Synthesis of molecular brushes by telomerization

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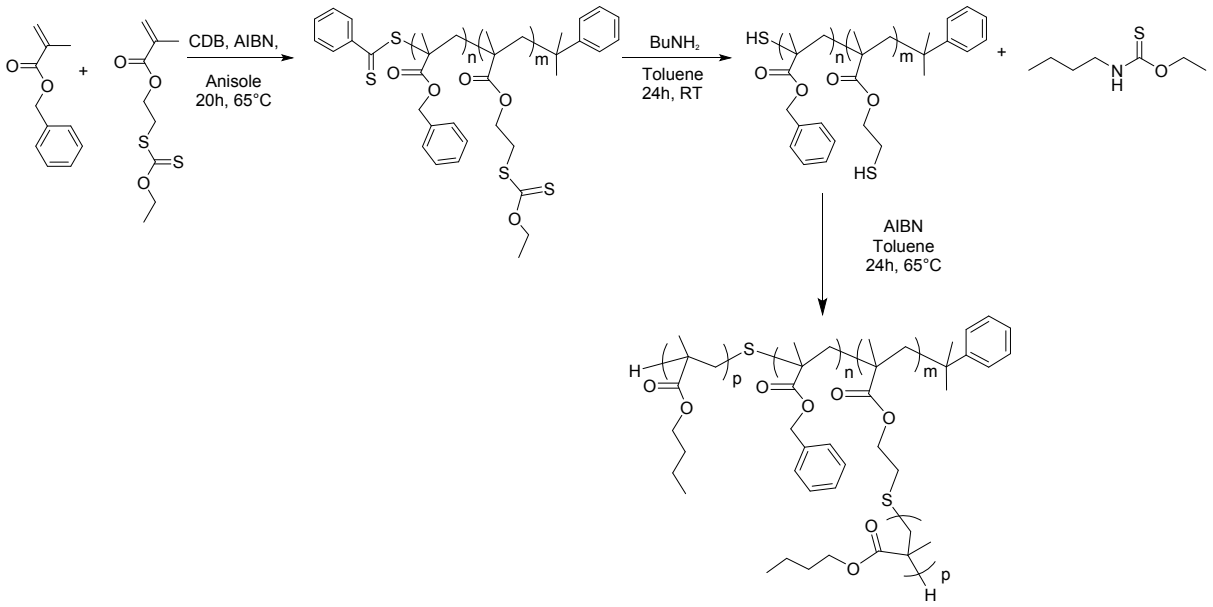
Supporting Information



Scheme S1 : Synthesis of PBMA brushes by telomerization via a two-pot two-step aminolysis and side-chain growth sequence

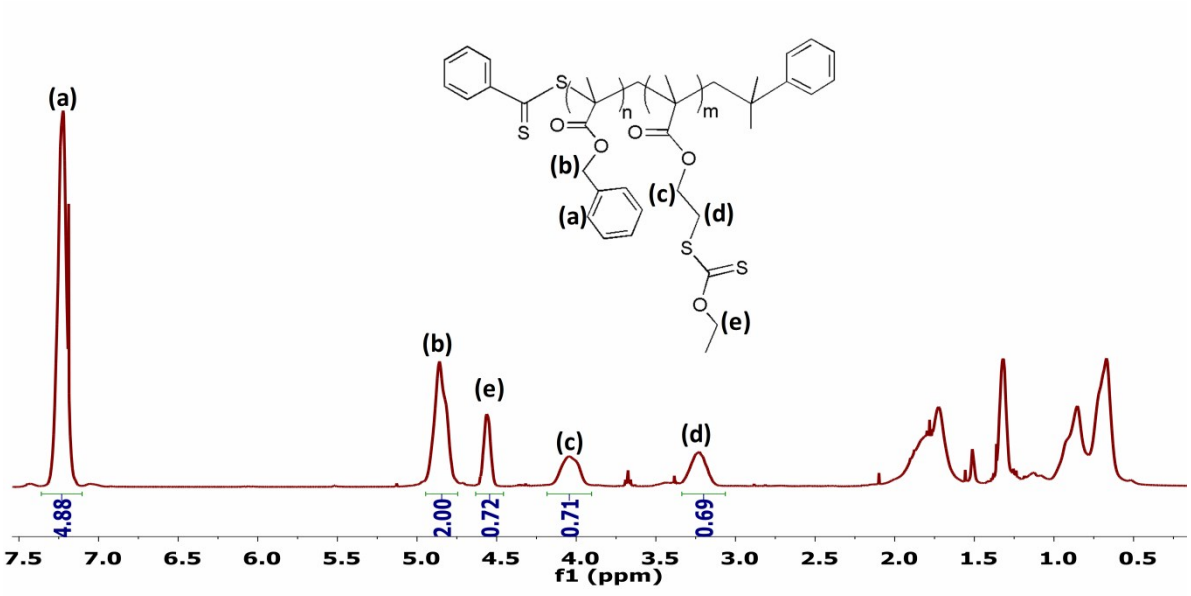


Figure S1: ^{1}H NMR spectrum of polymer **P1**. Experimental conditions: $[BenzMA]_0/[XEMA]_0/[CDB]_0/[AIBN]_0$ = 2.3/1/0.02/0.002 in anisole 40 vol%, 20 h at 65 °C

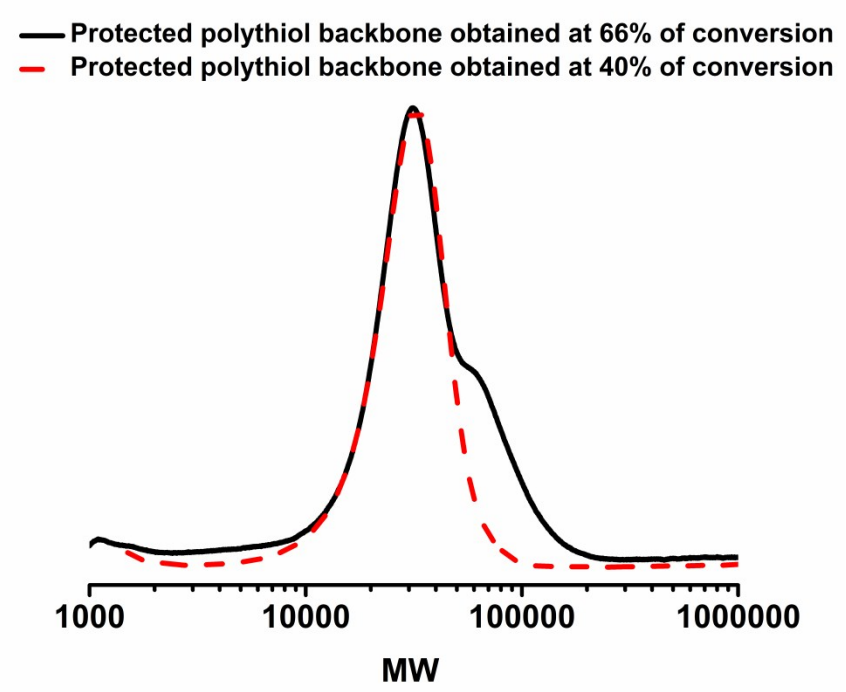


Figure S2: SEC traces of protected polythiol backbones. Black solid line experimental conditions: $[BenzMA]_0/[XEMA]_0/[CDB]_0/[AIBN]_0$ = 2.3/1/0.02/0.002 in anisole 40 vol%, 20 h at 65 °C; monomer conversion = 66%. Red dashed line experimental conditions: $[BenzMA]_0/[XEMA]_0/[CDB]_0/[AIBN]_0$ = 2.3/1/0.013/0.0013 in anisole 40 vol%, 20 h at 65 °C ; monomer conversion = 40%.

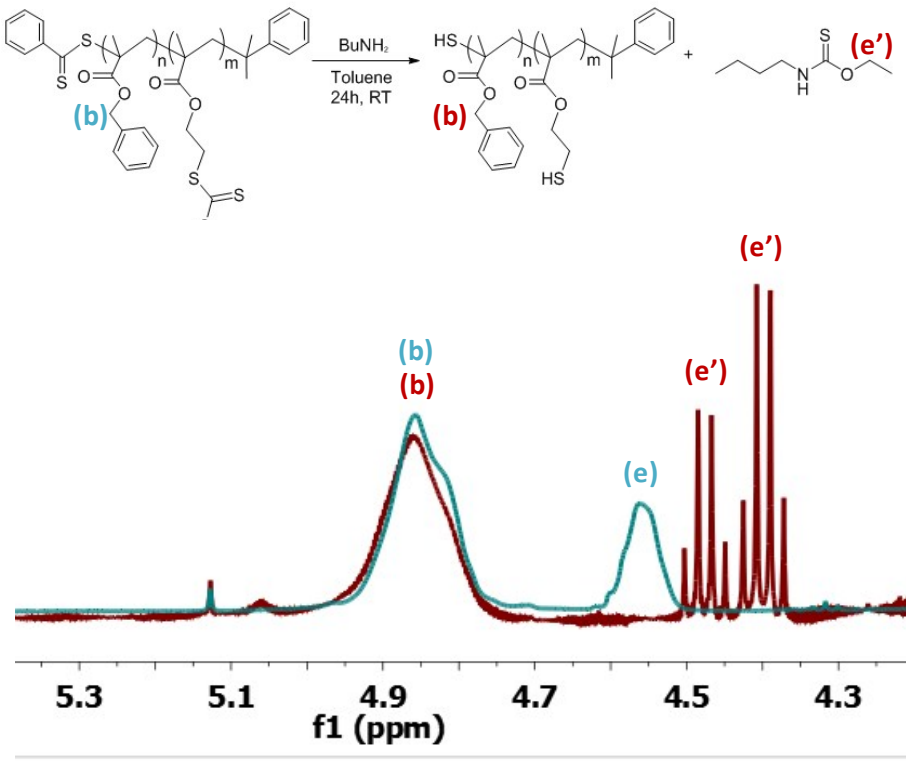


Figure S3: ^{1}H NMR spectra before (blue) and after (red) polythiol deprotection

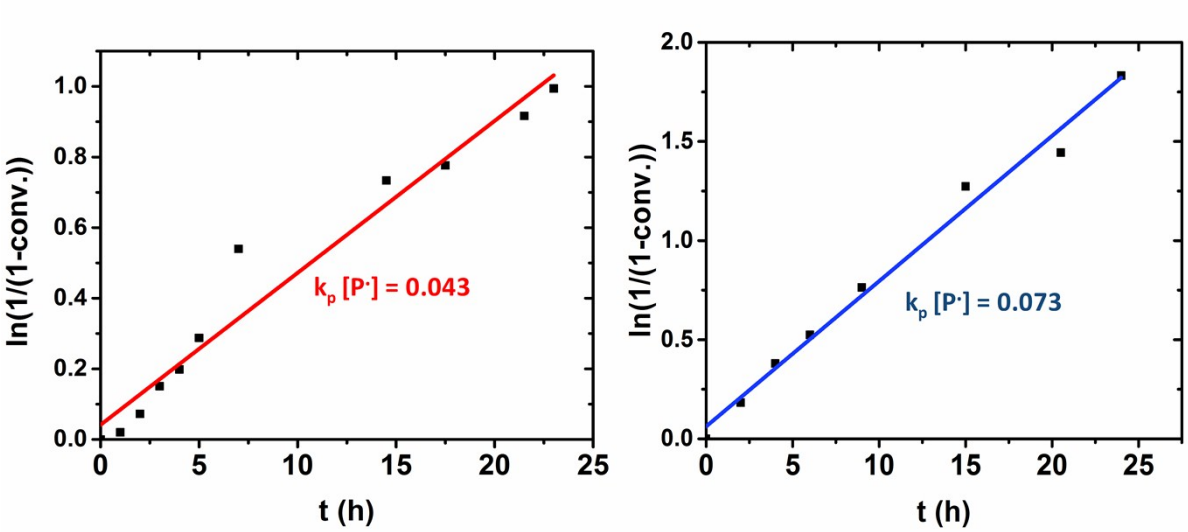
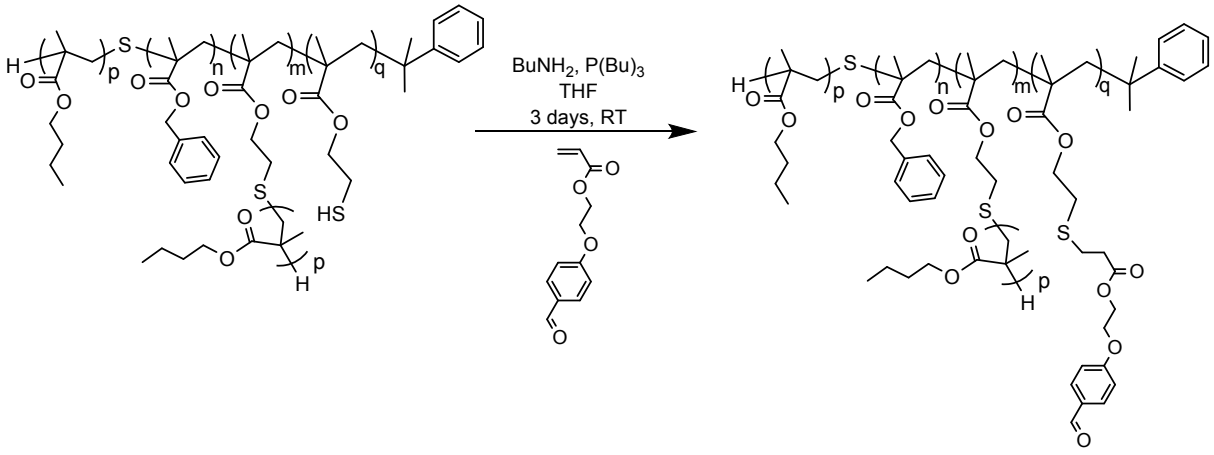


Figure S4: Kinetic plot for (a) **P5** polymerization in 50 % toluene solution at 65 °C with a ratio of $[BMA]_0/[SH]_0/[AIBN]_0$ = 60/1/0.01 and (b) **P7** polymerization in 50 % toluene solution at 65 °C with a ratio of $[BMA]_0/[SH]_0/[AIBN]_0$ = 40/1/0.01



Scheme S2: General procedure for thiol titration on bottlebrush polymers

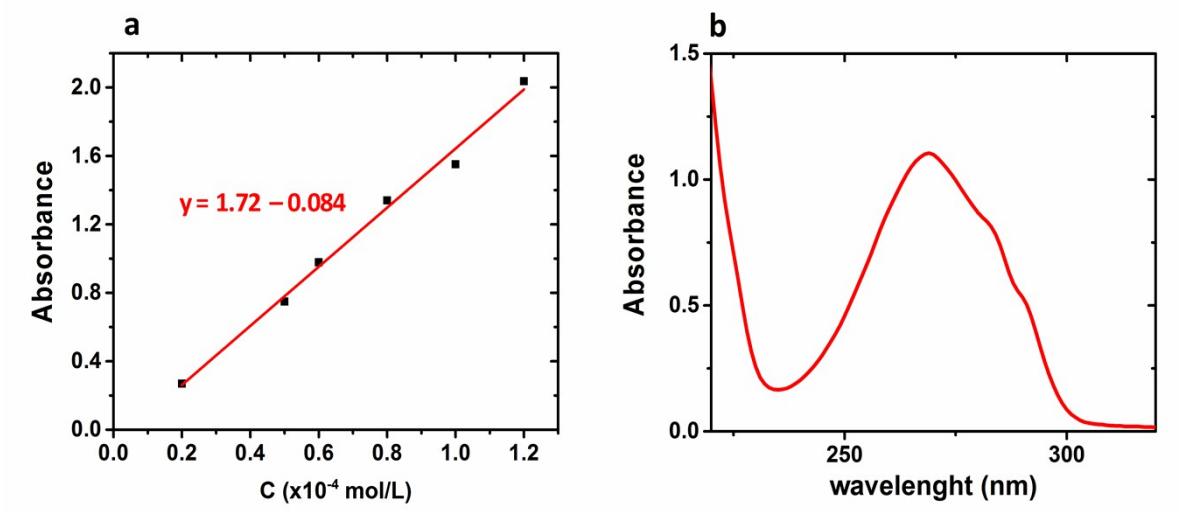


Figure S5: (a) Calibration curve of 4-(2-acryloxyethoxy)benzaldehyde at 270 nm – ε = 17 200 $M^{-1}.cm^{-1}$ (b) UV spectrum of polythiol **P1** after deprotection and functionalization with 4-(2-acryloxyethoxy)benzaldehyde.

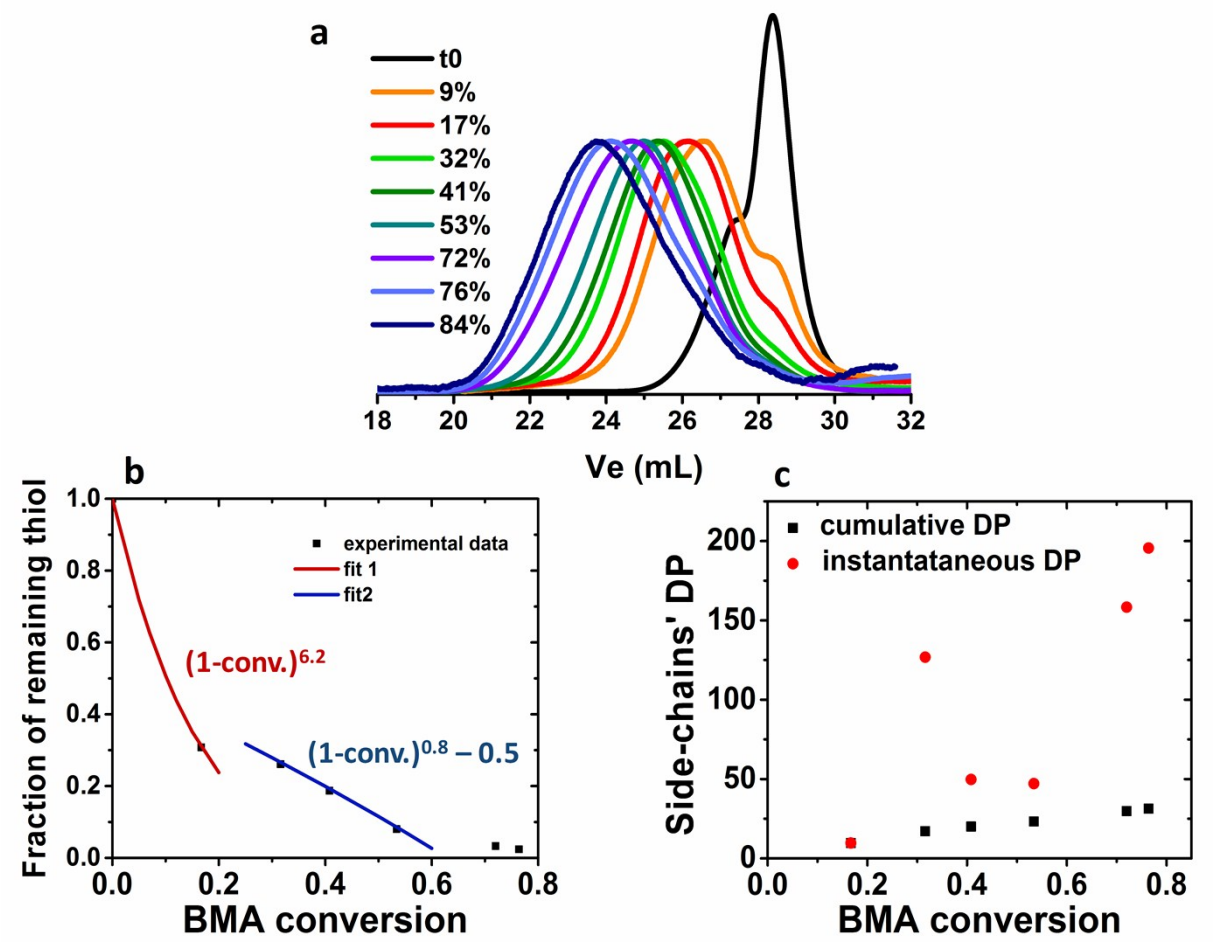


Figure S6: (a) Evolution of SEC traces of the crude reaction medium during the synthesis of brush **P7**. Polymerization conditions: $[BMA]_0/[SH]_0/[AIBN]_0$ = 40/1/0.01 in toluene 50 vol%, 24 h at 65 °C. (b) Plot of the remaining fraction of thiol vs BMA conversion during the synthesis of brush **P7** (c) Plot of side-chains cumulated DP (black squares) $([M]_0\text{-}[M]_t)/([S]_0\text{-}[S]_t)$ and instantaneous DP (red circles) $([M]_{t\text{-}1}\text{-}[M]_t)/([S]_{t\text{-}1}\text{-}[S]_t)$ vs BMA conversion during the synthesis of brush **P7**.

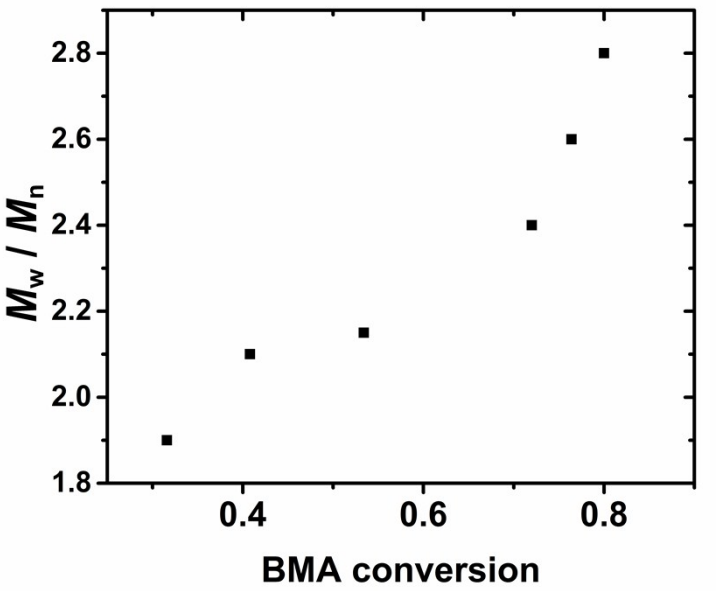


Figure S7: Plot of M_w/M_n vs conversion during brush **P7** polymerization. Polymerization conditions: $[BMA]_0/[SH]_0/[AIBN]_0$ = 40/1/0.01 in toluene 50 vol%, 24 h at 65 °C.

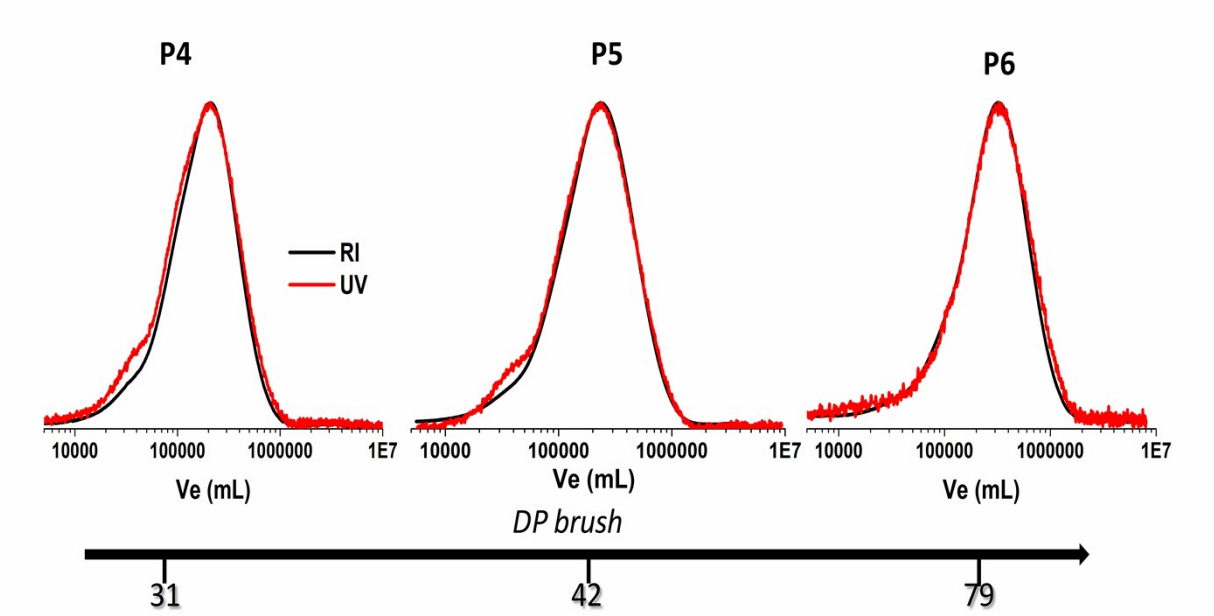


Figure S8: SEC traces of the crude reaction media at the end of the syntheses of brushes with different side-chain lengths.

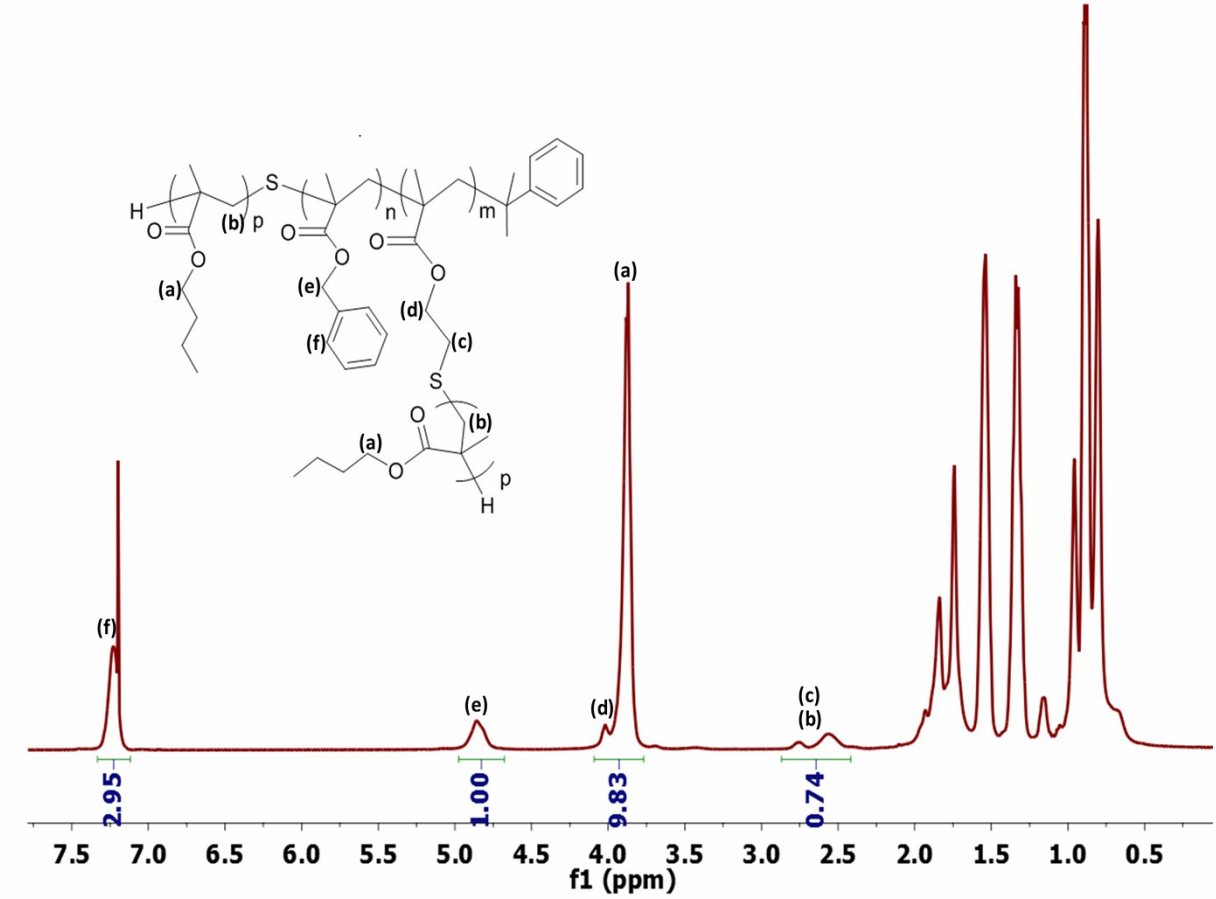


Figure S9: ^{1}H NMR spectrum of bottlebrush polymer **P4.** Polymerization conditions: $[BMA]_0/[SH]_0/[AIBN]_0$ = 40/1/0.01 in toluene 50 vol%, 24 h at 65 °C.

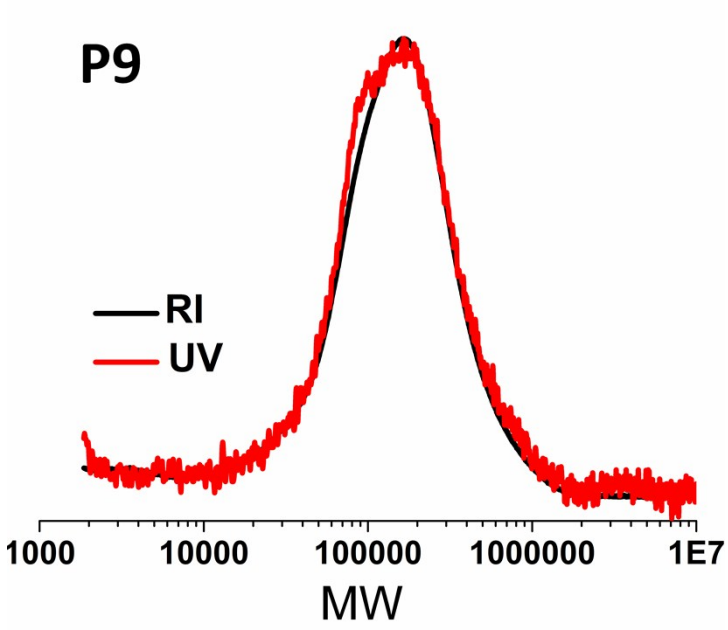


Figure S10: SEC traces of brush **P9** synthesized via a two-step process. Experimental conditions: $[NIPAM]_0/[SH]_0/[AIBN]_0$ = 40/1/0.01 in DMF 50 vol%, 1 h30 at 65 °C. SEC traces of the crude reaction medium.