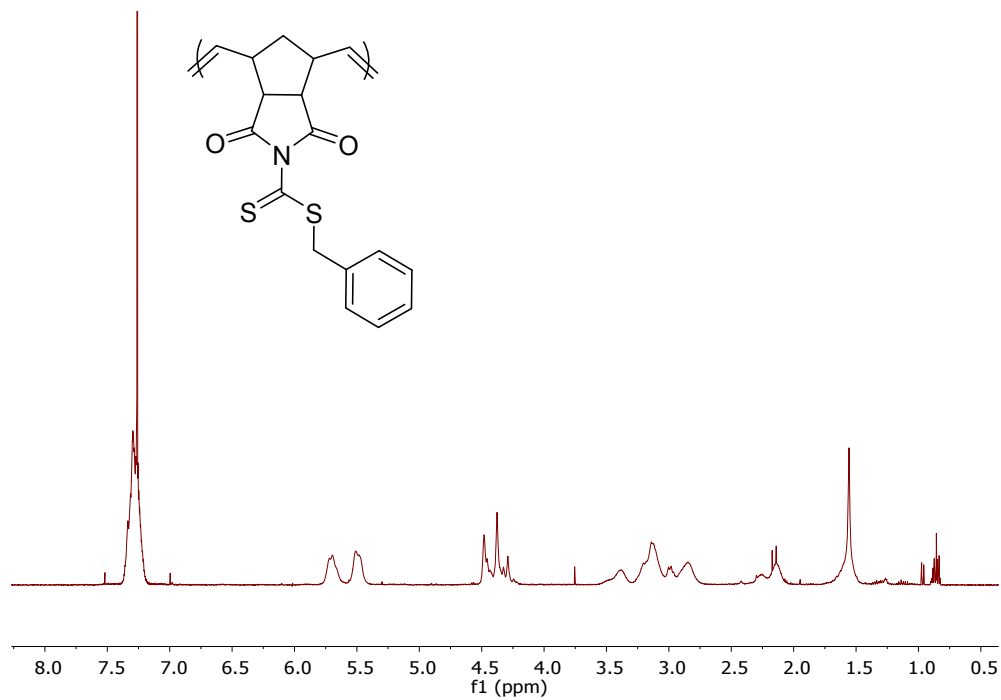


Figure S7: ¹H NMR of poly(CTA1)

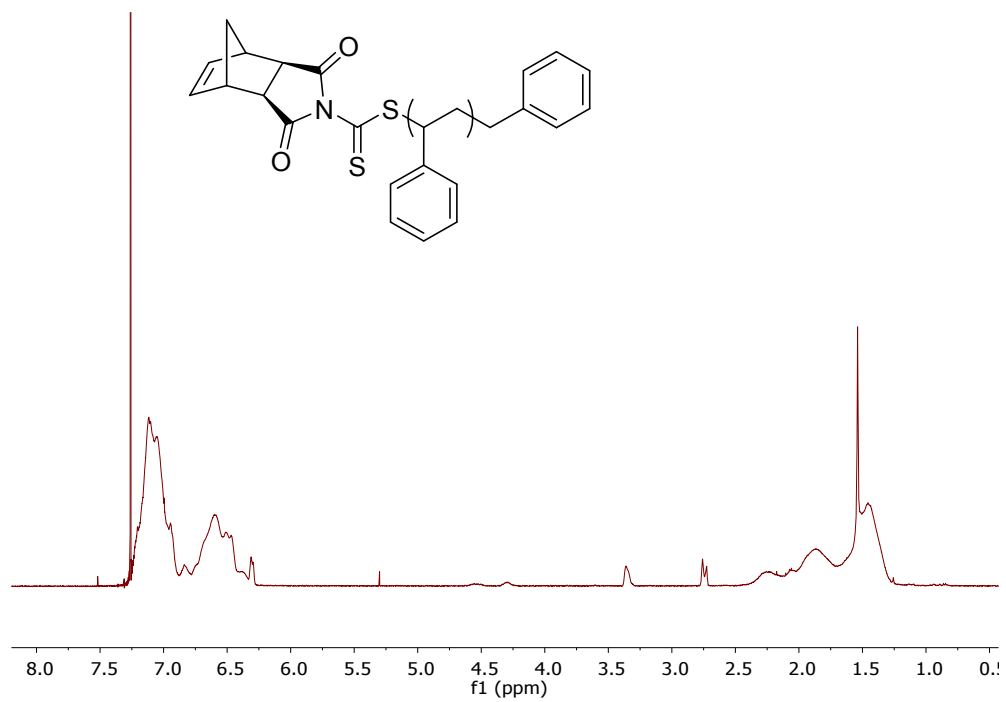


Figure S8: ¹H NMR of MM₂₉

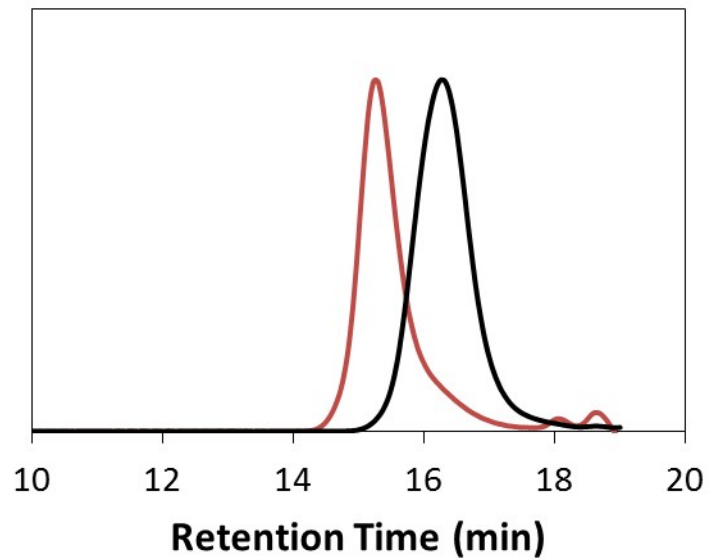


Figure S9: SEC traces of the RAFT chain extension with a PnBA Macro CTA (black line) with styrene to form a diblock copolymer (red line).

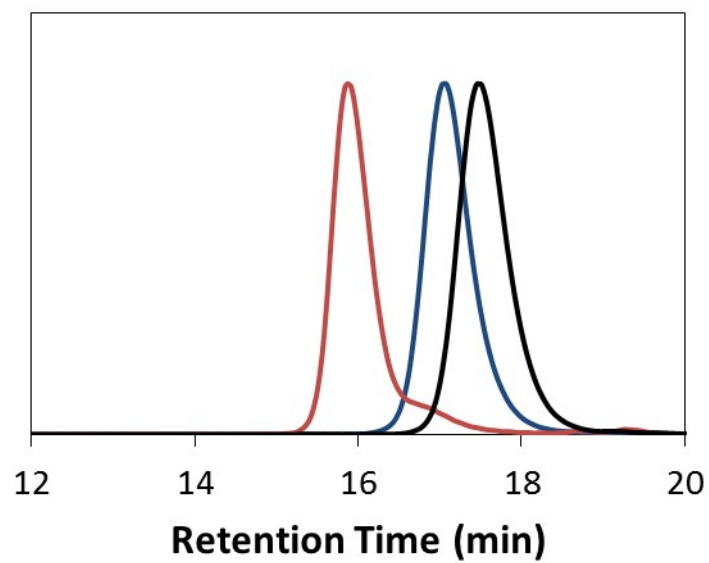


Figure S10: SEC traces of MM_{29} (black line), MM_{52} (blue line), and MM_{113} (red line).

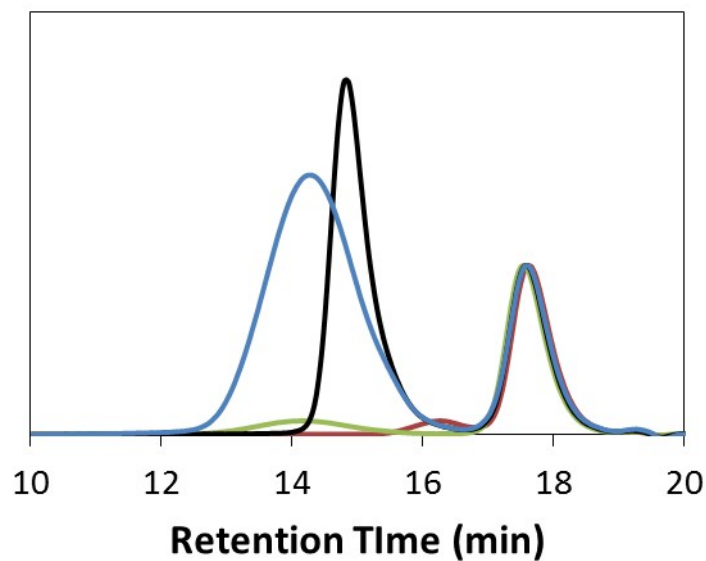


Figure S11: SEC traces of bottlebrush polymers prepared via grafting-through from MM_{29} using **G1** (red line), **G2** (green line), **G3** (black line), and **HG2** (blue line). Traces normalized to macromonomer peak height.

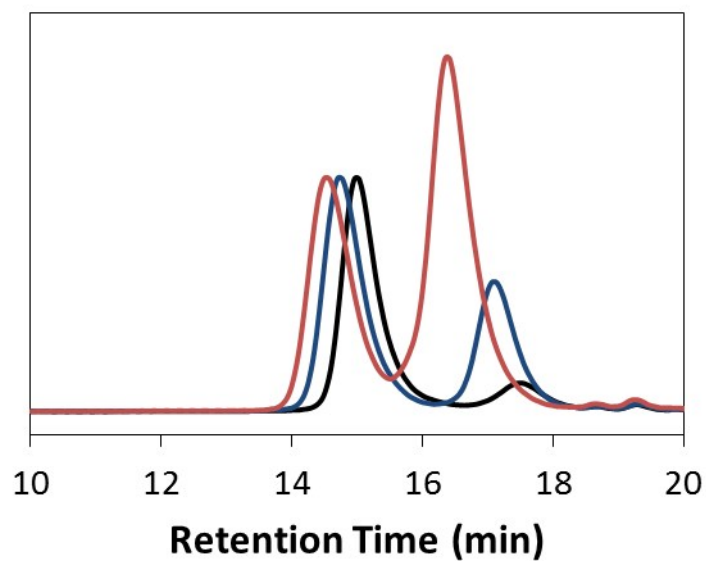


Figure S12: SEC traces of bottlebrush polymers prepared via grafting-through from MM_{29} (black line), MM_{52} (blue line), and MM_{113} (red line) using **G3**. Traces normalized to bottlebrush polymer peak height.

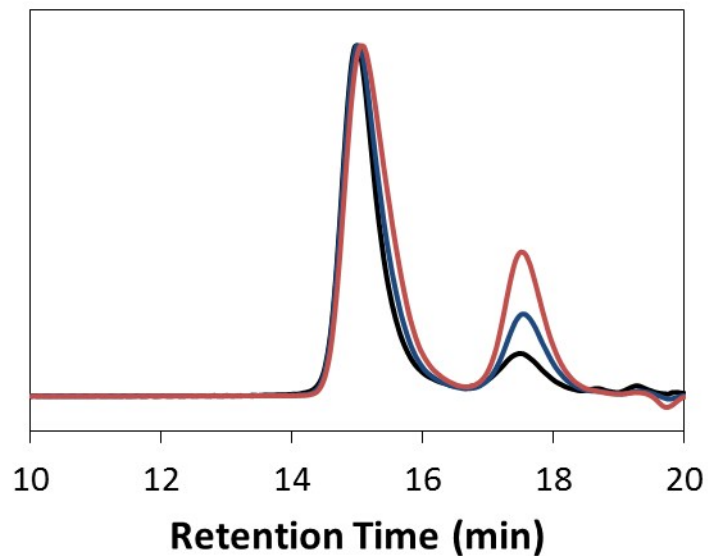


Figure S13: SEC traces of bottlebrush polymers prepared via grafting-through from MM_{29} at 100 mg/ml (black line), 50 mg/ml (blue line), and 25 mg/ml (red line). Traces normalized to bottlebrush polymer peak height.

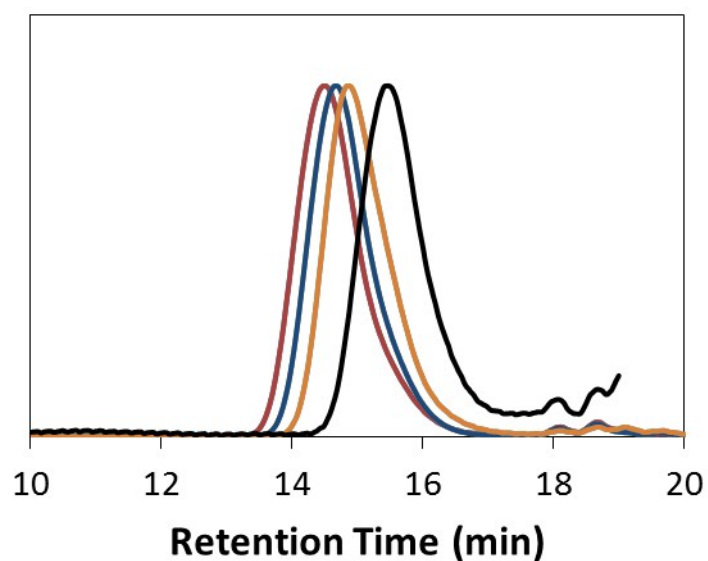


Figure S14: SEC traces of side chains aminolyzed from bottlebrush polymers prepared by transfer-to after 19 h (black line), 42 h (orange line), 67 h (blue line), and 91 h (red line).

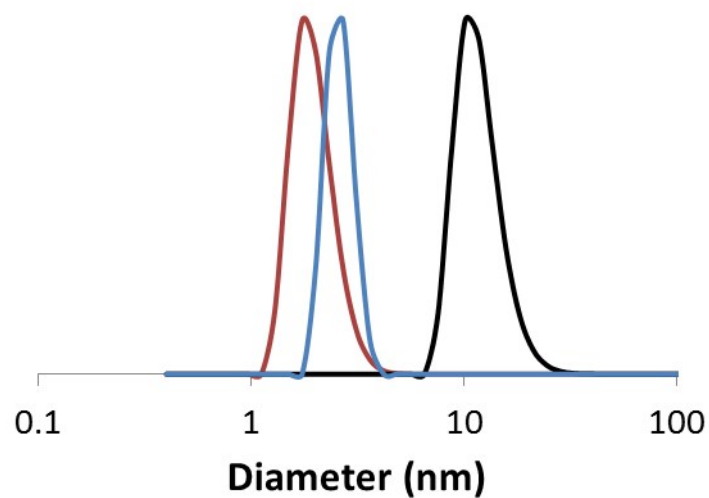


Figure S15: DLS traces of **MM₂₉** (red line), BB from **MM₂₉** (black line), and aminolysis product from the BB (blue line).

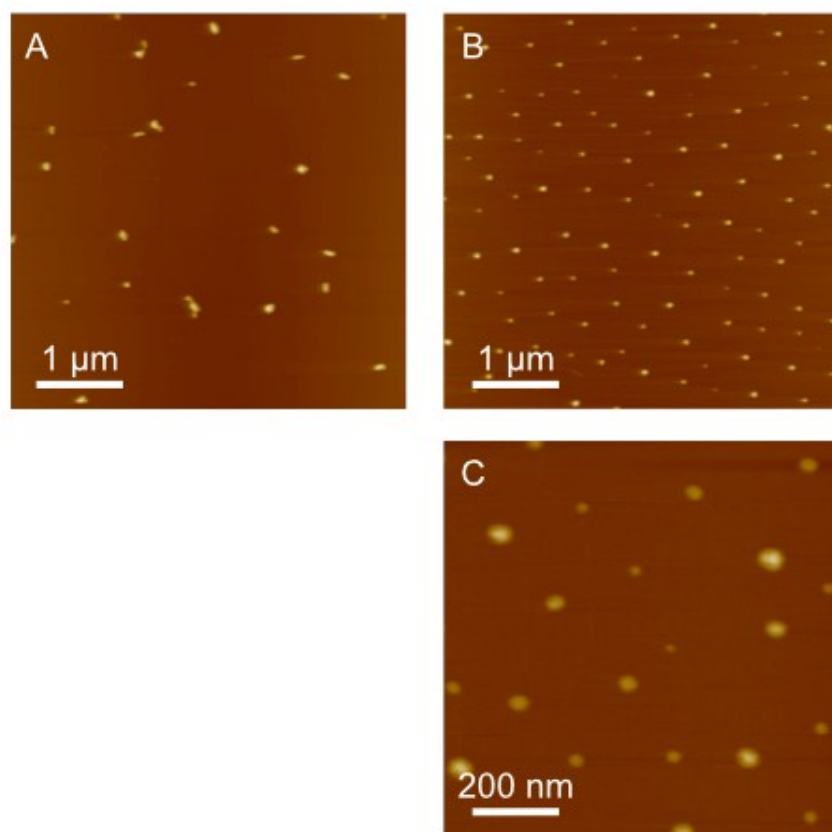


Figure S16: AFM height images of BB prepared from (A) transfer-to using **poly(CTA1)**, (B) and (C) grafting-through using **MM₂₉** (Table 2 entry 5).