Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

Desulfurization-bromination: direct chain-end modification of RAFT polymers

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Materials

Unless otherwise noted, all reagents were purchased from commercial sources and used without further purification. Radical inhibitors were removed from all monomers before use by running them through a basic aluminum oxide plug. All reactions were sparged with argon unless otherwise noted. Polystyrene-chain transfer agent (PS-CTA) and polystyrene-thiol (PS-SH) were prepared by previously reported RAFT and aminolysis procedures.[39] Polystyrene-*block*-poly(*tert*-butyl acrylate) (PS-*b*-P*t*BA) was synthesized by a Cu-catalyzed azide-alkyne "Click" reaction according to a previously reported procedure.[49] Poly(*N*,*N*-dimethylacrylamide)-*block*-polystyrene chain transfer agent (PDMA-*b*-PS-CTA) was prepared by a previously reported RAFT procedure.[53]

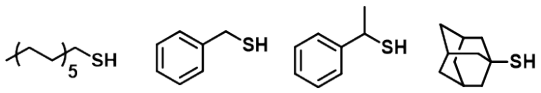
General analytical information

Nuclear magnetic resonance spectra were recorded on a Varian 600 MHz instrument. All ^{1}H NMR experiments are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm) in the deuterated solvent. All ^{13}C NMR spectra are reported in ppm relative to deuterochloroform (77.23 ppm), and all were obtained with ^{1}H decoupling. Size exclusion chromatography (SEC) was performed at ambient temperature using chloroform with 0.25% triethylamine as the mobile phase in a Waters 2695 separation module with a Waters 2414 refractive index detector. Number average molecular weights (M_n) and weight average molecular weights (M_w) were calculated relative to linear polystyrene standards. Dispersity (*Đ*) values are reported as the quotient of M_w/M_n.

Representative procedure for desulfurization-halogenation and disulfide bond formation of small molecule thiols

PPh_3X_2 (X = Br, Cl, and I; 0.5 mmol) was placed in a scintillation vial equipped with a magnetic stir bar. To the vial was added a small molecule thiol derivative (0.1 mmol) and DCM (1 or 2 ml). The mixture was bubbled with argon and stirred at room temperature overnight. For the desulfurization-halogenation of 1-adamantanethiol, TEA (0.5 mmol) was additionally added and the reaction mixture stirred at 40 °C for 10 hours to achieve full conversion of 1-adamantanethiol.

Small molecule thiols investigated:



Procedure for desulfurization-bromination of polystyrene-thiol (PS-SH)

PS-SH (0.01 mmol) and triphenylphosphine (5 mg, 0.02 mmol) were placed in a scintillation vial equipped with a magnetic stir bar. To the vial, degassed DCM (0.5 ml) and Br_2 (5 μl, 0.1 mmol) were added and allowed to stir at room temperature for 2 hours. Following the reaction, the crude reaction mixture was purified by precipitation into MeOH. The resulting white solid was filtered, redissolved in DCM and reprecipitated into MeOH.

Procedure for one-step transformation of polystyrene-chain transfer agent (PS-CTA) to polystyrene-bromide (PS-Br) using PPh_3Br_2 and NBS

PS-CTA (0.01 mmol), triphenylphosphine dibromide (8.4 mg, 0.02 mmol), and *N*-bromosuccinimide (5.3 mg, 0.03 mmol) were placed in a scintillation vial equipped with a magnetic stir bar. To the flask, degassed DCM (0.5 ml) was added and the mixture was allowed to stir at room temperature for 1 hour. Following the reaction, the crude reaction mixture was purified by the precipitation into MeOH. The resulting white solid was filtered, redissolved in DCM and reprecipitated into MeOH.

Procedure for one-step transformation of polystyrene-chain transfer agent (PS-CTA) to polystyrene-bromide (PS-Br) using Br_2

PS-CTA (0.01 mmol) was added to a scintillation vial equipped with a magnetic stir bar and dissolved in DCM (0.5 ml) before bubbling with argon for five minutes. To the vial, Br_2 (3 µl, 0.06 mmol) was added and stirred at room temperature for 3 hours. Following the reaction, the crude reaction mixture was purified by precipitation into MeOH. The resulting white solid was filtered, redissolved in DCM and reprecipitated into MeOH.

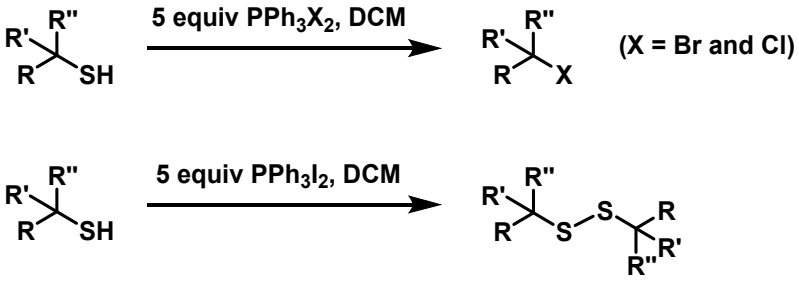


Figure S1. Schematic representation for the desulfurization-halogenation and disulfide bond formation of small molecule thiols

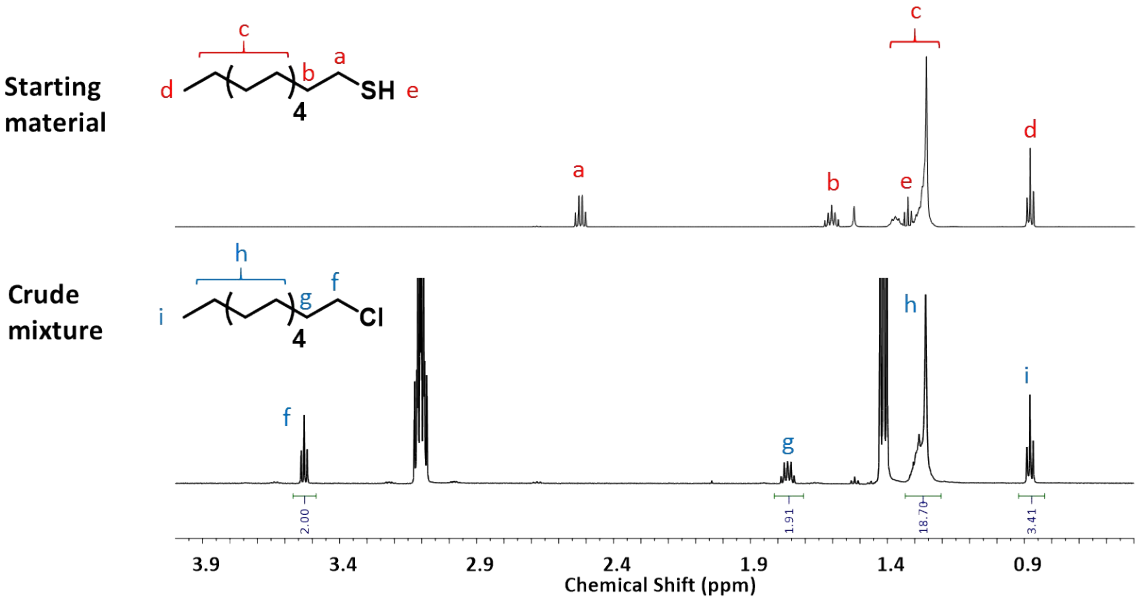


Figure S2. ^{1}H NMR confirming the desulfurization-chlorination of 1-dodecanethiol (Table 1, entry 1). ^{1}H NMR resonances match with literature values of 1-chlorododecane.[45]

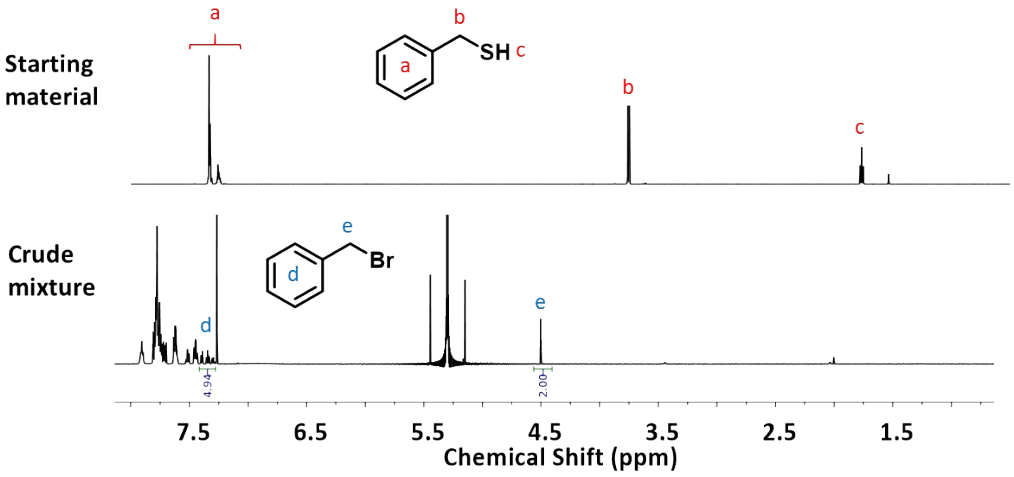


Figure S3. ^{1}H NMR confirming the desulfurization-bromination of benzyl mercaptan (Table 1, entry 2). ^{1}H NMR resonances match with literature values of benzyl bromide.[45]

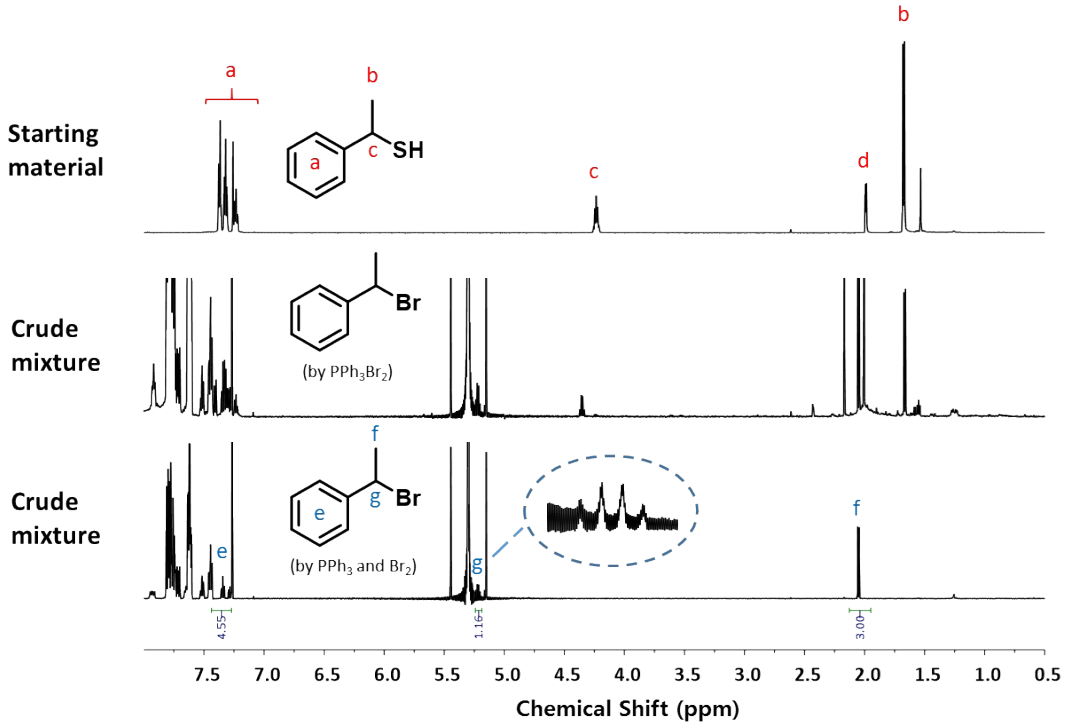


Figure S4. ^{1}H NMR confirming the desulfurization-bromination of α-methylbenzyl mercaptan (Table 1, entry 3). ^{1}H NMR resonances match with literature values of α-methylbenzyl bromide.[S1]

The different reactivity of well-defined PPh_3Br_2 and in situ generated PPh_3Br_2 (from PPh_3 and Br_2) has been shown in literature.[43]

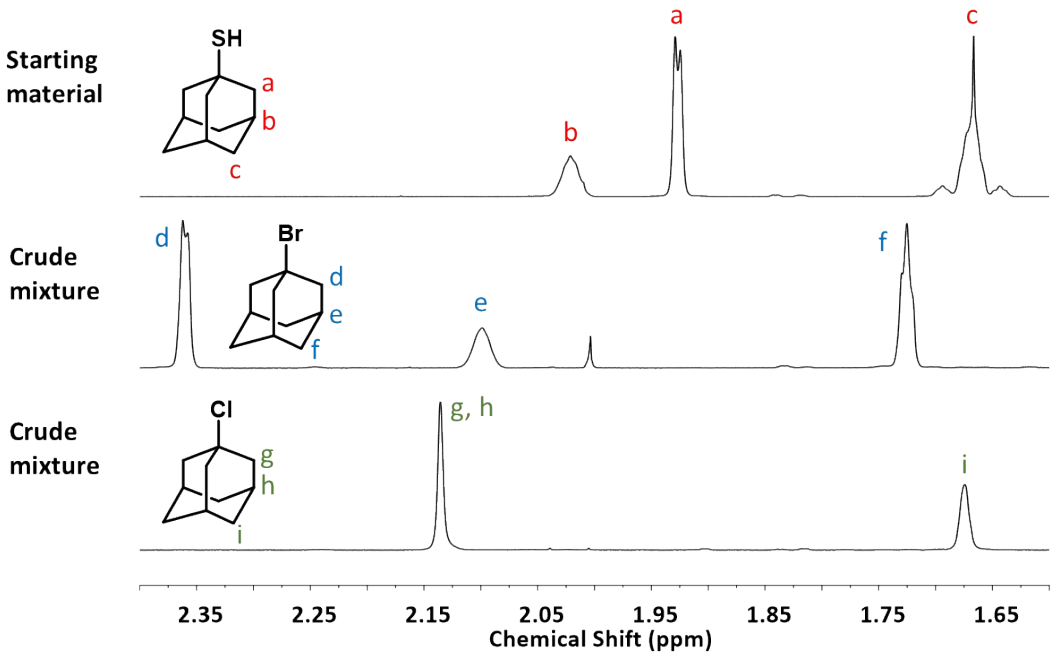


Figure S5. ^{1}H NMR confirming the desulfurization-halogenation of 1-adamantanethiol (Table 1, entry 4). ^{1}H NMR resonances match with literature values of 1-bromoadamantane[S2] and 1-chloroadamantane.[S3]

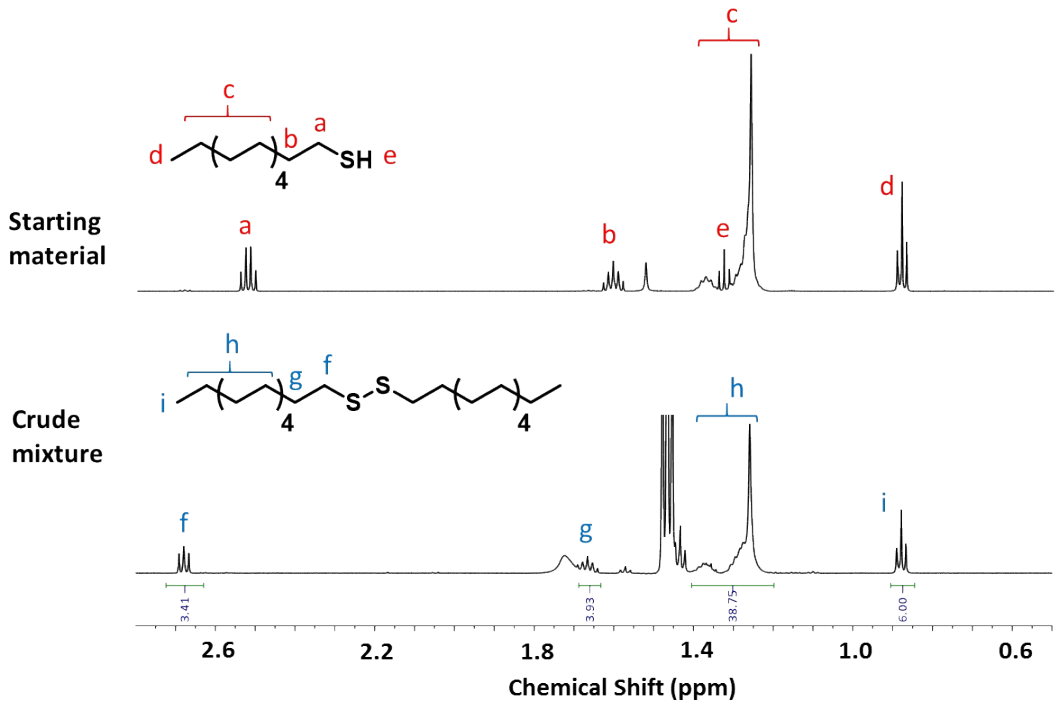


Figure S6. ^{1}H NMR confirming disulfide bond formation of 1-dodecanethiol (Table 1, entry 5). ^{1}H NMR resonances match with literature values of didododecyl disulfide.[S4]

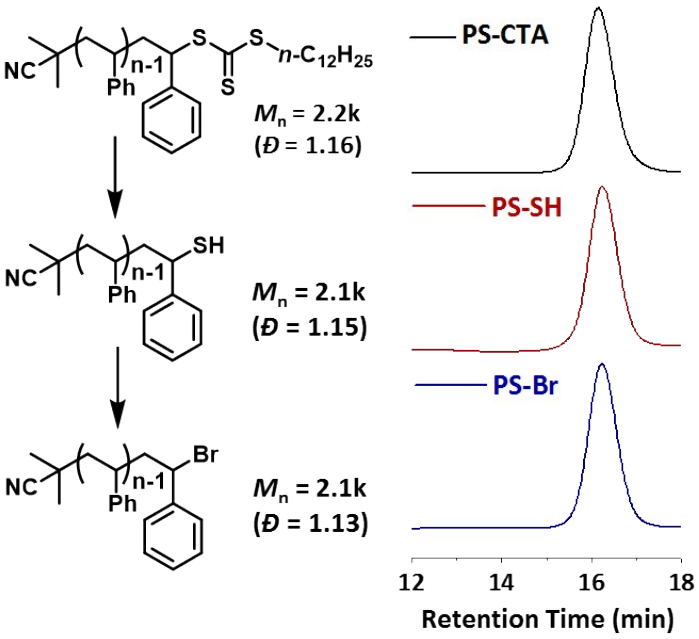


Figure S7. $CHCl_3$ SEC data for the stepwise transformation of PS-CTA to PS-SH to PS-Br.

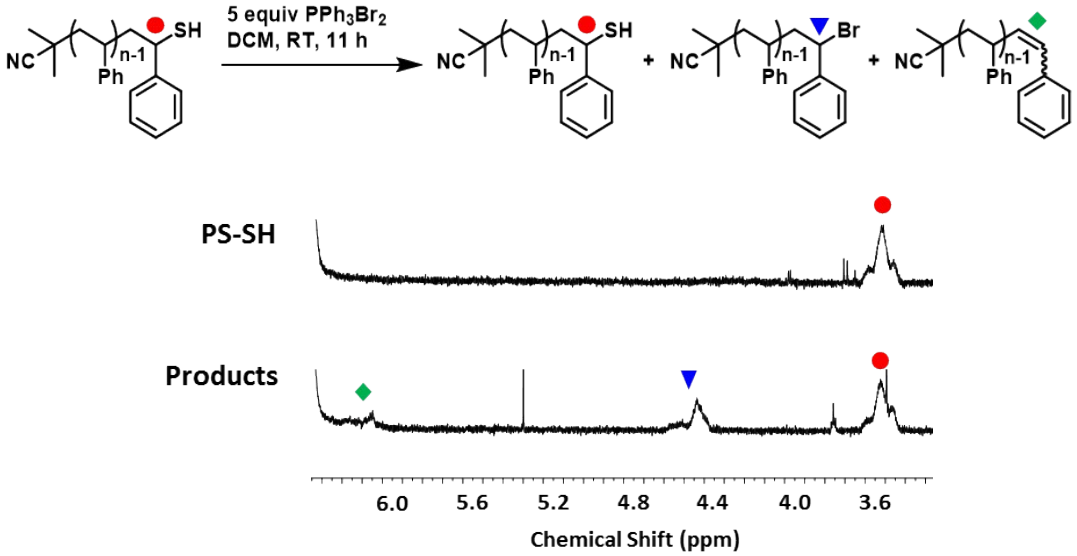


Figure S8. The desulfurization-bromination reaction of PS-SH (M_n = 2.1k, Đ =1.15) using PPh_3Br_2.

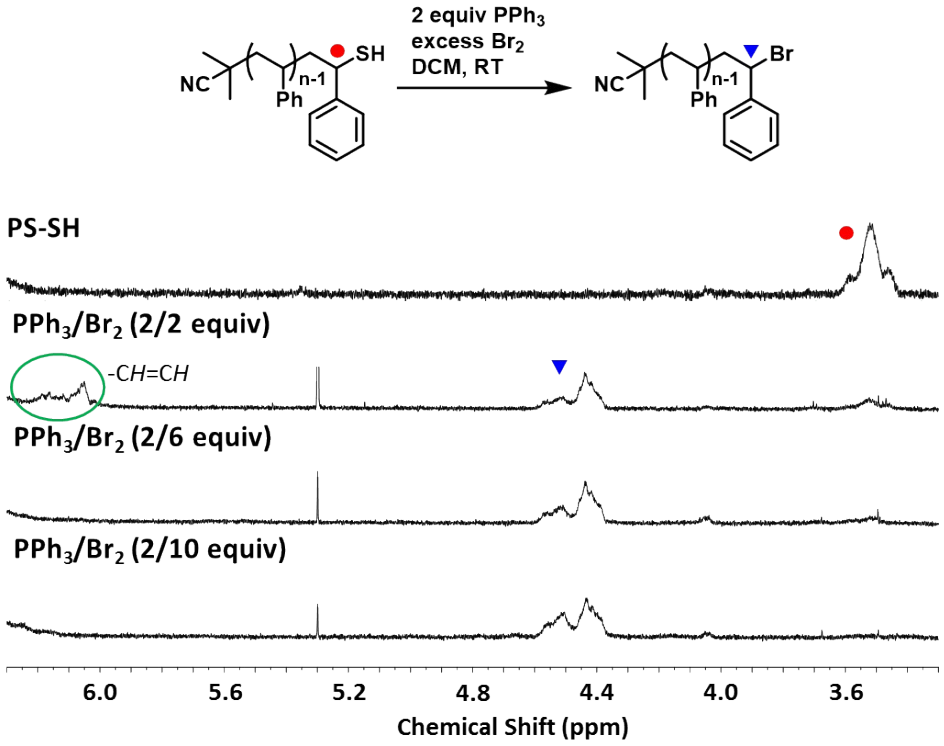


Figure S9. The desulfurization-bromination reaction of PS-SH (M_n = 2.1k, $Đ$ =1.15) using various ratios of PPh_3/Br_2.

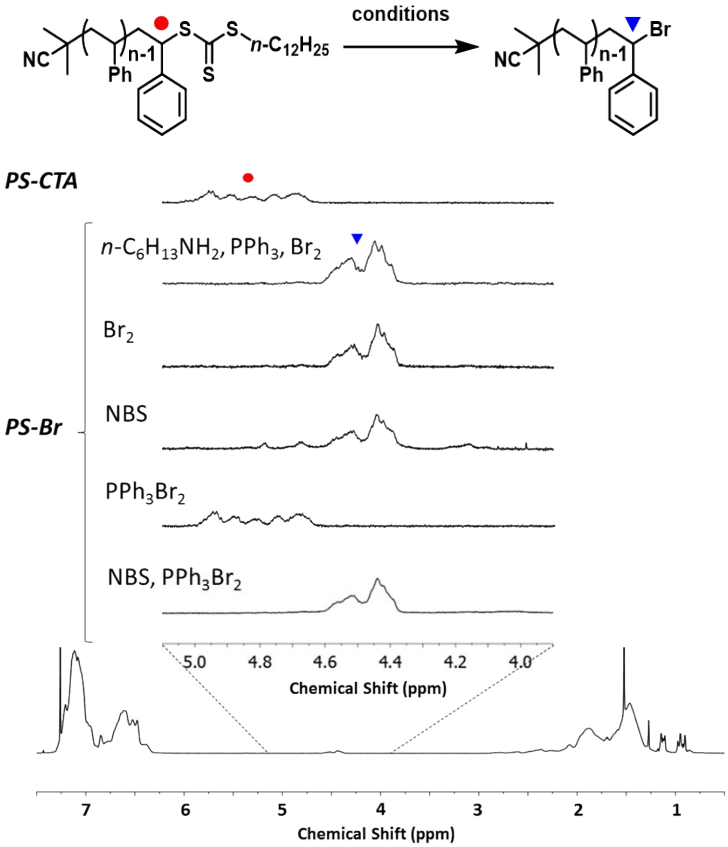
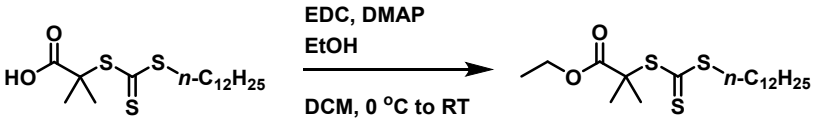
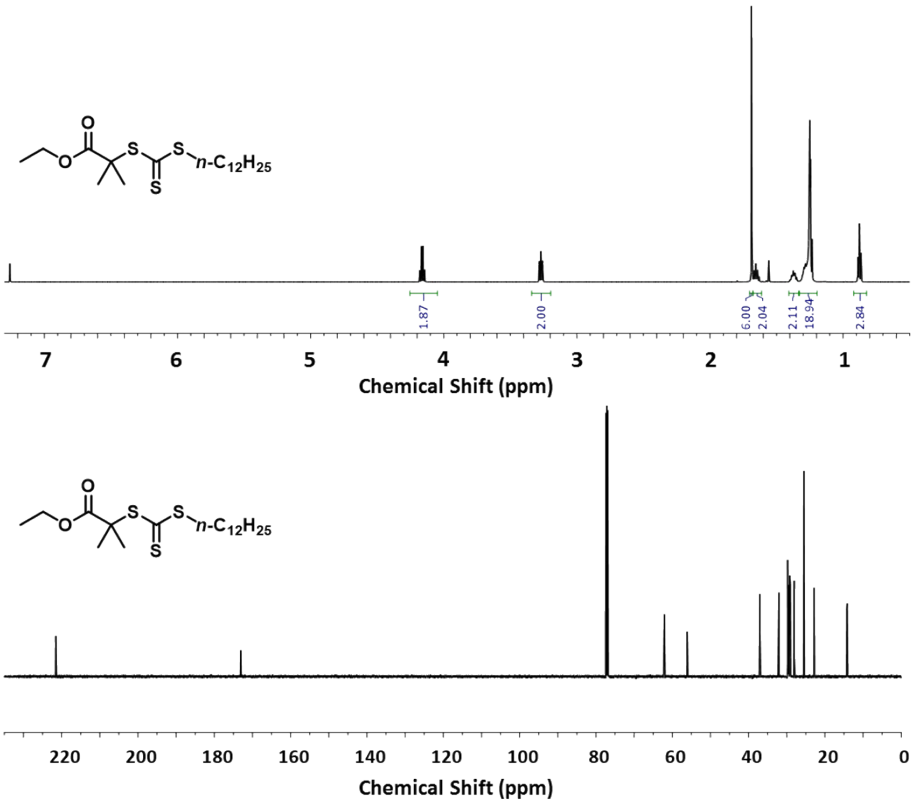


Figure S10. Direct transformation of PS-CTA (M_n = 2.2k, $Đ$ =1.16) to PS-Br under various bromination conditions.

Preparation of the chain transfer agent analogue of ethyl α-bromoisobutyrate



Chain transfer agent analogue of ethyl α-bromoisobutyrate was prepared using a slightly modified literature method.[S5] Added 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (1 g, 2.74 mmol) and 4-(dimethylamino)pyridine (0.033 g, 0.27 mmol) to a round bottom flask equipped with a magnetic stir bar and dissolved in DCM (8 ml). To the flask, *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide (0.582 g, 3.29 mmol) was added at 0 °C. After stirring at 0 °C for 15 minutes, EtOH (0.24 ml, 4.11 mmol) was added to the flask and allowed to stir at room temperature overnight. The crude reaction mixture was diluted with DCM, washed with water, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The compound was purified by silica gel column chromatography using ethyl acetate/*n*-hexane (v/v = 1/15) as an eluent.



^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 4.17 (q, 2H), 3.27 (t, 2H), 1.69 (s, 6H), 1.69–1.63 (m, 2H), 1.40-1.34 (m, 2H), 1.34-1.23 (m, 19H), 0.88 (t, 3H). ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 221.5, 173.1, 62.1, 56.1, 37.0, 32.0, 29.78, 29.76, 29.7, 29.6, 29.5, 29.3, 29.1, 28.0, 25.5, 22.8, 14.3, 14.2.

Figure S11. ^{1}H and ^{13}C NMR spectra confirming successful synthesis of RAFT CTA.

RAFT polymerization and the one-step transformation of PS-CTA to PS-Br (RAFT*)

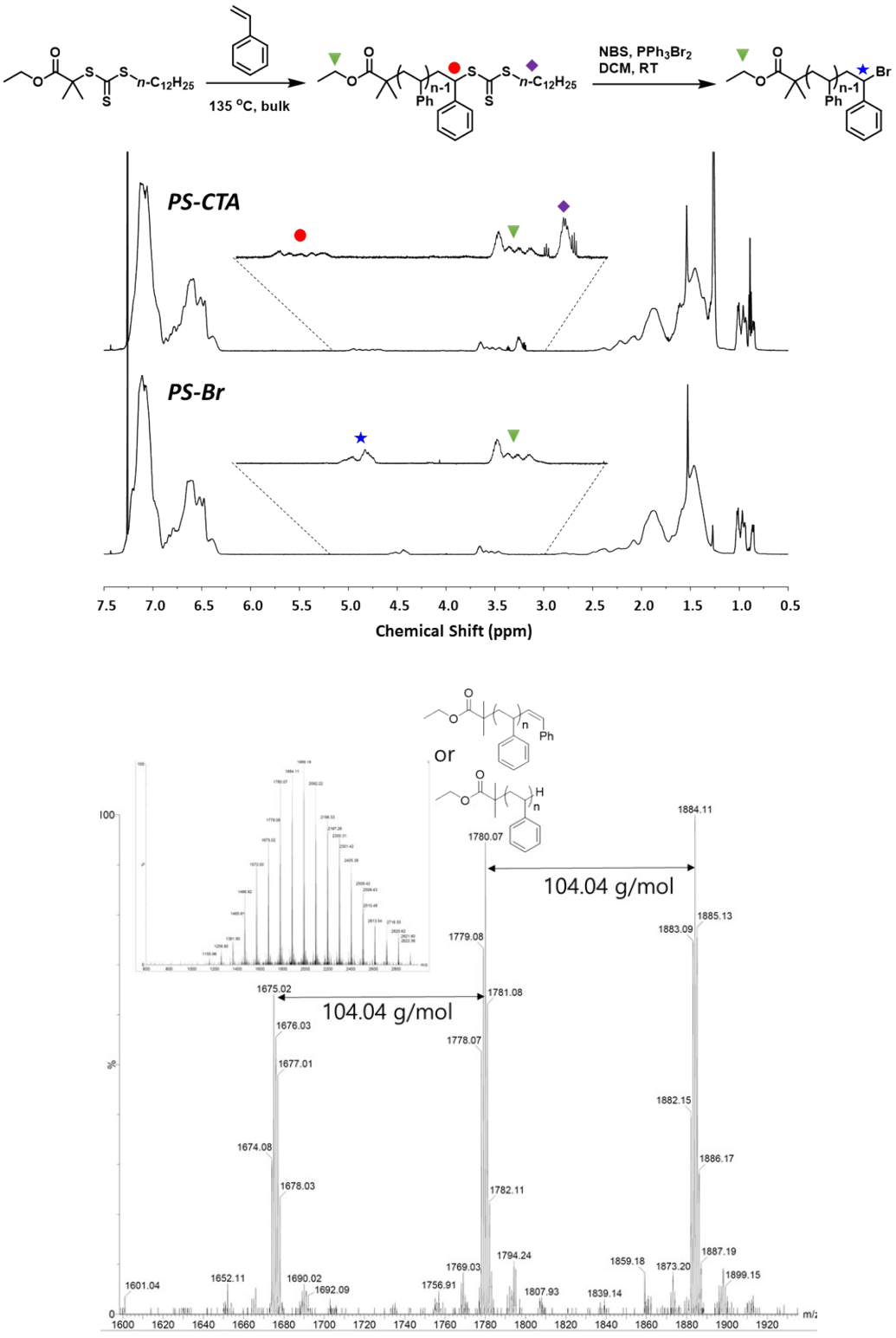


Figure S12. Chemical schematic of bulk polymerization of styrene using RAFT[39] followed by subsequent bromination in one-pot. ^{1}H NMR overlay confirms quantitative transformation to the bromide chain-end. Field desorption mass spectrometry (FD-MS) of PS-Br revealed the mass corresponding to PS-H due to the elimination of bromide during the measurement.[S6,S7]

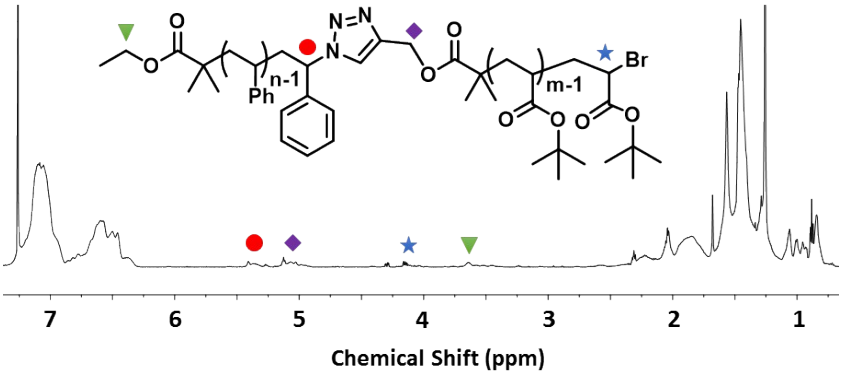


Figure S13. ^{1}H NMR spectrum of PS-*b*-P*t*BA prepared by Cu-catalyzed azide-alkyne "click" chemistry supporting successful diblock synthesis.[49]

Chain extension via ATRP

To a vial equipped with a magnetic stir bar and a teflon screw cap septum, PS-Br macroinitiator (16 mg, 0.007 mmol), styrene (0.24 ml, 2.1 mmol), CuBr (0.0014g, 0.01 mmol), and *N*,*N*′,*N*″,*N*‴-pentamethyldiethylenetriamine (4 ul, 0.02 mmol) were added and dissolved in anisole (0.5 ml). The vial was bubbled with argon for 10 minutes and placed into a preheated oil bath at 90°C for 13 hours. The crude reaction mixture was purified by the precipitation into MeOH, affording 38 mg of PS-*b*-PS-Br as a white solid.

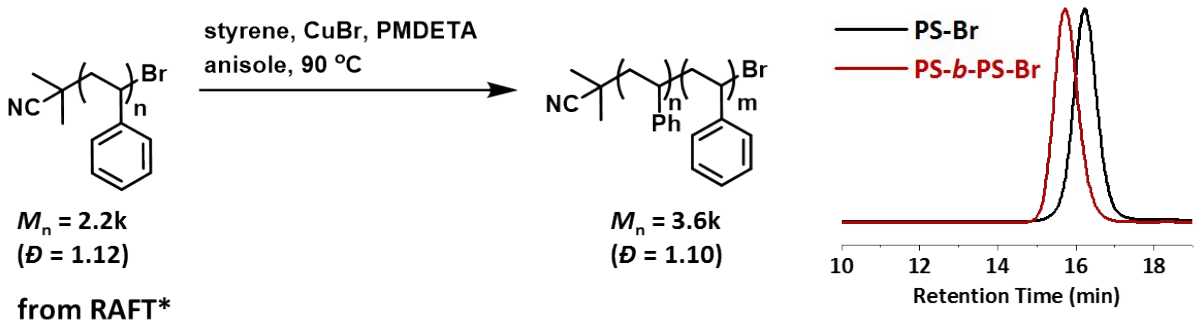


Figure S14. Schematic representation of chain extension of PS-Br from RAFT* with styrene using classical ATRP with corresponding GPC trace overlay confirming shift to higher molecular weight.

Preparation of PDMA-*b*-PS-CTA

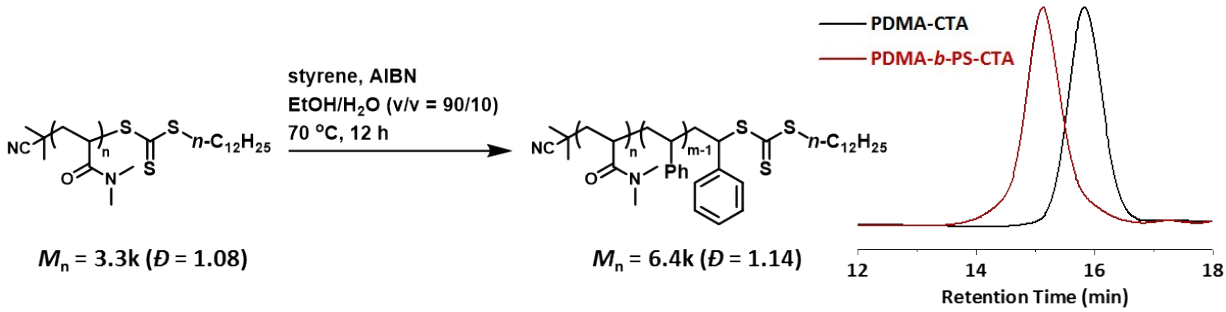


Figure S15. GPC characterization confirming successful preparation of PDMA-*b*-PS-CTA using thermally-initiated RAFT polymerization.[53]

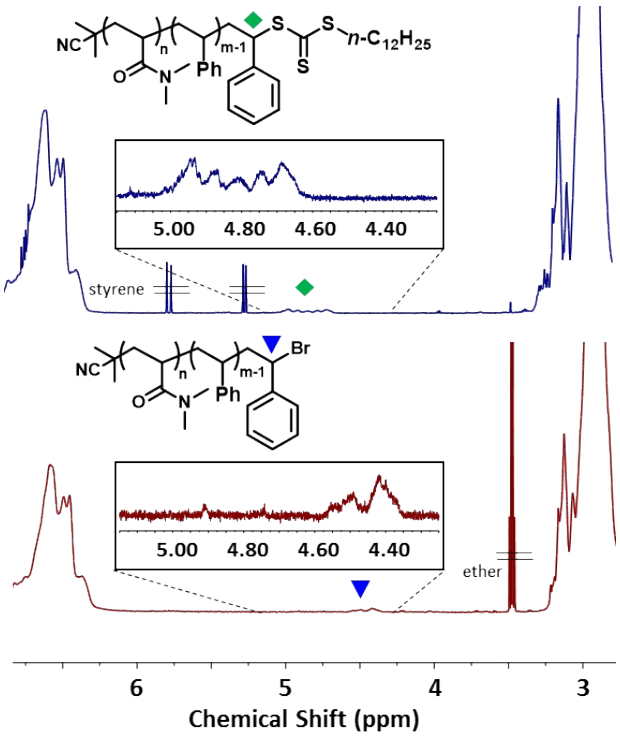


Figure S16. ^{1}H NMR spectrum of PDMA-*b*-PS-Br obtained via one-step transformation from PDMA-*b*-PS-CTA.

References

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