

RAFT polymerization with triphenylstannylcarbodithioates (Sn-RAFT)

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I. EXPERIMENTAL INFORMATION

A. Materials and instrumentation

Materials: THF, toluene, 1,4-dioxane and CS_2 were purified by distillation over CaH_2 , followed by passing through the column packed with molecular sieves 4 Å. Degassed solvents were stored over molecular sieves under Ar atmosphere in refrigerator. Li wire (Aldrich, $\geq 98\%$), N,N,N',N'-Tetramethylethylenediamine (TMEDA, Aldrich, $\geq 99.5\%$), triphenyltin chloride (Fluka, 95%), benzyl bromide (Acros, 98%) and (1-bromoethyl)benzene (Aldrich, 97%) were used as received.

The 2,2'-azobis(isobutyronitrile) initiator (AIBN, Fluka, $\geq 98\%$) was recrystallized twice from methanol prior to use. Styrene (St, Aldrich, $\geq 98\%$), methyl acrylate (MA, Acros, 99+%) were purified by passing through a column packed with neutral alumina. N-isopropylacrylamide (NIPAM, Aldrich, 97%) was recrystallized three times from a mixture of toluene/n-hexane (v/v = 1/1) prior to use. N-tert-octylacrylamide (TOA, Polysciences) was used as received.

Analytical techniques: NMR spectra were recorded using a Bruker AMX 300 spectrometer at 298K. Chemical shifts are expressed in parts per million with residual solvent signals as internal reference (^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR). The external chemical shift reference for ^{119}Sn is Me_4Sn . IR spectra were recorded using a Thermo Fischer Nexus 6700 FTIR spectrometer in ATR mode. Melting points were measured with a sealed capillary using the Stuart automatic melting point SMP40 apparatus.

The monomer conversion was determined by ^1H NMR in CDCl_3 and the number-average molar mass (M_n) values and dispersities (\bar{D}) of the polymer samples were obtained from size-exclusion chromatography analysis. Prior to injection, samples were diluted to a concentration of 5 mg mL^{-1} and filtered through $0.22 \mu\text{m}$ Nylon syringe filters (THF eluent) or $0.45 \mu\text{m}$ PTFE syringe filters (DMF eluent).

The SEC analyses of PSt, PMA and PTOA were conducted using a Waters 2414 refractive index detector, a mini DAWN TREOS Multi-Angle Light Scattering (MALS) detector (Wyatt Technology) equipped with a set of 2 columns (Shodex KF-802.5 and KF-804) in THF as eluent at a flow rate of 1.0 mL min^{-1} (35°C). The column system was calibrated with narrow PSt standards, obtained from Polymer Laboratories, ranging from 580 to $164500 \text{ g mol}^{-1}$. Values of M_n and \bar{D} for PSt and PMA are reported in PSt equivalents whereas PTOA

values are reported using SEC-MALS data ($dn/dc = 0.095 \text{ mL g}^{-1}$). Polystyrene calibration was applied for PMA samples with next Mark-Houwink-Sakurada (MHS) parameters: $K_{PSt} = 11.4 \times 10^{-5} \text{ dL g}^{-1}$ and $a_{PSt} = 0.716$ for polystyrene [Hutchinson, R. A.; Paquet Jr. D. A.; McMin, J. H.; Beuermann, S.; Fuller, R. E.; Jackson, C. *Dech. Monog.*, 1995, 131, 467-492.]; $K_{PMA} = 19.5 \times 10^{-5} \text{ dL g}^{-1}$ and $a_{PMA} = 0.660$ for poly(methyl acrylate) [Buback, M.; Kurz, C. H.; Schmaltz, C. *Macromol. Chem. Phys.*, 1998, 199, 1721-1727].

The SEC analyses of PNIPAM were carried out on a system comprising a Shodex KD-G guard column and three columns: Shodex KD-804 ($8 \text{ mm} \times 300 \text{ mm}$, $7 \mu\text{m}$), Shodex KD-802.5 ($8 \text{ mm} \times 300 \text{ mm}$, $6 \mu\text{m}$), Shodex KD-805L ($8 \text{ mm} \times 300 \text{ mm}$, $5 \mu\text{m}$); coupled with a refractometer (Optilab Rex, Wyatt technology) thermostated at 35°C , a UV detector (Prostar, Varian) set at 290 nm and a mini DAWN TREOS MALS detector (Wyatt Technology). DMF/LiBr (10 mM) was used as eluent at a flow rate of 1.0 mL min^{-1} (55°C). Values of M_n and \bar{D} are reported using SEC-MALS data, $dn/dc = 0.087 \text{ mL g}^{-1}$ [Read, E.; Guinaudeau, A.; Wilson, D. J.; Cadix, A.; Violleau, F.; Destarac, M. *Polym. Chem.*, 2014, 5, 2202-2207].

The dn/dc value for PTOA was measured using a PSS DnDc-2010 differential refractometer ($\lambda = 620 \text{ nm}$, 35°C) for polymer sample with M_n about 10 kDa. Polymer was purified by precipitation with ethanol, filtered off and dried in vacuo. Series of polymer solutions in THF with concentrations $0.5 - 10 \text{ mg mL}^{-1}$ were used.

All the syntheses were carried out using standard Schlenk and high vacuum line techniques under an argon atmosphere.

B. Synthesis of triphenylstannylecarbodithioates 1-2

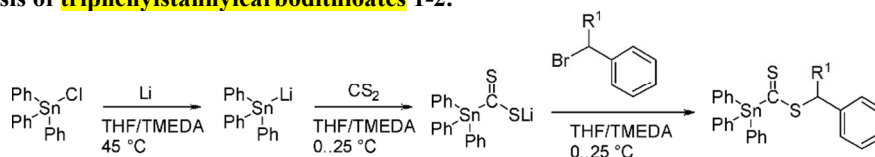
A solution of triphenyltin chloride (2.32 g , 6 mmol) and TMEDA (1 mL , 6.67 mmol) in 20 mL of THF was stirred with Li wire (84 mg , 12 mmol) at 45°C until it had totally dissolved. Then CS_2 (1.08 mL , 18 mmol) was added dropwise at 0°C and stirred for 30 min at room temperature. The resulting brown-red solution was slowly added to 7.5 mmol of the corresponding alkyl bromide at $0-10^\circ\text{C}$. After stirring for an additional 2 h at room temperature the solvent was evaporated. The residue was quickly chromatographed over silica gel using first petroleum ether as eluent to remove impurities and then diethyl ether to collect the pink fraction. Recrystallization from pentane led to crystalline products.

Benzyl triphenylstannylcarbodithioate 1 (2.26 g, 73%). Pink crystals, mp 94-96 °C (lit. 96 °C [Kunze, U.; Tischer, R. *Chem. Ber.*, 1987, 120, 1099-1104]); ¹H NMR (300.13 MHz, toluene-*d*₈, 298K): δ = 4.43 (t, ⁴J_{Sn,H} = 4.2 Hz, 2H, CH₂C₆H₅), 6.93 (m, 5H, CH₂C₆H₅), 7.09-7.19 (m, 9H, *m*-, *p*-(C₆H₅)₃Sn), 7.57-7.81 (m, ³J_{Sn,H} = 50.7 Hz, 6H, *o*-(C₆H₅)₃Sn); ¹³C{¹H} NMR (75.47 MHz, toluene-*d*₈, 298K) δ = 38.8 (t, ⁴J_{Sn,C} = 12.4 Hz, CH₂C₆H₅), 127.5 (s, *m*-CH₂C₆H₅), 128.8 (s, *p*-CH₂C₆H₅), 129.1 (t, ³J_{Sn,C} = 55.9 Hz, *m*-(C₆H₅)₃Sn), 129.5 (s, *o*-CH₂C₆H₅), 129.8 (t, ⁴J_{Sn,C} = 12.1 Hz, *p*-(C₆H₅)₃Sn), 135.7 (s, *ipso*-CH₂C₆H₅), 137.4 (t, ²J_{Sn,C} = 38.6 Hz, *o*-(C₆H₅)₃Sn), 137.9 (s, *ipso*-(C₆H₅)₃Sn), 264.8 ppm (s, C=S₂); ¹¹⁹Sn{¹H} NMR (98.2 MHz, toluene-*d*₈, 298K, external Me₄Sn) δ = -191.0 ppm; IR: 1046.6 cm⁻¹ (C=S); Figures S1-S3.

1-Phenylethyl triphenylstannylcarbodithioate 2 (1.79 g, 56%). Pink crystals, mp 93-95 °C; ¹H NMR (300.13 MHz,

toluene-*d*₈, 298K): δ = 1.44 (d, ³J_{H,H} = 7.1 Hz, 3H, CH(CH₃)C₆H₅), 5.84 (m, ³J_{H,H} = 7.1 Hz, ⁴J_{Sn,H} = 7.3 Hz, 1H, CH(CH₃)C₆H₅), 6.90-7.08 (m, 5H, CH(CH₃)C₆H₅), 7.09-7.19 (m, 9H, *m*-, *p*-(C₆H₅)₃Sn), 7.57-7.81 (m, ³J_{Sn,H} = 51.9 Hz, 6H, *o*-(C₆H₅)₃Sn); ¹³C{¹H} NMR (75.47 MHz, toluene-*d*₈, 298K) δ = 20.0 (s, CH(CH₃)C₆H₅), 46.3 (t, ⁴J_{Sn,C} = 13.3 Hz, CH(CH₃)C₆H₅), 127.6 (s, *p*-CH(CH₃)C₆H₅), 128.0 (s, *o*-CH(CH₃)C₆H₅), 128.8 (s, *m*-CH(CH₃)C₆H₅), 129.1 (t, ³J_{Sn,C} = 54.3 Hz, *m*-(C₆H₅)₃Sn), 129.8 (t, ⁴J_{Sn,C} = 12.1 Hz, *p*-(C₆H₅)₃Sn), 137.4 (t, ²J_{Sn,C} = 38.6 Hz, *o*-(C₆H₅)₃Sn), 138.0 (s, *ipso*-(C₆H₅)₃Sn), 141.3 (s, *ipso*-CH(CH₃)C₆H₅), 264.0 ppm (s, C=S₂); ¹¹⁹Sn{¹H} NMR (98.2 MHz, toluene-*d*₈, 298K, external Me₄Sn) δ = -192.7 ppm; IR: 1040.5 cm⁻¹ (C=S); Figures S4-S6.

Scheme S1. Synthesis of triphenylstannylcarbodithioates 1-2.



Sn-RAFT 1: R¹ = H; Sn-RAFT 2: R¹ = CH₃.

C. Polymerization techniques

RAFT polymerization: typical procedure. AIBN (1.3 mg (0.008 mmol), **Sn-RAFT 1** (48.1 mg, 0.093 mmol), TOA (1.81 g, 9.87 mmol) and 1,4-dioxane (2.62 g, 29.7 mmol) were stirred together until dissolution. The solution was divided into 4 × 2 mL glass tubes and degassed with three freeze-pump-thaw cycles before being flame-sealed under vacuum. The tubes were placed in a dry bath maintained at 60 °C. At given intervals, the tubes were quenched by freezing in liquid N₂.

Preparation of PNTOA-1 7.8K macro-RAFT agent: AIBN (3.7 mg (0.023 mmol), **Sn-RAFT 1** (57.1 mg, 0.11 mmol), TOA (1.065 g, 132 mmol) and 1,4-dioxane (3.11 g, 801 mmol) were mixed in a Schlenk tube, degassed with three freeze-pump-thaw cycles and heated during 7 h at 60 °C. Reaction was quenched by freezing in liquid N₂. Polymer was precipitated with ethanol, filtered off and dried in vacuo. Monomer conversion 83%, Mn = 7.77 kDa, Đ = 1.09 (Table 1, entry 13).

PNTOA-1 7.8K chain extension: AIBN (0.8 mg (0.005 mmol), **PNTOA-1 7.8K** (0.4 g, 0.052 mmol), TOA (1.5 g, 8.18 mmol) and 1,4-dioxane (4.37 g, 49.6 mmol) were stirred together. The solution was divided into 2 mL glass tubes and degassed with three freeze-pump-thaw cycles before being flame-sealed under vacuum. The tubes were placed in a dry bath maintained at 60 °C. At given intervals, the tubes were quenched by freezing in liquid N₂.

RAFT polymerization in NMR tubes: typical procedure. AIBN (11.6 mg, 0.071 mmol), **Sn-RAFT 1** (181.8 mg, 0.352 mmol), MA (2.42 g, 28.1 mmol) and benzene-*d*₆ (7.11 g, 84.5 mmol) were stirred together in a Schlenk tube. The solution was degassed with three freeze-pump-thaw cycles. NMR tubes were filled with 0.8 mL of solution under Ar atmosphere, sealed with rubber septa and immersed in an oil bath maintained at 60 °C. At given intervals, the tubes were quenched by freezing in liquid N₂ and analyzed by NMR.

II. Sn-RAFT AGENTS CHARACTERISATION

A. Benzyl triphenylstannylcarbodithioate Sn-RAFT 1 NMR spectra

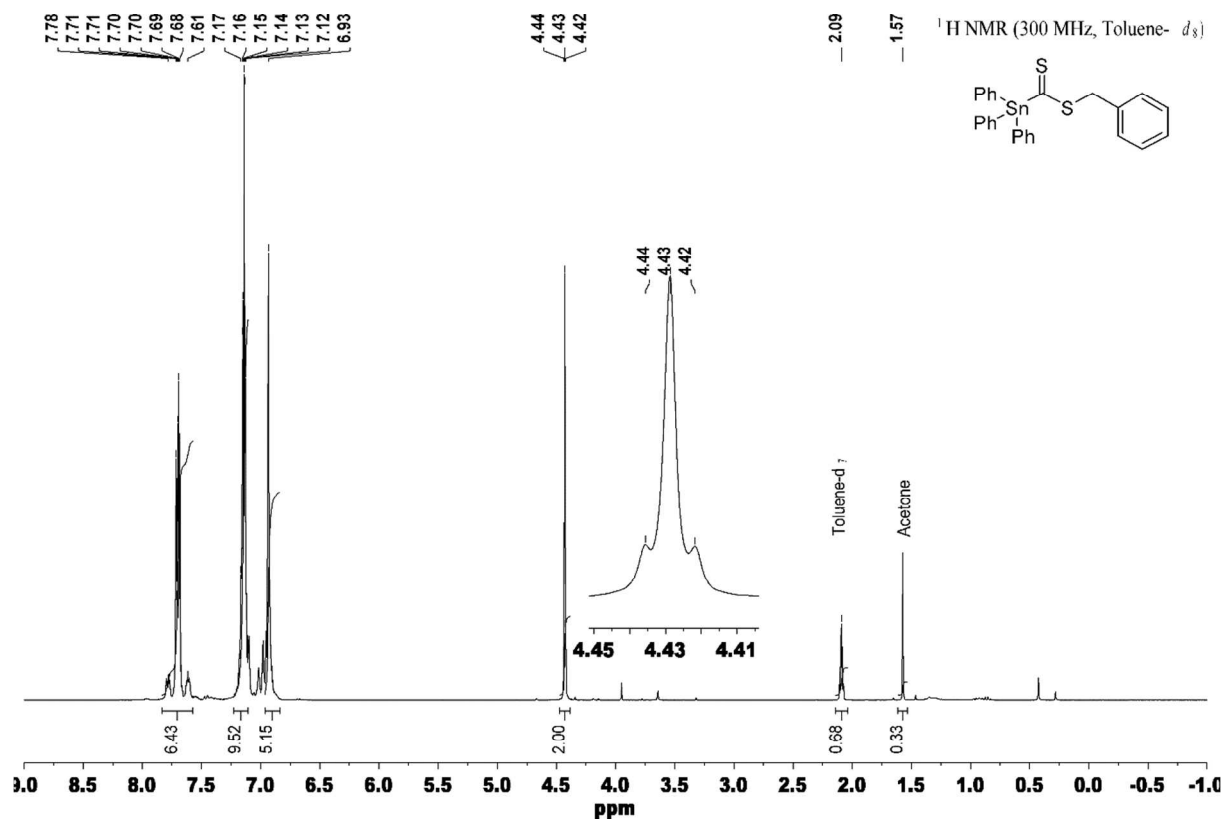


Figure S1. Benzyl triphenylstannylcarbodithioate Sn-RAFT 1 ¹H NMR spectrum.

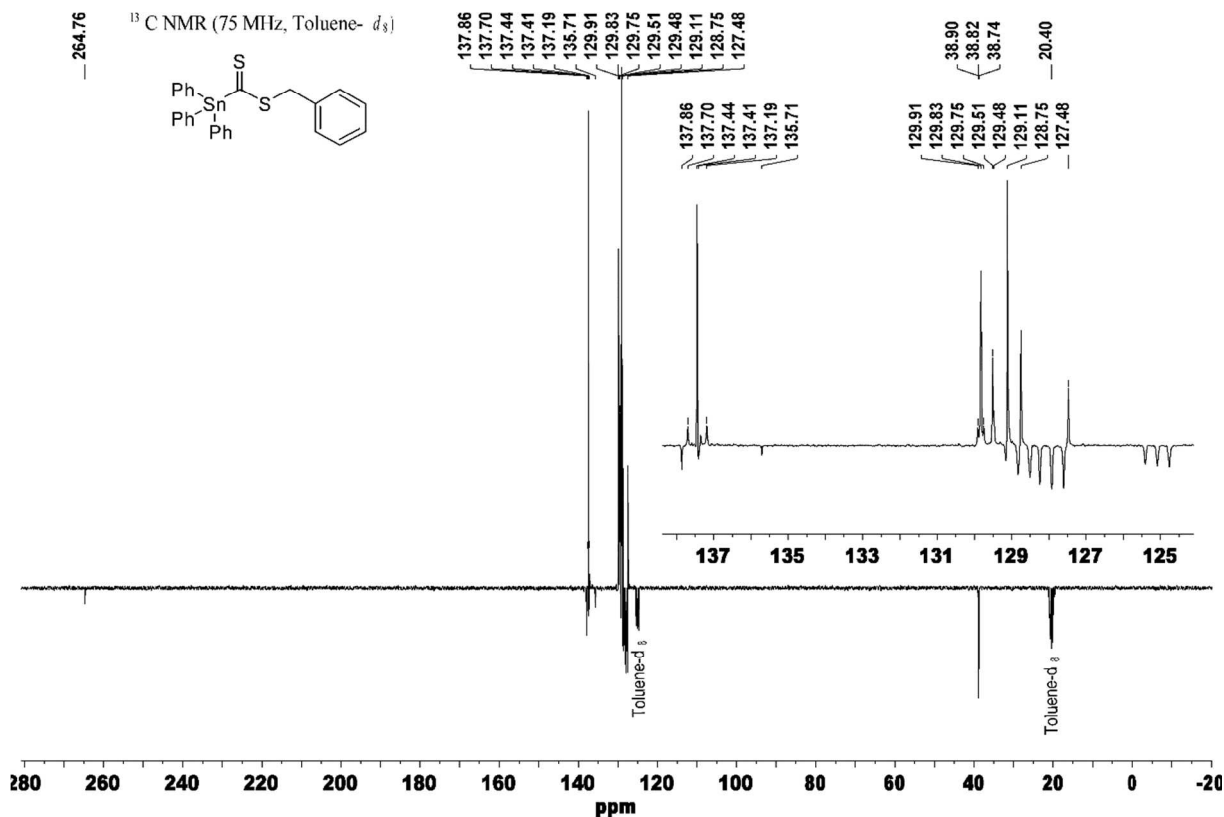


Figure S2. Benzyl triphenylstannylcarbodithioate Sn-RAFT 1 ¹³C NMR spectrum.

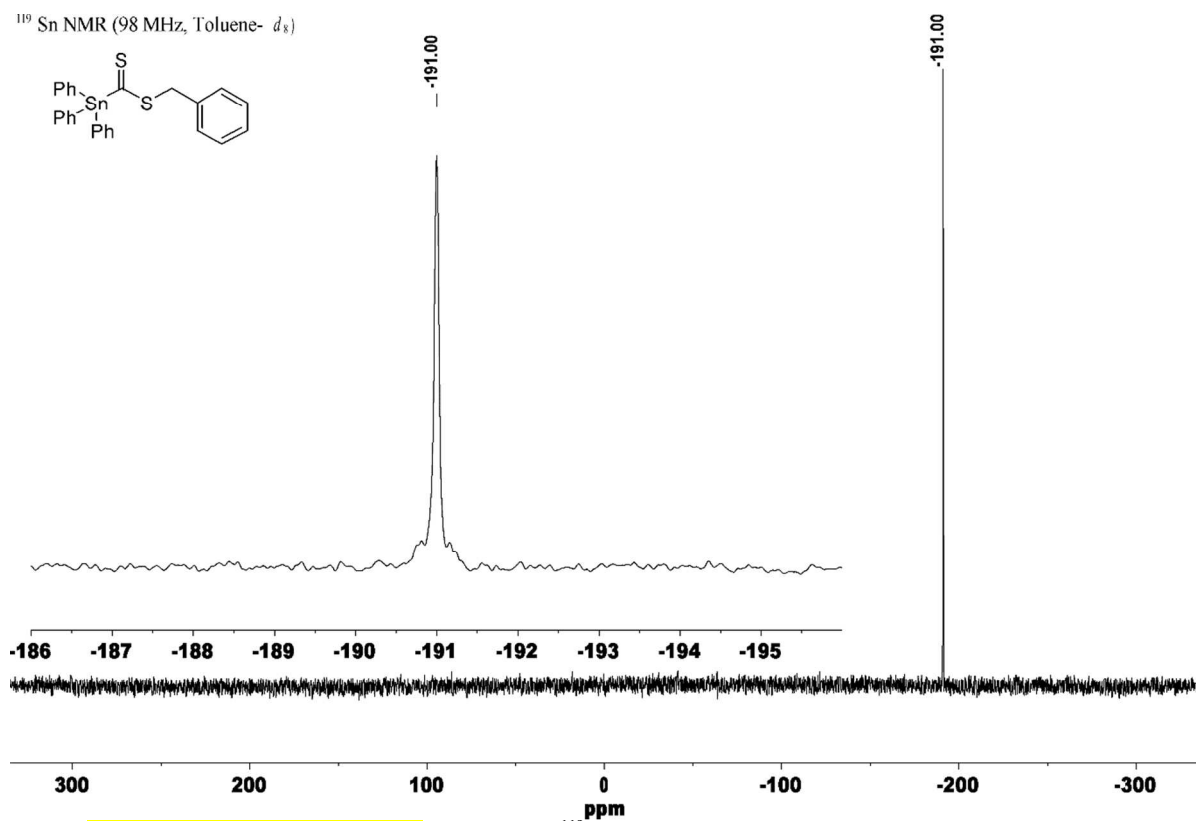


Figure S3. Benzyl triphenylstannylcarbodithioate Sn-RAFT 1 ¹¹⁹Sn NMR spectrum.

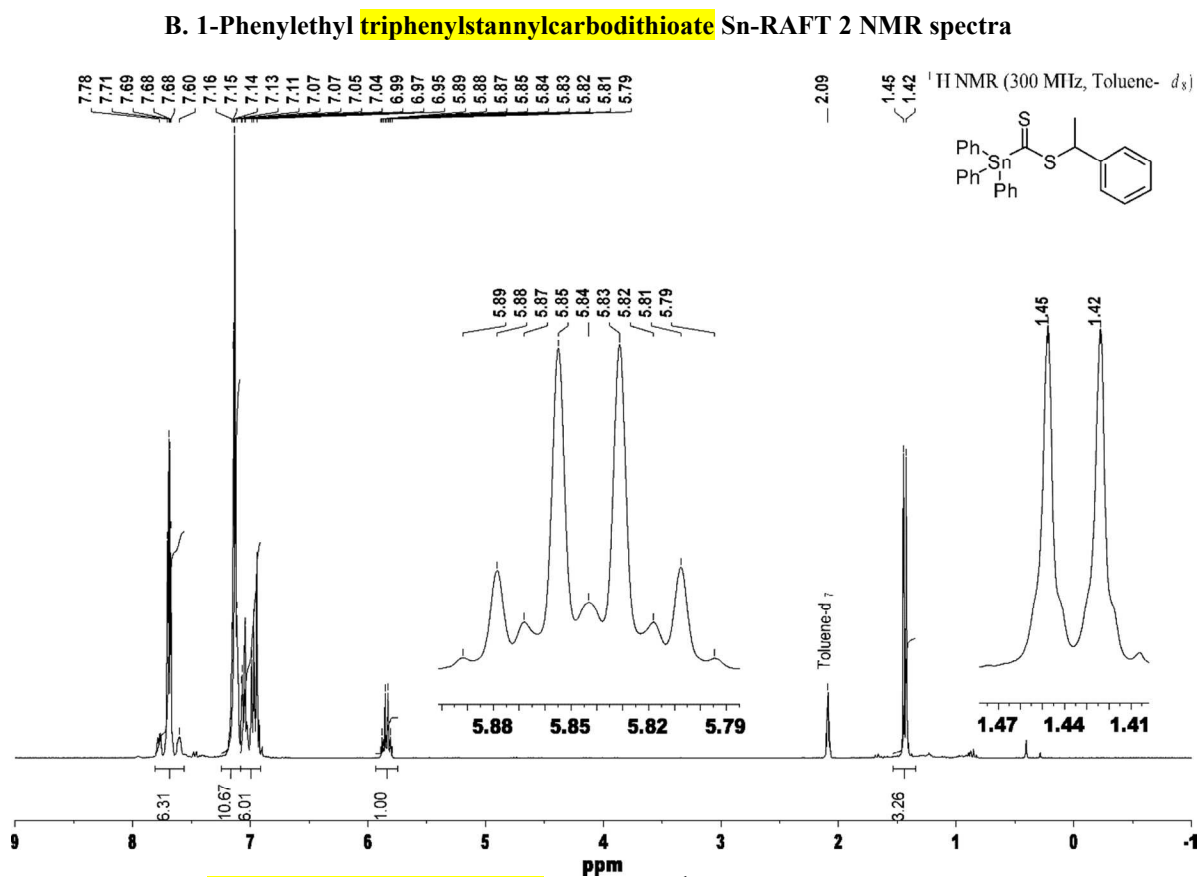


Figure S4. 1-Phenylethyl triphenylstannylcarbodithioate Sn-RAFT 2 ¹H NMR spectrum.

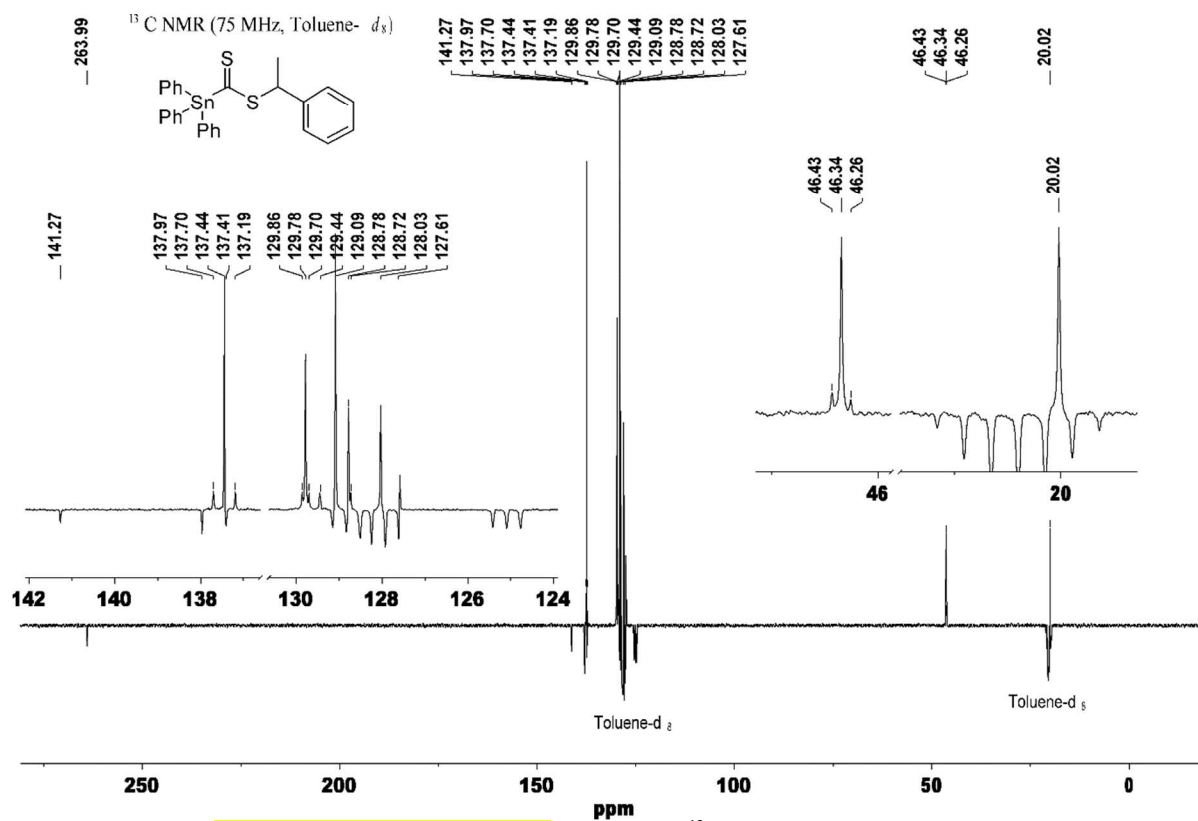


Figure S5. 1-Phenylethyl triphenylstannylcarbodithioate Sn-RAFT 2 ¹³C NMR spectrum.

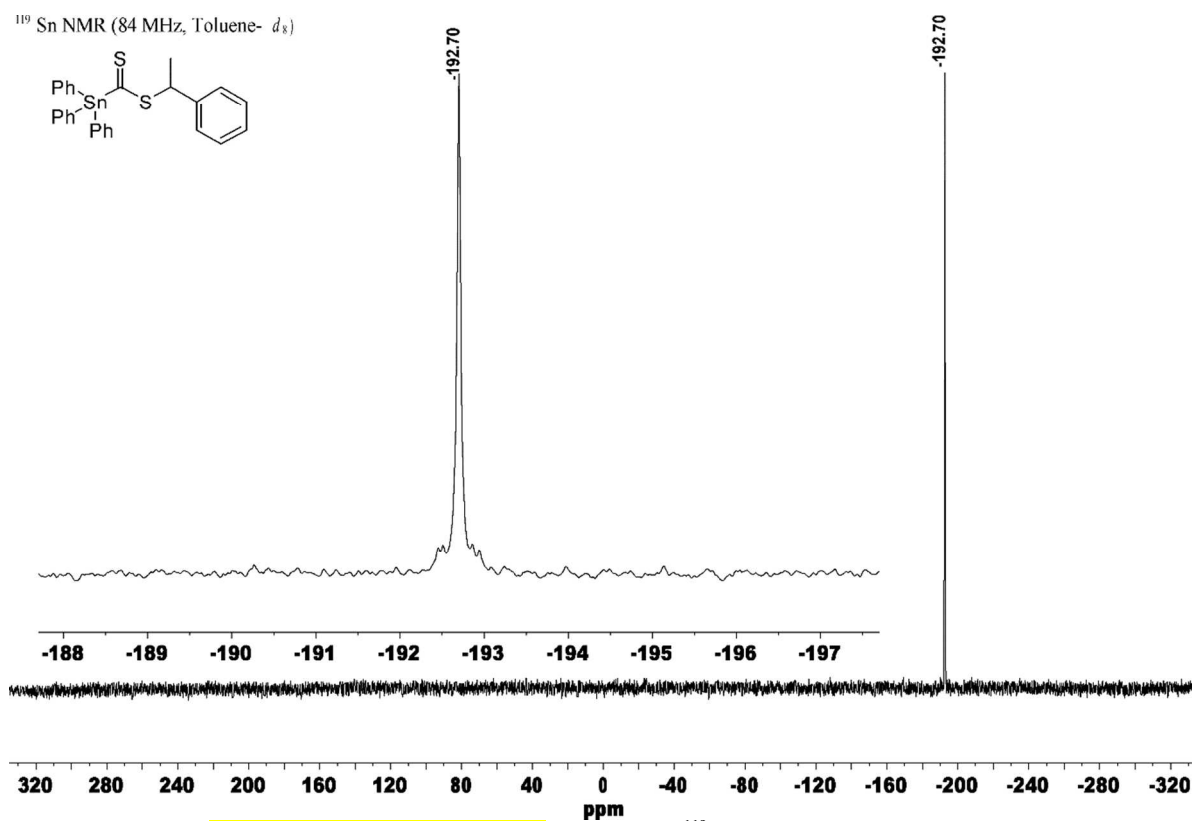


Figure S6. 1-Phenylethyl triphenylstannylcarbodithioate Sn-RAFT 2 ¹¹⁹Sn NMR spectrum.

III. POLYMERIZATION RESULTS

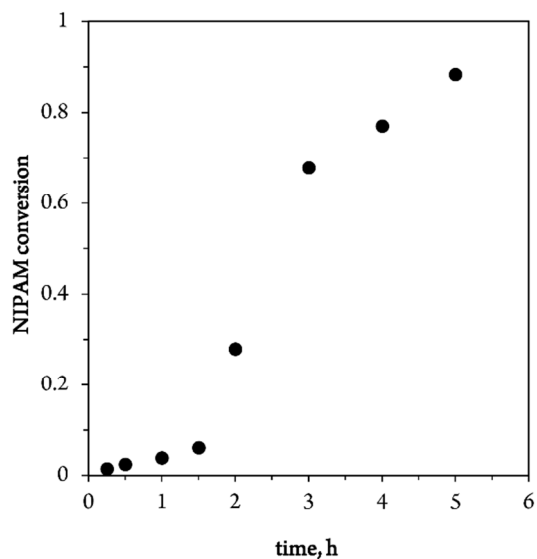


Figure S7. Kinetic plot for the polymerization of NIPAM mediated by Sn-RAFT 1 (Entries 1-4, Table 1).

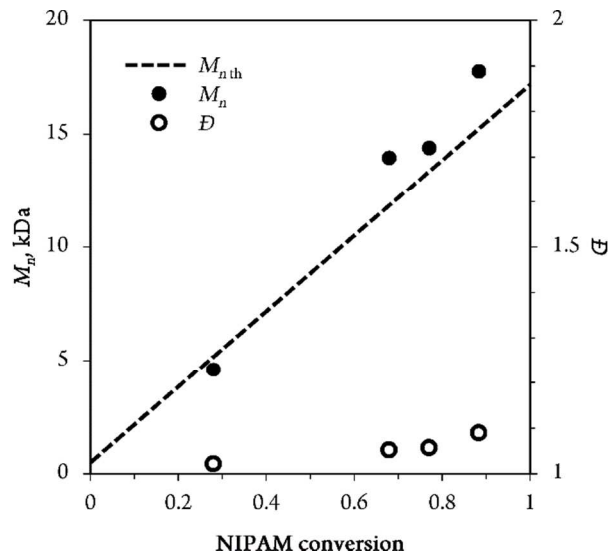


Figure S8. Evolution of M_n and \bar{D} during the polymerization of NIPAM mediated by Sn-RAFT 1 (Entries 1-4, Table 1).

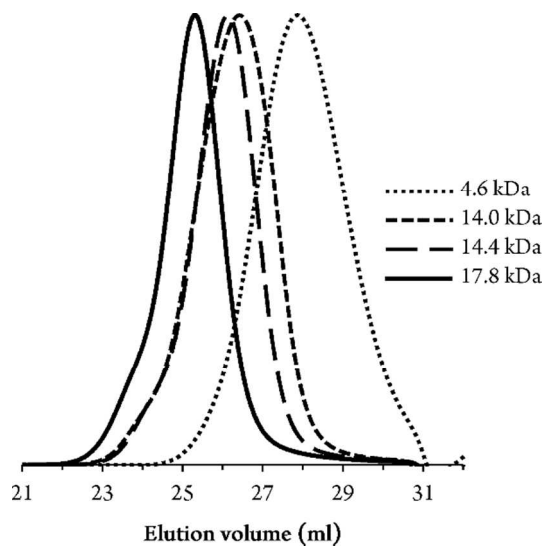


Figure S9. Overlay of SEC chromatograms for the polymerization of NIPAM mediated by Sn-RAFT 1 (Entries 1-4, Table 1).

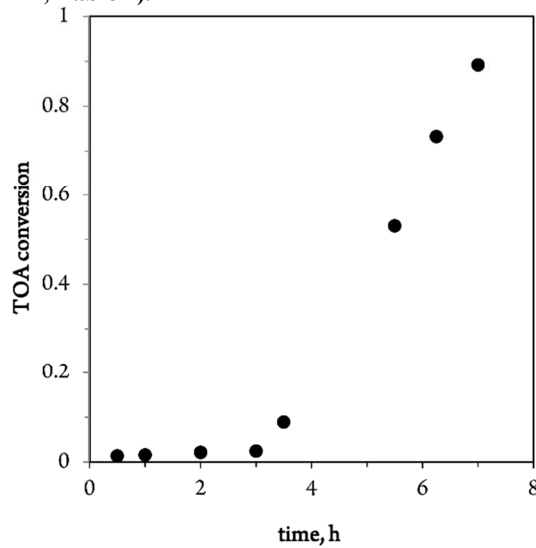


Figure S10. Kinetic plot for the polymerization of TOA mediated by Sn-RAFT 1 (Entries 5-8, Table 1).

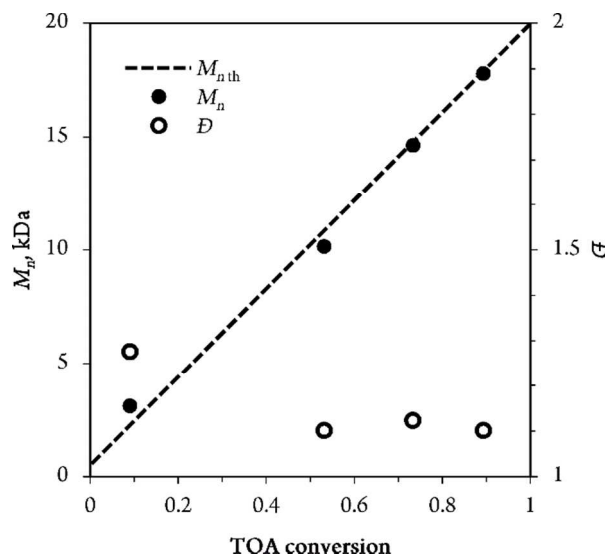


Figure S11. Evolution of M_n and \bar{D} during the polymerization of TOA mediated by Sn-RAFT 1 (Entries 5-8, Table 1).

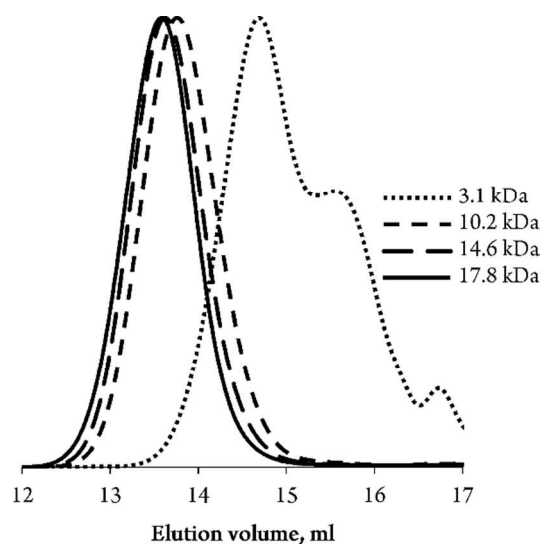


Figure S12. Overlay of SEC chromatograms for the polymerization of TOA mediated by Sn-RAFT 1 (Entries 5-8, Table 1).

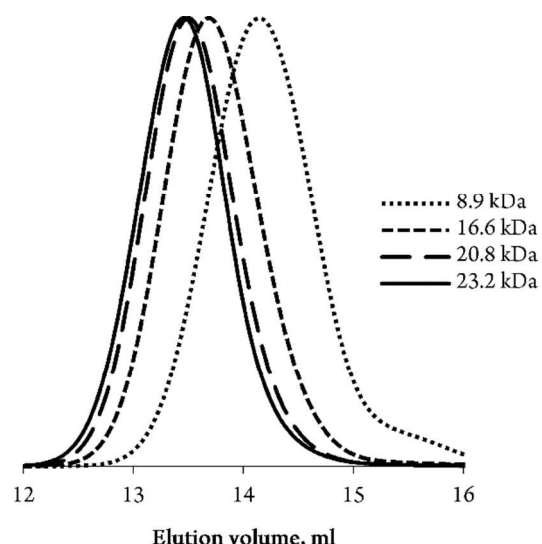


Figure S15. Overlay of SEC chromatograms for the polymerization of TOA mediated by Sn-RAFT 2 (Entries 9-12, Table 1).

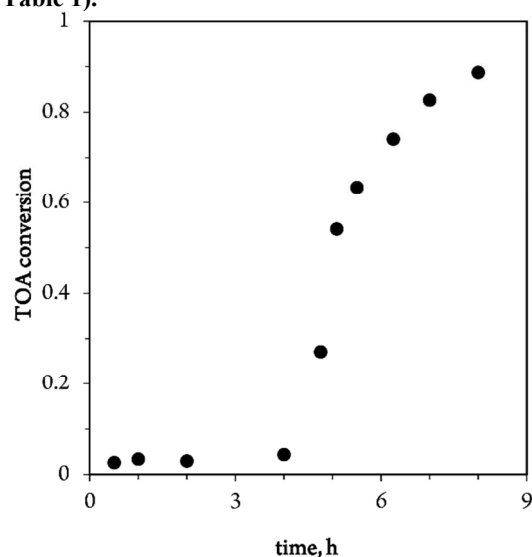


Figure S13. Kinetic plot for the polymerization of TOA mediated by Sn-RAFT 2 (Entries 9-12, Table 1).

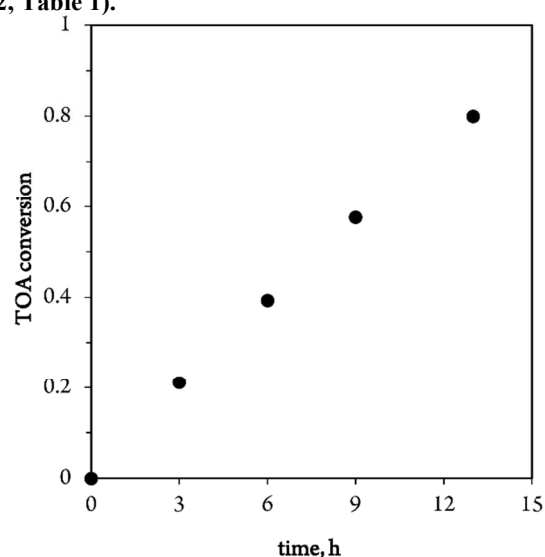


Figure S16. Kinetic plot for the chain extension of PTOA-1 7.8K (Entries 13-17, Table 1).

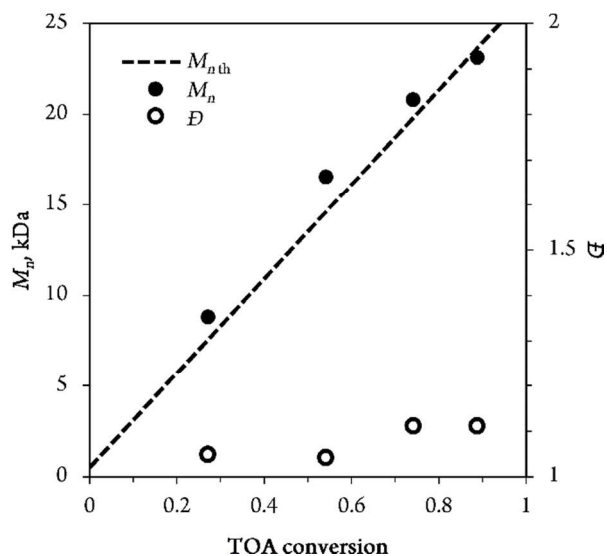


Figure S14. Evolution of M_n and \bar{D} during the polymerization of TOA mediated by Sn-RAFT 2 (Entries 9-12, Table 1).

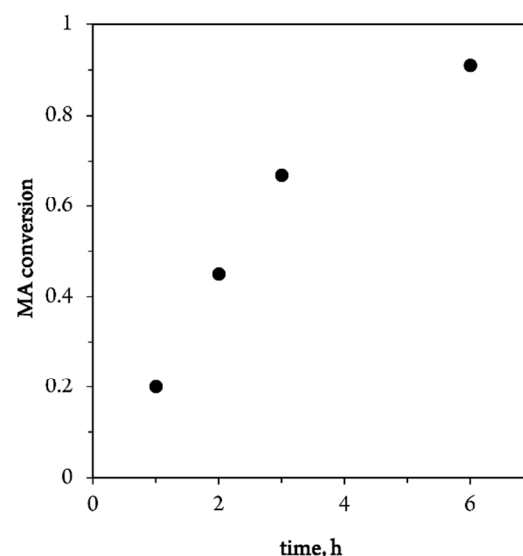


Figure S17. Kinetic plot for the polymerization of MA mediated by Sn-RAFT 2 (Entries 18-21, Table 1).

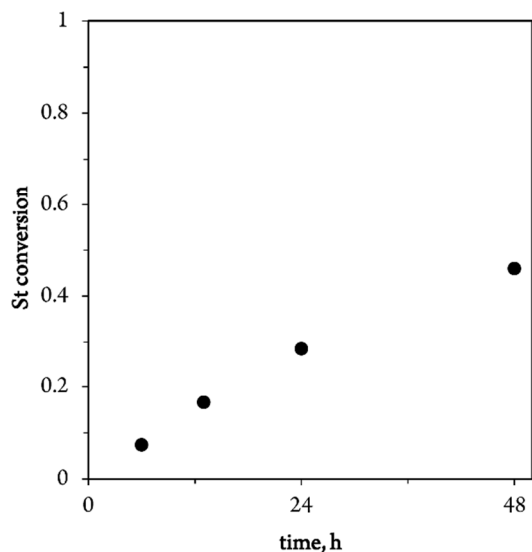


Figure S18. Kinetic plot for the polymerization of St mediated by Sn-RAFT 1 (Entries 22-25, Table 1).

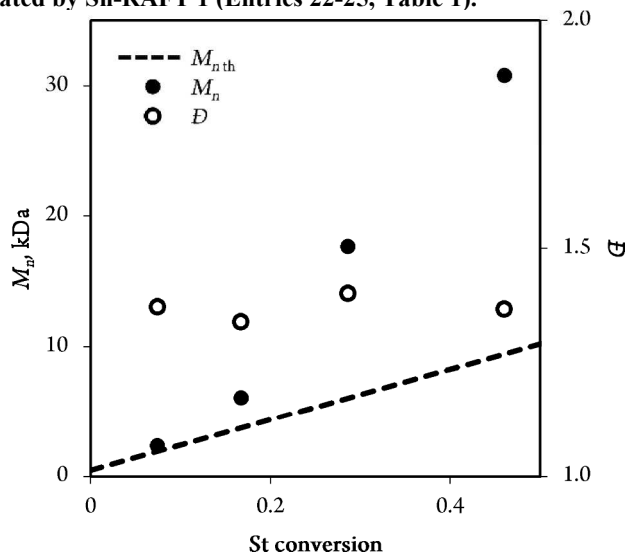


Figure S19. Evolution of M_n and \bar{D} during the polymerization of St mediated by Sn-RAFT 1 (Entries 22-25, Table 1).

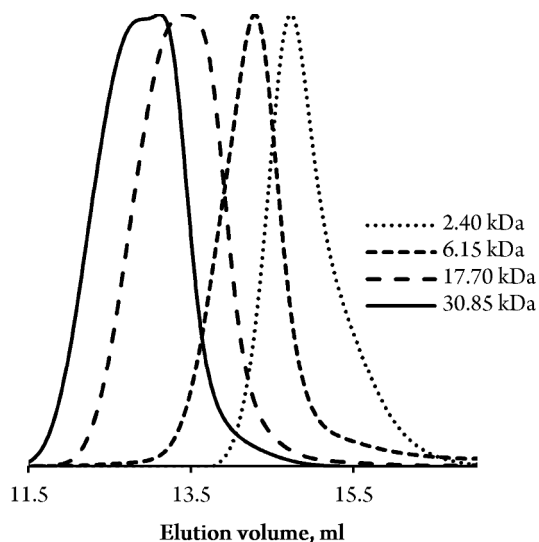


Figure S20. Overlay of SEC chromatograms for the polymerization of St mediated by Sn-RAFT 1 (Entries 22-25, Table 1).

IV. POLYMERIZATIONS WITH ^{119}Sn NMR MONITORING

Table S1. Polymerization of MA in C_6D_6 with Sn-RAFT 1 initiated with AIBN at 60 °C in NMR tubes.

t (h)	MA conv. (%)	1 conv. (%)	$M_{n,th}$ (kDa)	M_n (kDa)	\bar{D} M_w/M_n	[MA] mM	[1] mM	ln[MA]	ln[1]
0.5	0.8	31.5	0.73	N/A	N/A	8284.4	60.2	9.022	4.097
1	3.3	55	1.01	N/A	N/A	8075.7	39.5	8.997	3.677
1.5	6.2	68	1.26	0.95	1.27	7833.5	28.1	8.966	3.336
2	11.1	86	1.57	1.31	1.32	7424.3	12.3	8.913	2.509
3	23.1	98.5	2.44	2.78	1.42	6422.1	1.3	8.768	0.276
3.5	29.4	99	2.95	3.50	1.42				
4	42.8	99.5	4.04	4.29	1.29				
6	63.0	100	5.67	5.71	1.38				
8	77.5	100	6.86	8.88	1.38				

*[MA]₀ = 8.35 M, [1]₀ = 87.8 mM, [AIBN]₀ = 10.3 mM; Conversions and concentrations of Sn-RAFT 1 and MA were determined using ^{119}Sn and ^1H NMR respectively. M_n and \bar{D} were determined by SEC.

Table S2. Polymerization of St in C_6D_6 with Sn-RAFT 1 initiated with AIBN at 60 °C in NMR tubes.

t (h)	St conv. (%)	1 conv. (%)	$M_{n,th}$ (kDa)	M_n (kDa)	\bar{D} M_w/M_n	[St] mM	[1] mM	ln[St]	ln[1]
1	1.6	21	1.06	N/A	N/A	6783.5	79.2	8.822	4.373
2	2.4	39.5	0.95	N/A	N/A	6728.3	60.7	8.814	4.106
4	4.4	55.5	1.08	1.02	1.32	6590.5	44.6	8.793	3.799

6	7.9	66	1.37	1.35	1.35
8	11.3	77	1.57	1.55	1.37
15	24.0	92	2.38	2.24	1.40
24	34.8	95	3.14	3.68	1.44
39	51.5	99.5	4.22	5.64	1.39
54	60.0	100	4.81	7.15	1.38

*[St]₀ = 6.89 M, [1]₀ = 100.3 mM, [AIBN]₀ = 10.2 mM; Conversions and concentrations of Sn-RAFT 1 and MA were determined using ¹¹⁹Sn and ¹H NMR respectively. *M_n* and *Đ* were determined by SEC.

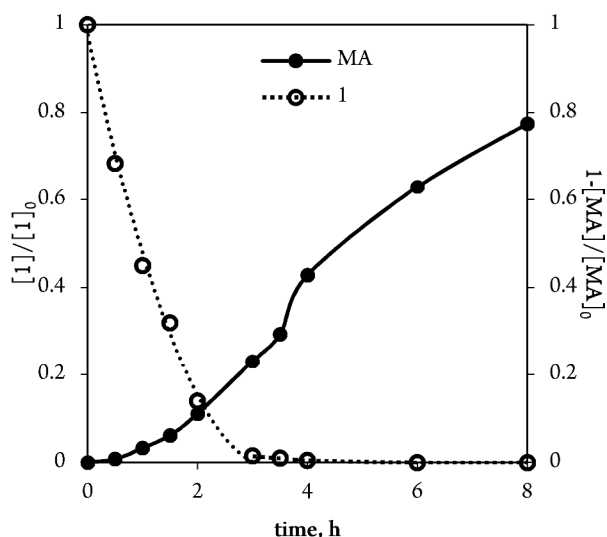


Figure S21. Kinetic plot for the polymerization of MA mediated by Sn-RAFT 1 in NMR tubes (Table S1).

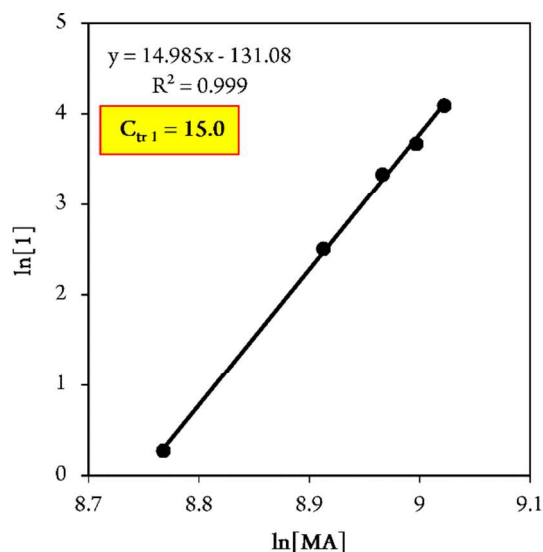


Figure S22. Determination of Ctr for the polymerization of MA mediated by Sn-RAFT 1 in NMR tubes (Table S1).

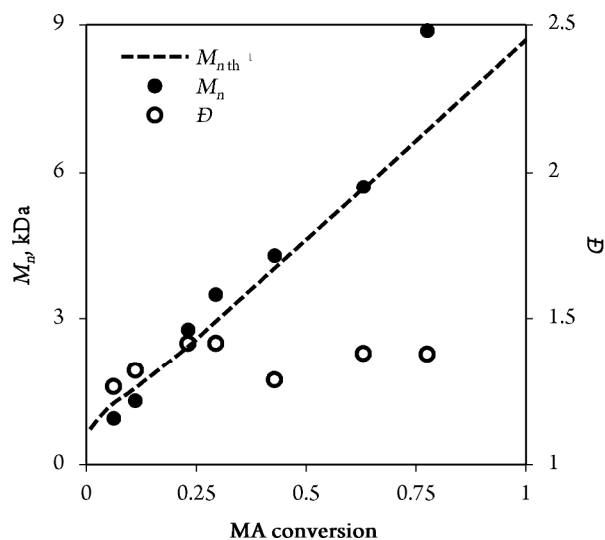


Figure S23. Evolution of *M_n* and *Đ* during the polymerization of MA mediated by Sn-RAFT 1 in NMR tubes (Table S1).

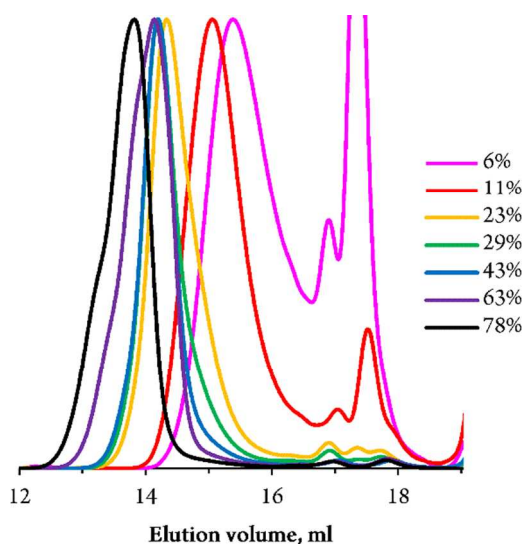


Figure S24. Overlay of SEC chromatograms for the polymerization of MA mediated by Sn-RAFT 1 in NMR tubes (Table S1).

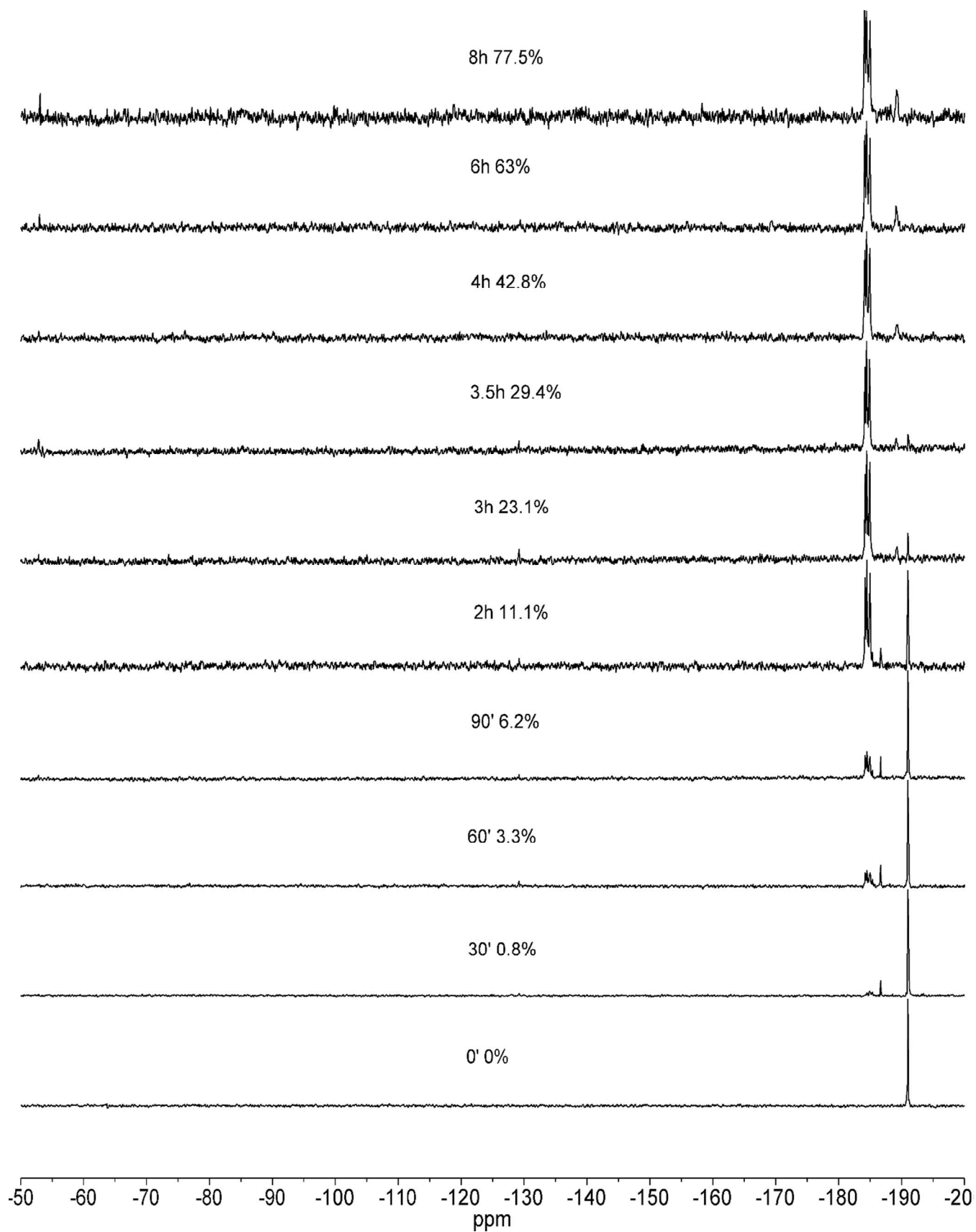


Figure S25. Overlay of ^{119}Sn NMR spectra for the polymerization of MA mediated by Sn-RAFT 1 in NMR tubes (Table S1).

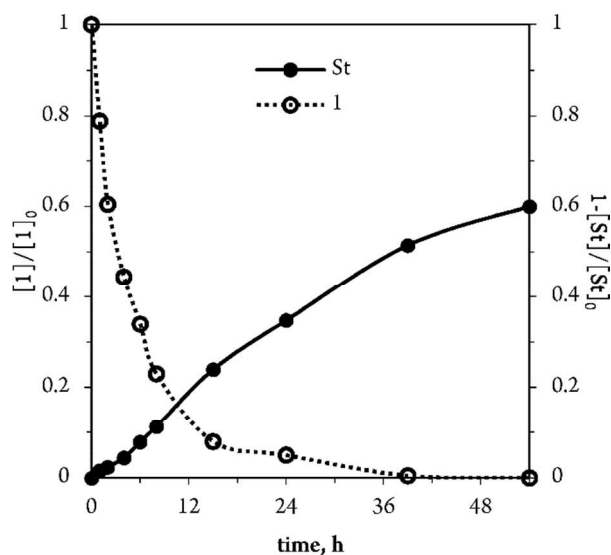


Figure S26. Kinetic plot for the polymerization of St mediated by Sn-RAFT 1 in NMR tubes (Table S2).

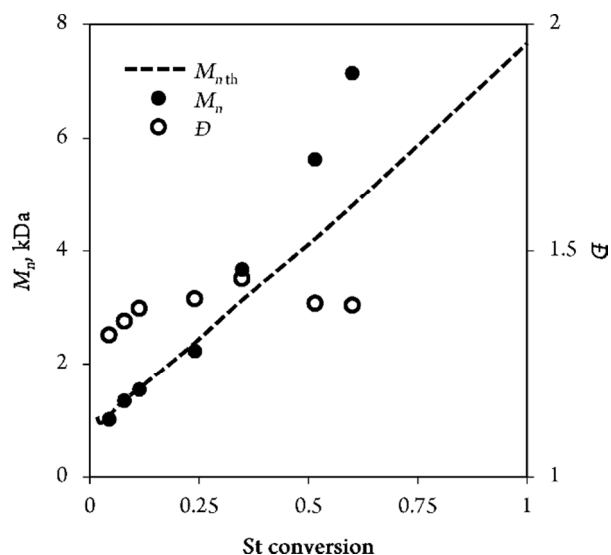


Figure S28. Evolution of M_n and \bar{D} during the polymerization of St mediated by Sn-RAFT 1 in NMR tubes (Table S2).

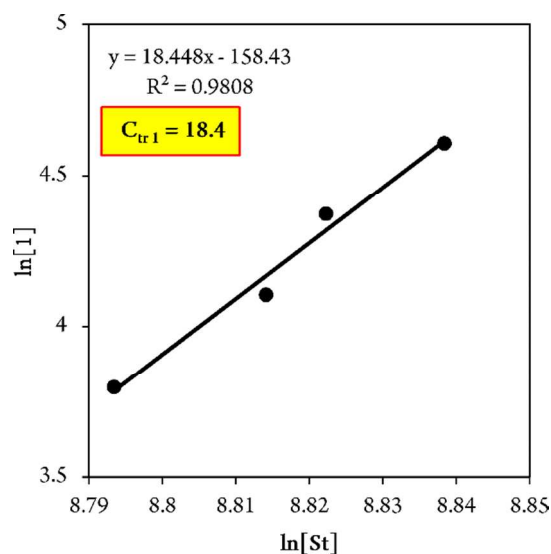


Figure S27. Determination of C_{tr} for the polymerization of St mediated by Sn-RAFT 1 in NMR tubes (Table S2).

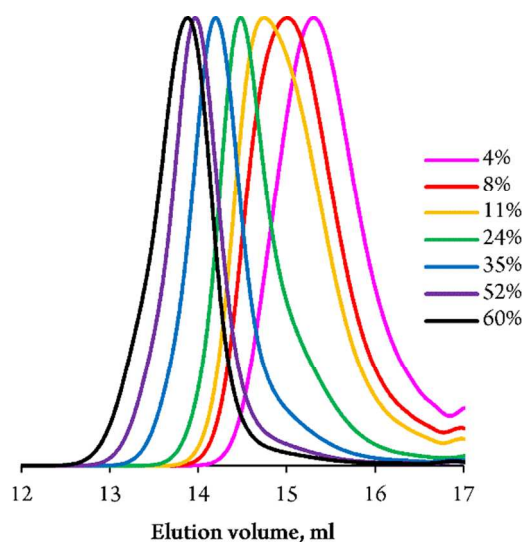


Figure S29. Overlay of SEC chromatograms for the polymerization of St mediated by Sn-RAFT 1 in NMR tubes (Table S2).

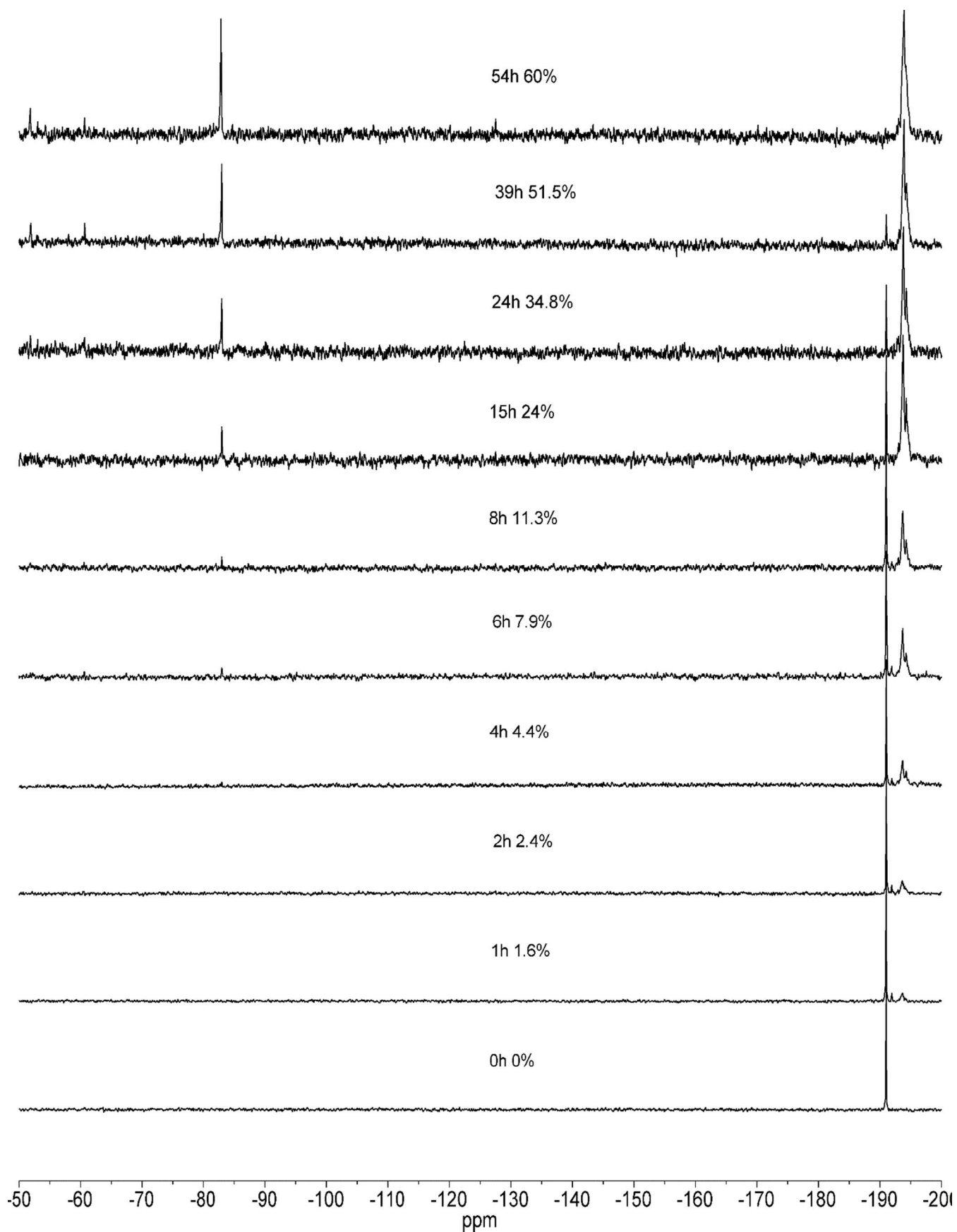


Figure S30. Overlay of ^{119}Sn NMR spectra for the polymerization of St mediated by Sn-RAFT 1 in NMR tubes (Table S2).