Supporting Information

Molecular Weight Distribution of Living Chains in Polystyrene Prepared by Reversible Addition-Fragmentation Chain Transfer Polymerization

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Synthesis and Characterization of the RAFT agent

4,4'-azobis(4-cyano-1-pentanol) (5)

To a solution of hydrazine sulfate salt (2.0 g, 15.4 mmol) and 5-hydroxy-2-pentanone (3.1 g, 30.8 mmol) in water (25 mL) was added a solution of potassium cyanide (2.0 g, 30.8 mmol) in water (14 mL) dropwise over 1 hr at room temperature. After stirring for 19 hr at room temperature, the resulting solution was cooled to 0 °C and 15% aq. HCl was added to the solution until its pH dropped to 2. Then, bromine (4.5 g, 28.0 mmol) was added dropwise over 1 hr. After the solution was stirred for 5 hr at 0 °C, sodium hydrosulfide hydrate was added to remove the remaining bromine until a precipitate was generated and the resulting mixture was maintained at 0 °C for 20 hr. The solid precipitate was filtered off and the filtrate was extracted with EtOAc, dried over MgSO\(_4\) and concentrated. The residue was subjected to column chromatography with CH\(_2\)Cl\(_2\)/EtOAc (1/4) as eluent to give the desired product 5 (1.7 g, 45%) as a white solid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 3.72 (t, \(J = 6.1\) Hz, 4H), 2.29-2.23 (m, 2H), 2.18-2.11 (m, 2H), 1.82-1.75 (m, 2H), 1.73 (s, 6H), 1.57-1.54 (m, 2H), 1.45 (br s, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 118.3, 72.4, 61.5, 34.6, 27.2, 24.0.

![Figure S1. \(^1\)H NMR and \(^{13}\)C NMR spectrum of 4,4'-azobis(4-cyano-1-pentanol).]

11-((tert-butyldimethylsilyl)oxy)undecane-1-thiol (6)

To a solution of 11-mercapto-1-undecanol (2.0 g, 9.8 mmol) and imidazole (0.7 g, 10.8 mmol) in dry THF (20 mL) at 0 °C was added tert-butyldimethylsilyl chloride (TBDMSCl, 1.6 g, 10.8 mmol). The resulting solution was warmed to room temperature and allowed to stir for 16 hr. The reaction mixture was concentrated by rotary evaporator. The residue was partitioned with water and CH\(_2\)Cl\(_2\). The organic layer was separated,
dried over MgSO₄ and concentrated to give the desired product 6 (3.7 g, 99%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 3.60 (t, J = 6.7 Hz, 2H), 2.53 (q, J = 7.2 Hz, 2H), 1.61 (quin, J = 7.1 Hz, 2H), 1.53-1.48 (m, 2H), 1.39-1.28 (m, 16H), 0.90 (s, 9H), 0.05 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 63.4, 34.2, 33.0, 29.7, 29.6, 29.5, 29.2, 28.5, 26.1, 25.9, 24.8, 18.5, -5.2.

**Figure S2.** ¹H NMR and ¹³C NMR spectrum of 11-((tert-butylimethyldimethylsilyl)oxy)undecane-1-thiol.

**bis(((11-tert-butyldimethylsilyl)oxy)undecylmercaptothiocarbonyl) disulfide (7)**

This compound was prepared according to the modified procedure of the previous report.² To a solution of 11-(tert-butyldimethylsilyloxy)undecane-1-thiol (6, 2.0 g, 6.3 mmol) in water (20 mL) and acetone (5 mL) was added 50% aq. KOH (0.8 mL) dropwise at 0 °C. After the resulting solution was warmed to room temperature, carbon disulfide (1.0 g, 12.6 mmol) was added to the solution and stirred for 30 min. To the resulting mixture was added p-toluenesulfonyl chloride (0.6 g, 3.1 mmol). After stirring for 2 hr at room temperature, the reaction temperature was warmed to 45 °C and stirred for 10 min. The reaction mixture was concentrated by rotary evaporator. The residue was partitioned with water and CH₂Cl₂. The organic layer was separated, dried over MgSO₄ and concentrated to give the desired product 7 (2.0 g, 80%) as a pale reddish oil. ¹H NMR (400 MHz, CDCl₃) δ 3.61 (t, J = 6.7 Hz, 2H), 3.31 (t, J = 8.0 Hz, 2H), 1.70 (quin, J = 7.4 Hz, 2H), 1.53-1.48 (m, 2H), 1.42-1.27 (m, 16H), 0.91 (s, 9H), 0.06 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 221.5, 63.3, 39.2, 38.3, 32.9, 29.6, 29.5, 29.2, 29.0, 28.5, 27.3, 26.0, 25.8, 18.3, -5.3.
Figure S3. $^1$H NMR and $^{13}$C NMR spectrum of bis(((11-tert-butyldimethylsilyl)oxy)undecyl mercaptothiocarbonyl) disulfide (3)

11-((tert-butyldimethylsilyl)oxy)undecyl (2-cyano-5-hydroxypentan-2-yl) carbonotrithioate (8)

A solution of bis((11-tert-butyldimethylsilyl)oxy)undecylmercaptothiocarbonyl) disulfide (7, 2.0 g, 2.5 mmol) and 4,4'-azobis(4-cyano-1-pentanol) (5, 0.7 g, 2.8 mmol) in EtOAc (35 mL) was heated to reflux for 24 hr. The reaction mixture was concentrated by rotary evaporator and the residue was subjected to column chromatography with hexane/EtOAc (2/1) as eluent to give the desired product 8 (0.5 g, 40%) as a pale reddish oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.73 (t, $J = 5.3$ Hz, 2H), 3.60 (t, $J = 6.6$ Hz, 2H), 3.33 (t, $J = 7.6$ Hz, 2H), 2.33-2.23 (m, 1H), 2.15-2.08 (m, 1H), 1.90 (s, 3H), 1.88-1.82 (m, 2H), 1.70 (quin, $J = 7.4$ Hz, 2H), 1.51 (quin, $J = 7.4$ Hz, 2H), 1.42-1.28 (m, 16H), 0.89 (s, 9H), 0.05 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 217.5, 119.5, 63.3, 61.7, 47.0, 37.0, 36.0, 32.8, 29.5, 29.4, 29.0, 28.9, 27.9, 27.7, 26.0, 25.7, 25.6, 24.9, 18.4, -5.3.

Figure S4. $^1$H NMR and $^{13}$C NMR spectrum of 11-((tert-butyldimethylsilyl)oxy)undecyl (2-cyano-5-hydroxypentan-2-yl) carbonotrithioate.
2-cyano-5-hydroxypentan-2-yl (11-hydroxyundecyl) carbonotrithioate (2)

To a solution of 11-((tert-butyldimethylsilyl)oxy)undecyl (2-cyano-5-hydroxypentan-2-yl) carbonotrithioate (8, 1.0 g, 2.0 mmol) in EtOH (15 mL) at 0 °C was added 48-51% aq. HF (0.8 mL). The resulting solution was stirred for 2 hr at room temperature, then quenched with 5 mL of sat’d NaHCO₃ solution. The solution was partitioned with water and CH₂Cl₂. The organic layer was separated, dried over MgSO₄ and concentrated to give the desired product 2 (0.7 g, 90%) as a pale reddish oil. ¹H NMR (400 MHz, CDCl₃) δ 3.73 (t, J = 6.6 Hz, 2H), 3.65 (t, J = 6.7 Hz, 2H), 3.33 (t, J = 7.5 Hz, 2H), 2.33-2.25 (m, 1H), 2.15-2.07 (m, 1H), 1.90 (s, 3H), 1.88-1.82 (m, 2H), 1.70 (quin, J = 7.4 Hz, 2H), 1.57 (quin, J = 6.7 Hz, 2H), 1.42-1.28 (m, 16H). ¹³C NMR (100 MHz, CDCl₃) δ 217.5, 119.6, 62.9, 61.6, 58.3, 46.9, 36.9, 35.7, 32.7, 29.5, 29.32, 29.3, 29.0, 28.8, 27.8, 27.6, 25.7, 24.8, 18.3. HRMS (ESI Q-TOF) Calcd for C₁₈H₃₃NO₂S₃Na [M + Na]⁺: 414.1571. Found: 414.1569.

Figure S5. ¹H NMR and ¹³C NMR spectrum of 2-cyano-5-hydroxypentan-2-yl (11-hydroxyundecyl) carbonotrithioate.

¹H NMR (400 MHz, CDCl₃) δ 3.73 (t, J = 6.6 Hz, 2H), 3.65 (t, J = 6.7 Hz, 2H), 3.33 (t, J = 7.5 Hz, 2H), 2.33-2.25 (m, 1H), 2.15-2.07 (m, 1H), 1.90 (s, 3H), 1.88-1.82 (m, 2H), 1.70 (quin, J = 7.4 Hz, 2H), 1.57 (quin, J = 6.7 Hz, 2H), 1.42-1.28 (m, 16H). ¹³C NMR (100 MHz, CDCl₃) δ 217.5, 119.6, 62.9, 61.6, 58.3, 46.9, 36.9, 35.7, 32.7, 29.5, 29.32, 29.3, 29.0, 28.8, 27.8, 27.6, 25.7, 24.8, 18.3. HRMS (ESI Q-TOF) Calcd for C₁₈H₃₃NO₂S₃Na [M + Na]⁺: 414.1571. Found: 414.1569.
**Figure S6.** MALDI-TOF mass spectra of as-prepared polystyrene (black), the living chains (blue, F1 and red, F3) and dead chains (green, F2 and dark yellow, F4).
Figure S7. Weight fraction vs. molecular weight plot of SEC (black) and theoretical Poisson distribution (red) of the PS prepared by anionic polymerization. They show the band-broadening of SEC becomes serious as MW increases, For the MW below 7k, the MWD determined by SEC follows the Poisson distribution quite well indicating that the band-broadening of SEC is not serious at low MW.
Preparation of PS1, PS2 and PS3.

Three polystyrene samples, were prepared at three different [initiator]/[RAFT agent] ratios, 0.05 (PS1), 0.10 (PS2) and 0.2 (PS3) as follows. For PS1, styrene (2.72g, 26 mmol), RAFT agent 2 (0.10g, 0.26 mmol) and AIBN (2.2 mg, 0.013 mmol) were dissolved in anisole (1.5 g) in a 25 mL flask and the solution was degassed with freezing-pump-thawing for four times. Then, the flask was placed in an oil bath at 80 °C for 18 h under nitrogen atmosphere. The conversion of the monomer in the reaction was monitored using gas chromatography. Finally, the polymerization was quenched in an ice bath after the conversion of 39%. The polymer was not reprecipitated to preserve the low molecular weight polymer species for the characterization. Number-average molecular weight, $M_n = 4,320$ and dispersity, $D = 1.05$. PS2 and PS3 were synthesized under the identical condition with the only difference in the amount of AIBN, 4.3 mg (0.026 mmol) and 8.6 mg (0.052 mmol) for PS2 and PS3, respectively. Number-average molecular weight of PS2, $M_n = 4,380$ and $D = 1.06$. Number-average molecular weight of PS3, $M_n = 4,340$ and $D = 1.07$. 

Figure S8. MALDI-MS spectrum of the fractionated R-PS-Z and fit to the Poisson distribution.
**Figure S9.** Solvent gradient HPLC fractionation of the as-prepared PS samples at 3 different [initiator]/[RAFT agent] ratios. Column: Nucleosil bare silica, 250 × 4.6 mm, 50 Å, 5 μm. Eluent: THF/n-hexane (TEA 0.2%), 40/60 (v/v) → 100/0 (v/v) at a flow rate of 0.6 mL/min.

**Figure S10.** Comparison of the SEC chromatograms of as-prepared PS (black) and the living chains (blue, F1 and red, F3) with equally adjusted peak heights for the PS samples prepared at three different [initiator]/[RAFT agent] ratios.