Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for

Role of Lewis Acids in Preventing the Degradation of Dithioester-Dormant Species in the RAFT Polymerization of Acrylamides in Methanol to Enable the Successful Dual Control of Molecular Weight and Tacticity

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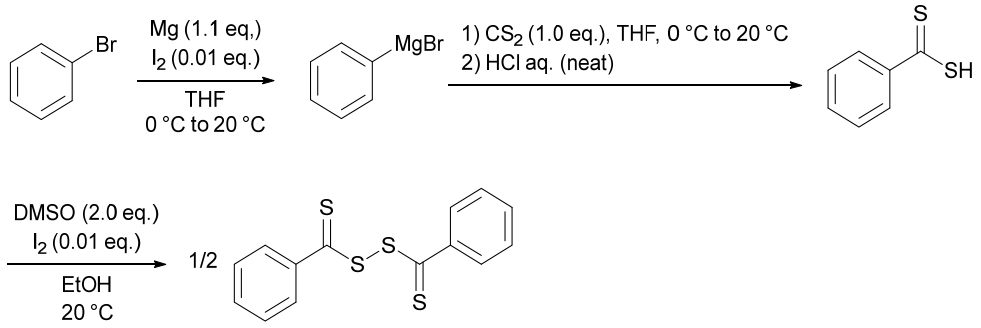
Table of Contents

1. Syntheses of CTAs 2a and 2b

1-1. Synthesis of bis(dithiobenzoyl) disulfide[1]

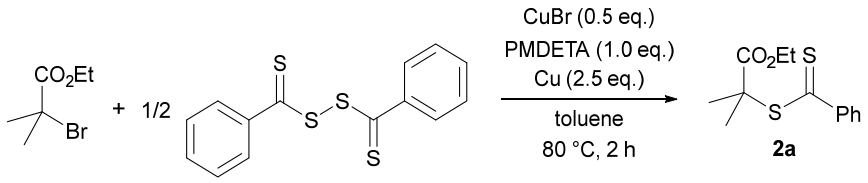


To a suspension of Mg turning (2.0 g, 82 mmol) and iodine (250 mg, 1.0 mmol) in 10 mL of THF was added bromobenzene (0.84 mL, 8.0 mmol) at 0 °C. The resulting mixture was stirred for at 0 °C till the reaction started (ca. 10 min). To this mixture was added a solution of bromobenzene (7.5 mL, 72 mmol) in 30 mL of THF for 30 min at 0 °C, and the resulting mixture was stirred for 1 h at room temperature. To this solution was added CS_2 (4.8 mL, 79 mmol) for 10 min at 0 °C, and the resulting solution was stirred for 1.5 h at room temperature. The solution was quenched by cooled water (100 mL) and was passed through a glass filter packed with celite with the aid of water. The solvent (THF) was removed under reduced pressure. To the remaining liquid was added concentrated aqueous HCl solution (12 mol L^{-1}, 10 mL), and benzodithioic acid was extracted by diethyl ether (200 mL × 3). The combined ether solution was dried over anhydrous magnesium sulfate and was filtrated. The solvent was removed under reduced pressure to give crude oil (12.6 g).

The crude oil was dissolved in EtOH (100 mL), and dimethyl sulfoxide (11.4 mL, 161 mmol) and iodine (250 mg, 1.0 mmol) were added. The resulting mixture was stirred for 25 h at room temperature. The precipitate was collected by suction filtration with the help of cooled EtOH. The product was dried under reduced pressure to give the title compound as reddish purple solid. (2.2 g, 18% yield). The product was sufficiently pure and used for the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) 7.43-7.48 (m, 4H, Ar*H*), 7.59-7.64 (m, 2H, Ar*H*), 8.07-8.10 (m, 4H, Ar*H*).

1-2. Synthesis of CTA 2a[2]

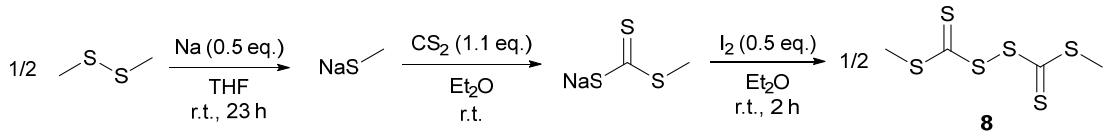


To a solution of bis(dithiobenzoyl) disulfide (0.49 g, 1.6 mmol), Cu (260 mg, 4.1 mmol) and CuBr (115 mg, 0.80 mmol) in toluene (20 mL) was added ethyl 2-bromoisobutyrate (470 μL, 3.2 mmol) and

N,*N*,*N*′,*N*′′,*N*′′-pentamethyldiethylenetriamine (PMDETA, 334 μL, 1.6 mmol) under nitrogen. The mixture was stirred for 2 h at 80 °C. The solution was passed through a glass filter packed with alumina with the aid of Et_2O, and solvent was removed under reduced pressure. Purification by preparative SEC (eluent: THF) gave pure **2a** (552 mg, 64% yield) as viscous red oil.

^{1}H NMR (400 MHz, $CDCl_3$) 1.24 (t, 7.2, 7.0 Hz, 3H, -CH_2CH_3), 1.76 (s, 6H, -$C(CO_2Et)(CH_3)_2$), 4.17 (q, 2H, 7.2, 7.0 Hz, -CH_2CH_3), 7.34-7.39 (m, 2H, Ar*H*), 7.50-7.55 (m, 1H, Ar*H*), 7.92-7.96 (m, 2H, Ar*H*).

1-3. Synthesis of disulfide 8[3]

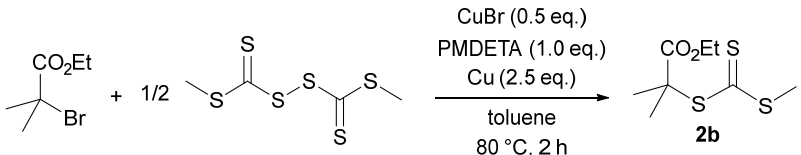


8

To a suspention of sodium (1.47 g, 64 mmol) in THF (150 mL) was added dimethyidisulfide (11.3 mL, 127 mmol), and the reaction mixture was stirred for 23 h at room temperature. The precipitated sodium methanethiolate was filtrated by suction filteration with an aid of Et_2O and dried under reduced pressure giving a white solid (4.31 g).[4] To a solution of this solid in Et_2O (180 mL) was added anhydrous CS_2 (4.1 mL, 68 mmol), and the mixture was stirred for 2 h at room temperature. Removal of the solvent under reduced pressure afforded sodium methyl trithiocarbonate (4.3 g, 48% yield).[5] A solution of sodium methyl trithiocarbonate (1.30 g, 8.9 mmol) and iodine (1.14 g, 4.5 mmol) in Et_2O (40 mL) was stirred for 2 h at room temperature. The solution was washed with aqueous saturated sodium thiosulfate solution (100 mL) and water (100 mL). The combined water phase was washed with Et_2O (50 mL × 3), and the combined organic phase was washed with aqueous saturated sodium chloride solution (50 mL) and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure giving disulfide **8** (1.01 g, 92% yield) as a yellow solid.[6] It was used for the next step without further purification (purity >97%).

^{1}H NMR (400 MHz, $CDCl_3$) 2.72 (s, 6H, -SCH_3).

1-4. Synthesis of CTA 2b

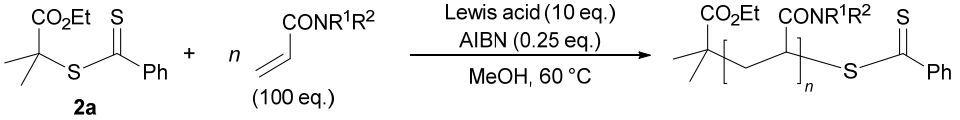


8 **2b**

To a solution of **8** (492 mg, 2.0 mmol), Cu (318 mg, 5.0 mmol) and CuBr (143 mg, 1.0 mmol) in toluene (25 mL) was added ethyl 2-bromoisobutyrate (557 μL, 3.8 mmol) and PMDETA (420 μL, 2.0 mmol), and the resulting mixture was stirred for 2 h at 80 °C. The solution was passed through a glass filter

packed with alumina with the aid of Et_2O, and the solvent was removed under reduced pressure to give oil. Purification by preparative SEC (eluent: THF) gave pure **2b** (100 mg, 11% yield) as yellow oil. IR (neat); 1732, 1466, 1421, 1381, 1364, 1261; HRMS (EI) *m/z*: Calcd for $C_8H_{14}O_2S_3$ $(M)^+$, 238.0156; Found 238.0154; ^{1}H NMR (400 MHz, $CDCl_3$) 1.25 (t, *J* = 7.0, 7.2 Hz, 3H, -CH_2CH_3), 1.70 (s, 6H, -CCH_3), 2.67 (s, 3H, -SCH_3), 4.17 (q, *J* = 7.0, 7.2 Hz, 2H, -CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) 14.16, 20.09, 25.48, 56.18, 62.15, 173.05, 222.03.

2. Polymerization



DEAA: $R^1 = R^2 = Et$, DMAA: $R^1 = R^2 = Me$, NIPAM: $R^1 = {}^iPr$, $R^2 = H$

2-1. RAFT polymerization of DEAA using YCl_3. A solution of **2a** (8.4 μl, 1.49 mol L^{-1} in methanol, 0.0125 mmol), DEAA (171 μl, 1.25 mmol), AIBN (40 μl, 0.078 mol L^{-1} in methanol, 0.0031 mmol), α,α,α-trifluorotoluene (15 μl, 0.125 mmol as an internal standard), YCl_3 (24 mg, 0.125 mmol) in methanol (0.80 mL) was heated at 60 °C. The monomer conversion was reached to 92% after 6 h. The polymer was purified by dyalysis and was dried under reduced pressure at 100 °C for overnight (126 mg, 79% yield). The SEC analysis determined M_n (= 12,600) and *Đ* (= 1.14). The ^{1}H NMR analysis (DMSO-d_6, 130 °C) determined *meso* diad selectivity (81% *m*).

2-2. RAFT polymerization of DMAA using $Y(OTf)_3$. A solution of **2a** (8.4 μl, 1.49 mol L^{-1} in methanol, 0.0125 mmol), DMAA (128 μl, 1.25 mmol), AIBN (40 μl, 0.078 mol L^{-1} in methanol, 0.0031 mmol), α,α,α-trifluorotoluene (15 μl, 0.125 mmol as an internal standard), $Y(OTf)_3$ (67 mg, 0.125 mmol) in methanol (0.36 mL) was heated at 60 °C. The monomer conversion was reached to 87% after 4.5 h. The crude mixture was diluted with 1 mL of methanol and the solution was poured into vigorously stirred of diethylether (100 mL). The product collected by suction filtration was dried under reduced pressure at 100 °C for overnight (120 mg, 97%). The SEC analysis determined M_n (= 17,500) and *Đ* (= 1.14), respectively. The ^{1}H NMR (DMSO-d_6, 130 °C) analysis determined *meso* diad selectivity (84% *m*).

2-3. RAFT polymerization of NIPAM using $Y(OTf)_3$. A solution of **2a** (5.1 μl, 1.49 mol L^{-1} in methanol, 0.0076 mmol), NIPAM (86 mg, 0.76 mmol), AIBN (24 μl, 0.078 mol L^{-1} in methanol, 0.0019 mmol), α,α,α-trifluorotoluene (19 μl, 0.15 mmol as an internal standard), $Y(OTf)_3$ (41 mg, 0.076 mmol) in methanol (0.49 mL) was heated at 60 °C. The monomer conversion was reached to 84% after 11 h. The crude mixture was diluted with 1 mL of methanol and the solution was poured into vigorously

stirred of diethylether (100 mL). The product collected by suction filtration was dried under reduced pressure at 100 °C for overnight (93 mg, 108%). The SEC analysis determined M_n (= 21,000) and $Đ$ (= 1.11), respectively. The ^{1}H NMR analysis (DMSO-d_6, 145 °C) determined *meso* diad selectivity (84% *m*).

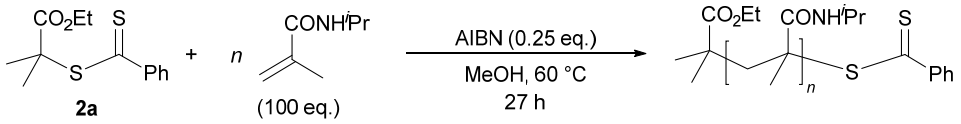
2-4. RAFT polymerization of DEAA using LiOTf. A solution of **2a** (8.4 μl, 1.49 mol L^{-1} in methanol, 0.0125 mmol), DEAA (171 μl, 1.25 mmol), AIBN (40 μl, 0.078 mol L^{-1} in methanol, 0.0031 mmol), α,α,α-trifluorotoluene (15 μl, 0.125 mmol as an internal standard), LiOTf (20 mg, 0.125 mmol) in methanol (0.80 mL) was heated at 60 °C. The monomer conversion was reached to 94% after 18 h. The crude mixture was diluted with 1 mL of methanol and the solution was poured into vigorously stirred of hexane (100 mL). The insoluble part was collected with acetone. The solution was evaporated and dried under reduced pressure at 100 °C for overnight (83 mg, 52%). The SEC analysis determined M_n (= 13,400) and $Đ$ (= 2.29), respectively. The ^{1}H NMR analysis (DMSO-d_6, 130 °C) determined *meso* diad selectivity (58% *m*).

Table S1. RAFT polymerization of DEAA in the presence of different metal triflates.[a]

run	Lewis acid	time (h)	conv. (%)[b]	$t_{1/2}$ (h)	$M_{n(SEC)}$[c] ×10^{-3}	$M_{n(NMR)}$[d] ×10^{-3}	$M_{n(theo)}$[e] ×10^{-3}	$Đ$[c]	*m* (%)[d]
1	LiOTf	18	94	3.2	13.4	14.3	12.2	2.29	58
2	NaOTf	10	81	4.7	12.7	15.8	10.6	2.48	54
3	KOTf	10	86	3.7	12.8	18.6	11.2	2.30	57
4	$Mg(OTf)_2$	18	97	3.0	10.8	12.2	12.6	2.30	56
5	$Ca(OTf)_2$	6	96	1.4	21.2	12.5	12.5	2.56	56
6	$Cu(OTf)_2$	22	2	–[f]	–[f]	–[f]	0.5	–[f]	–[f]
7	$Zn(OTf)_2$	18	82	6.2	10.4	10.2	10.7	1.30	56

[a]Polymerization was carried out by heating a solution of monomer, CTA **2a**, and AIBN in methanol at 60 °C with $[DEAA]_0$ = 1.56 mol L^{-1}. [b]Determined by ^{1}H NMR in DMSO-d_6 at 25 °C. [c]Determined by SEC with DMF containing LiBr (0.010 mol L^{-1}) at 40 °C against PMMA standards. [d]Determined by ^{1}H NMR in DMSO-d_6 at 130 °C. [e]Determined based on conversion of monomer. [f]Data could not be obtained.

2-5. RAFT polymerization of NIPMAM.



A solution of **2a** (8.4 μl, 1.49 mol L^{-1} in methanol, 0.0125 mmol), NIPMAM (159 mg, 1.25 mmol), AIBN (40 μl, 0.078 mol L^{-1} in methanol, 0.0031 mmol), α,α,α-trifluorotoluene (15 μl, 0.125 mmol as an internal standard), in methanol (0.80 mL) was heated at 60 °C. The monomer conversion was reached to 50% after 27 h. The SEC analysis determined M_n (= 8,200) and $Đ$ (= 1.21), respectively. The crude mixture was diluted with 1.0 mL of methanol and the 1.0 mL of the solution was poured into vigorously stirred of diethylether (40 mL). The product collected by suction filtration was dried under reduced pressure at 100 °C for 4 h (13 mg, 16%). The ^{1}H NMR analysis (DMSO-d_6, 100 °C) determined $M_{n(NMR)}$ of 7,100 which was close to $M_{n(theo)}$ (= 6,600). The ^{13}C NMR analysis (DMSO-d_6, 100 °C) determined triad selectivity (*mm*:*mr*:*rr* = ~0:29:71).

3. Supplementary material

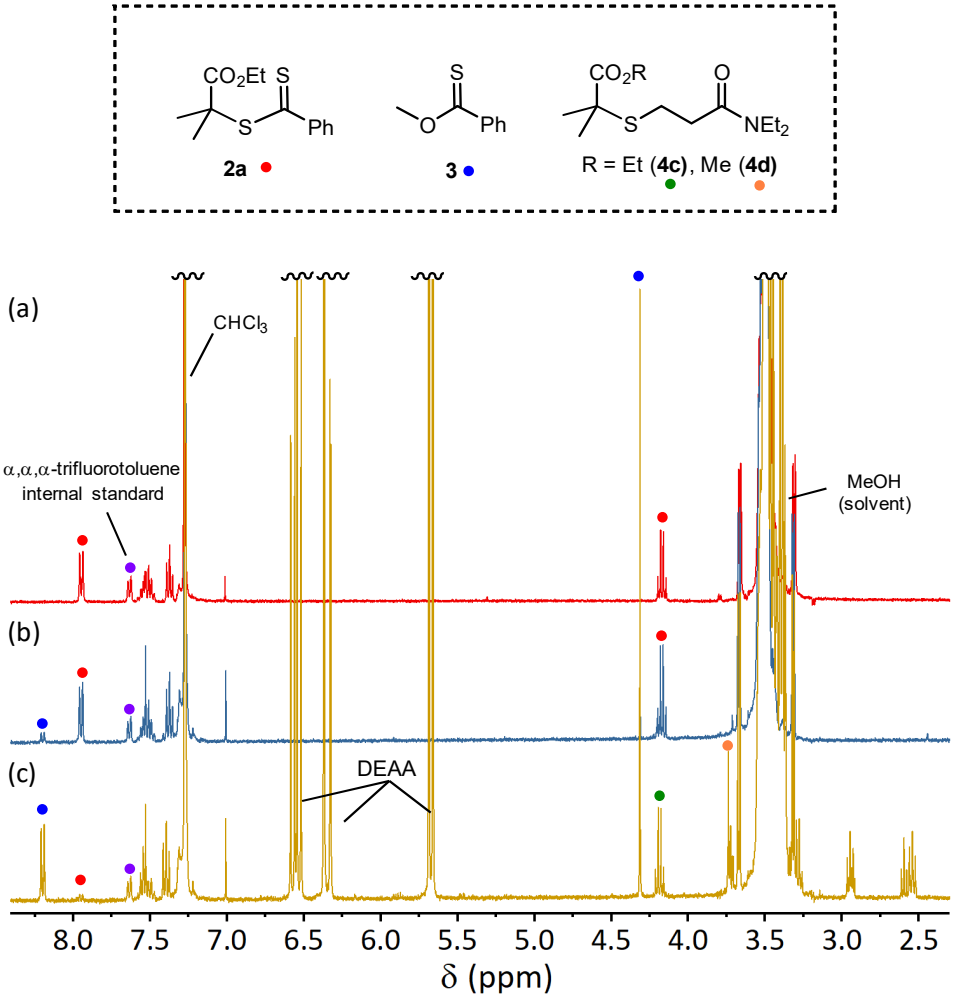


Figure S1. ^{1}H NMR spectra of reaction mixture during degradation of **2a** (a) before heating, (b) after heating at 60 °C for 21 h without DEAA, (c) after heating at 60 °C for 20 h with DEAA ($CDCl_3$, 25 °C).

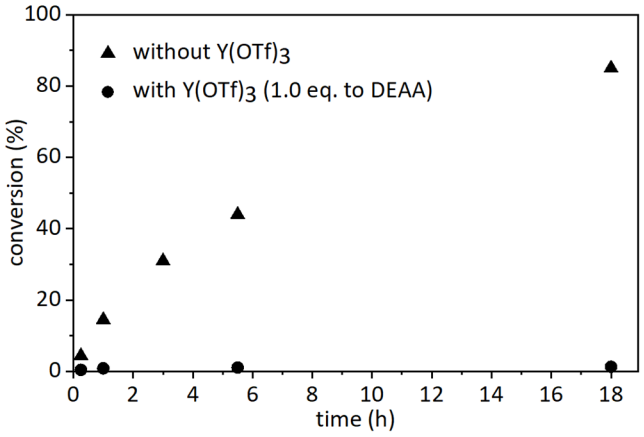


Figure S2. Effect of $Y(OTf)_3$ on the degradation of **2a**.

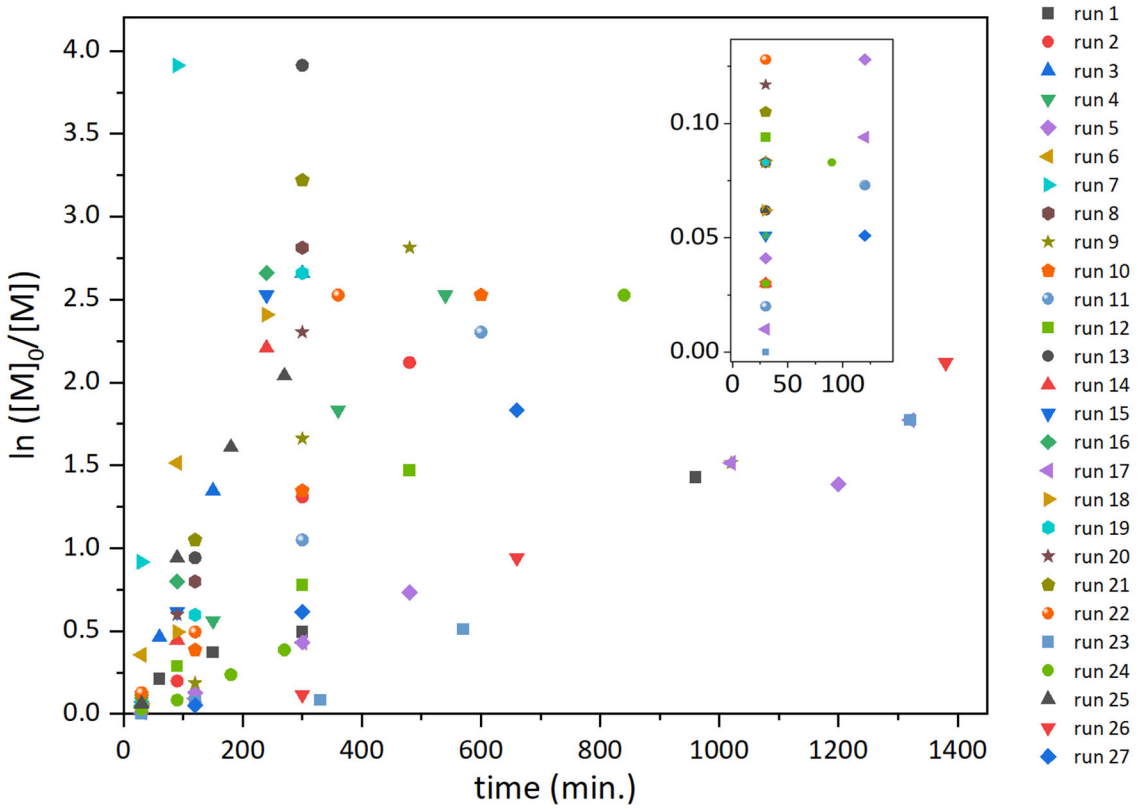


Figure S3. Kinetics of RAFT polymerization of DEAA, DMAA and NIPAM in the presence or absence of Lewis acids (Table 1, runs 1-27).

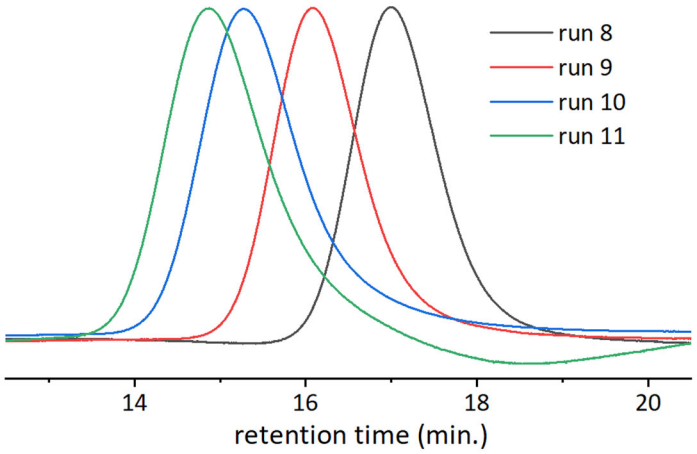


Figure S4. SEC traces of PDEAA with higher molecular weight (runs 8-11).

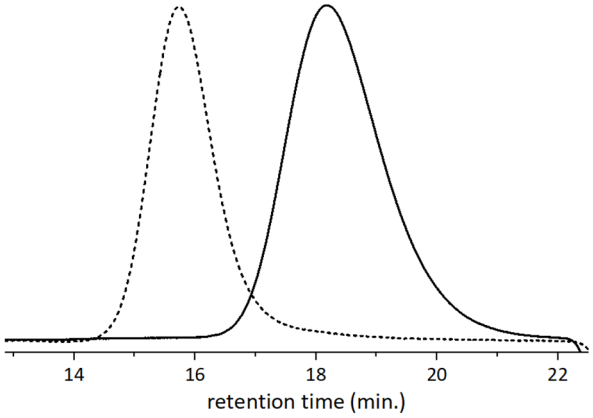


Figure S5. SEC traces of PDEAA synthesized with CTA **2b** [before (solid line) and after (dotted line) chain extension reaction (run 7)].

4. Spectra data

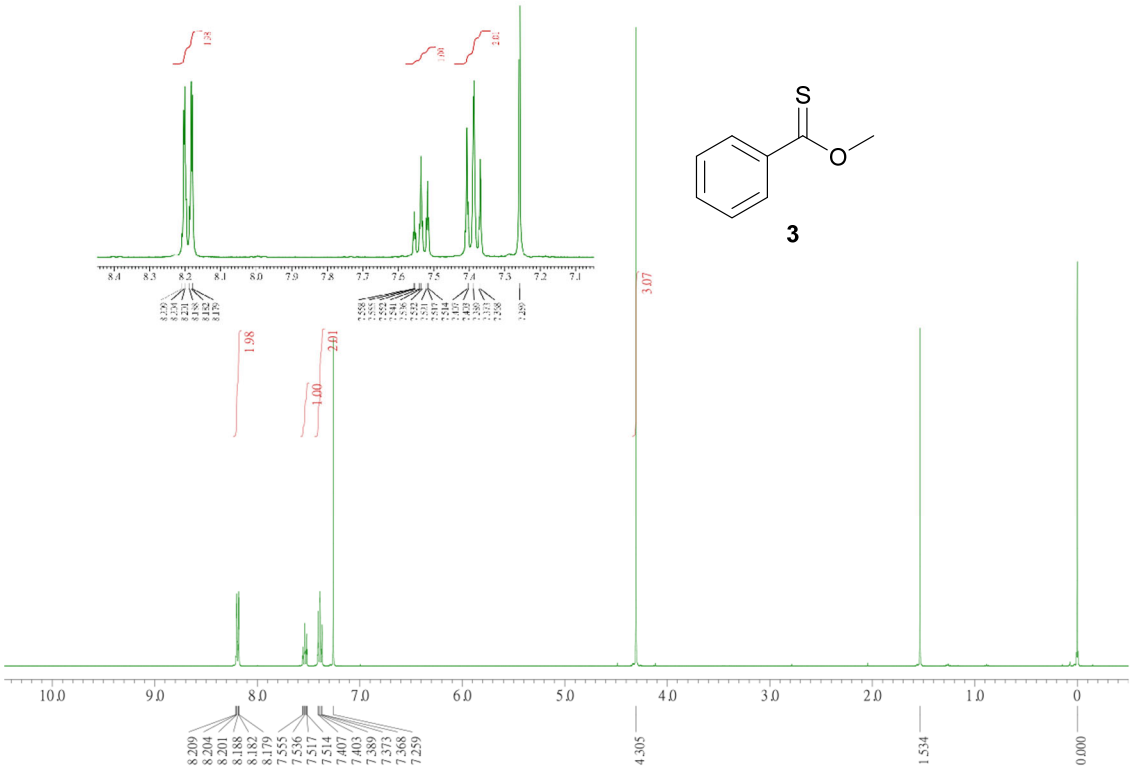


Figure S6a. ^{1}H NMR spectrum of **3**.

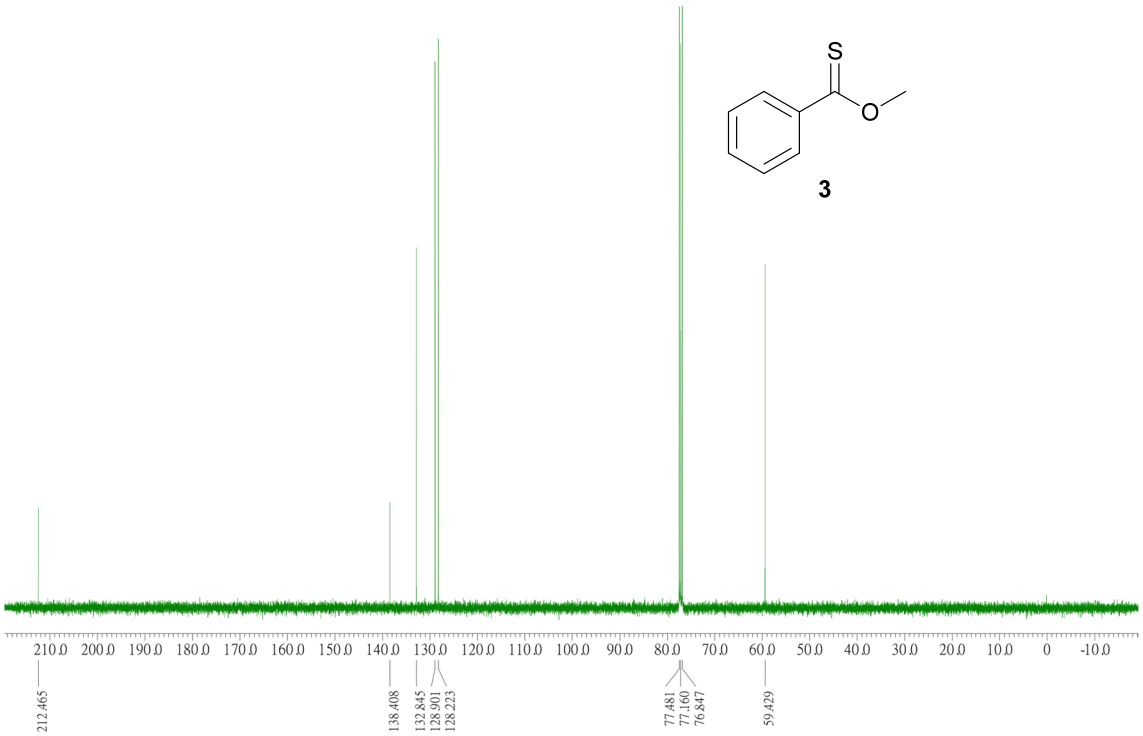


Figure S6b. ^{13}C NMR spectrum of **3**.

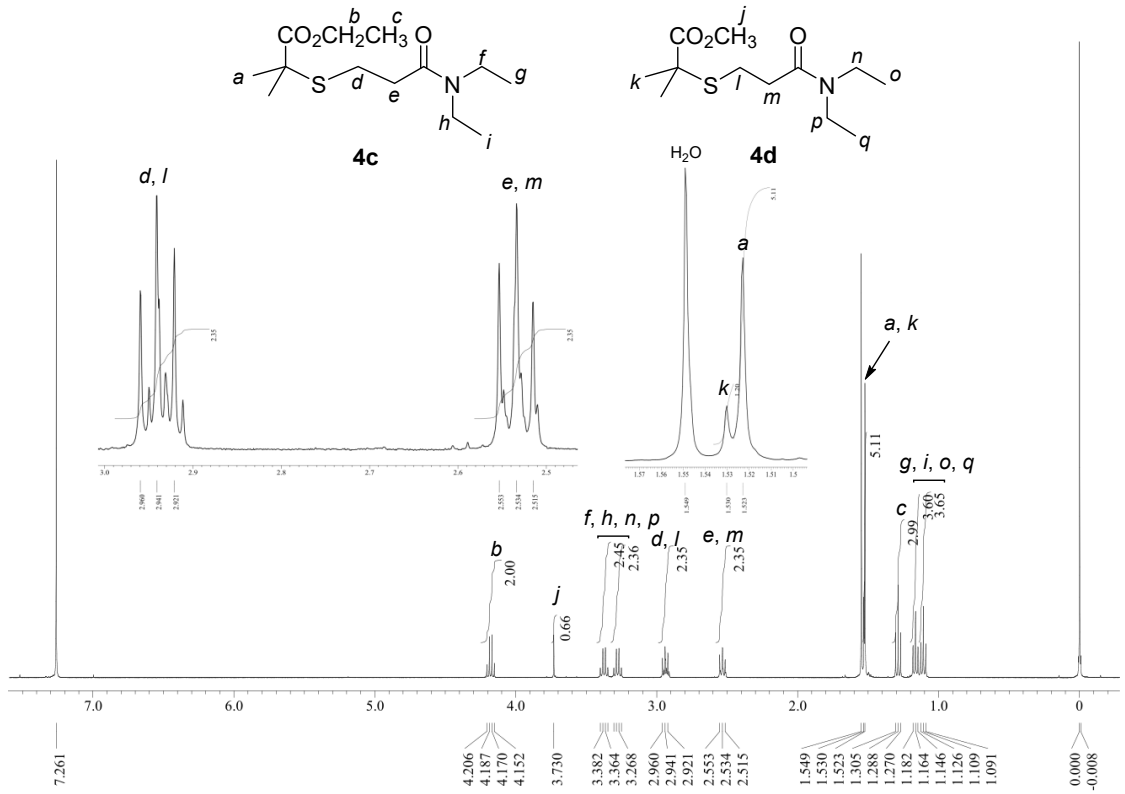


Figure S7a. ^{1}H NMR spectrum of mixture of **4c** and **4d**.

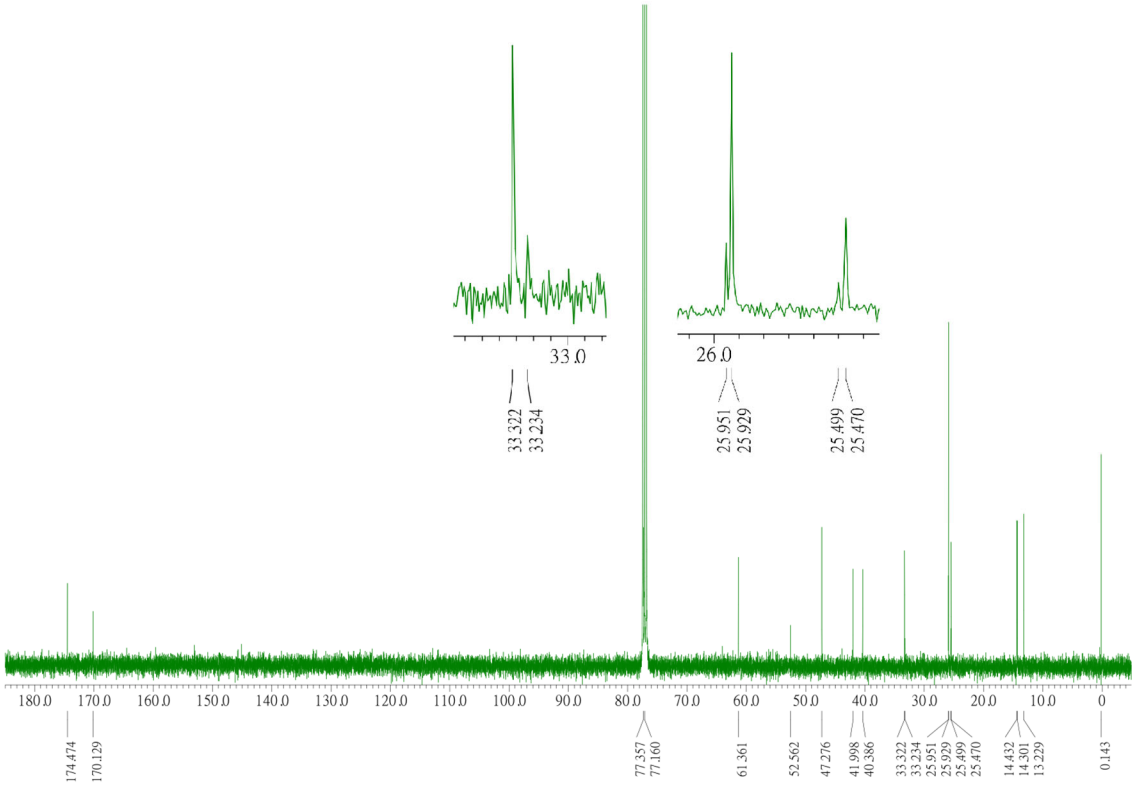


Figure S7b. ^{13}C NMR spectrum of mixture of **4c** and **4d**.

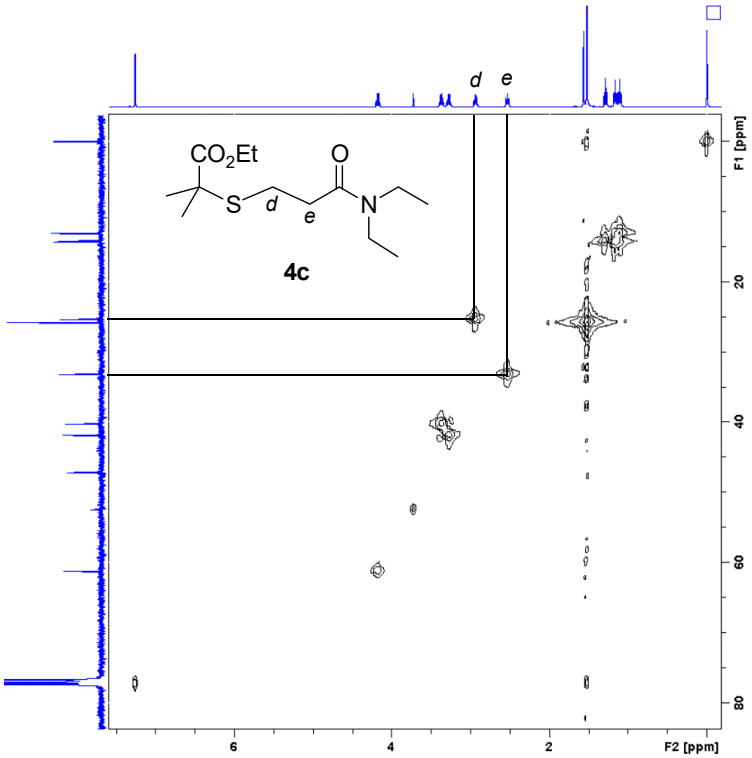


Figure S7c. HMQC spectrum of mixture of **4c** and **4d**.

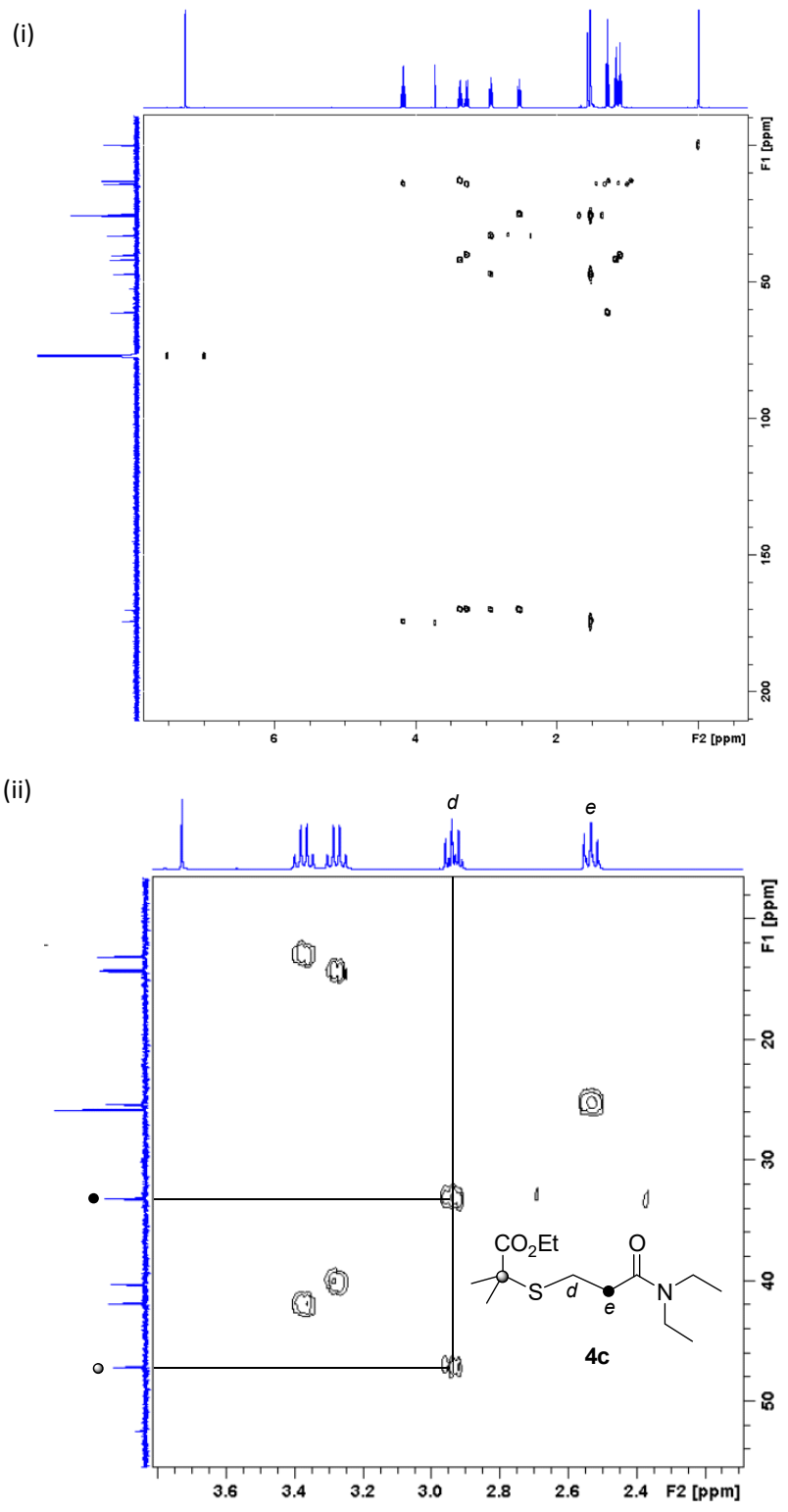


Figure S7d. HMBC spectrum of mixture of **4c** and **4d** [(i) whole (ii) part].

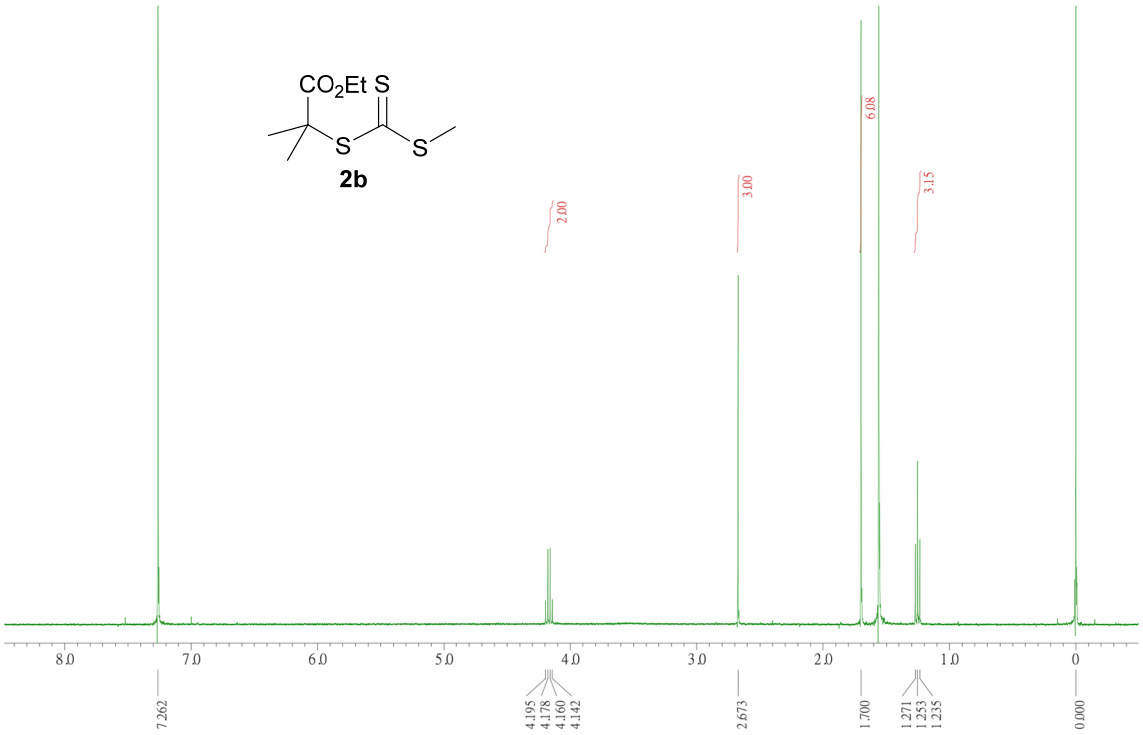


Figure S8a. ^{1}H NMR spectrum of **2b**.

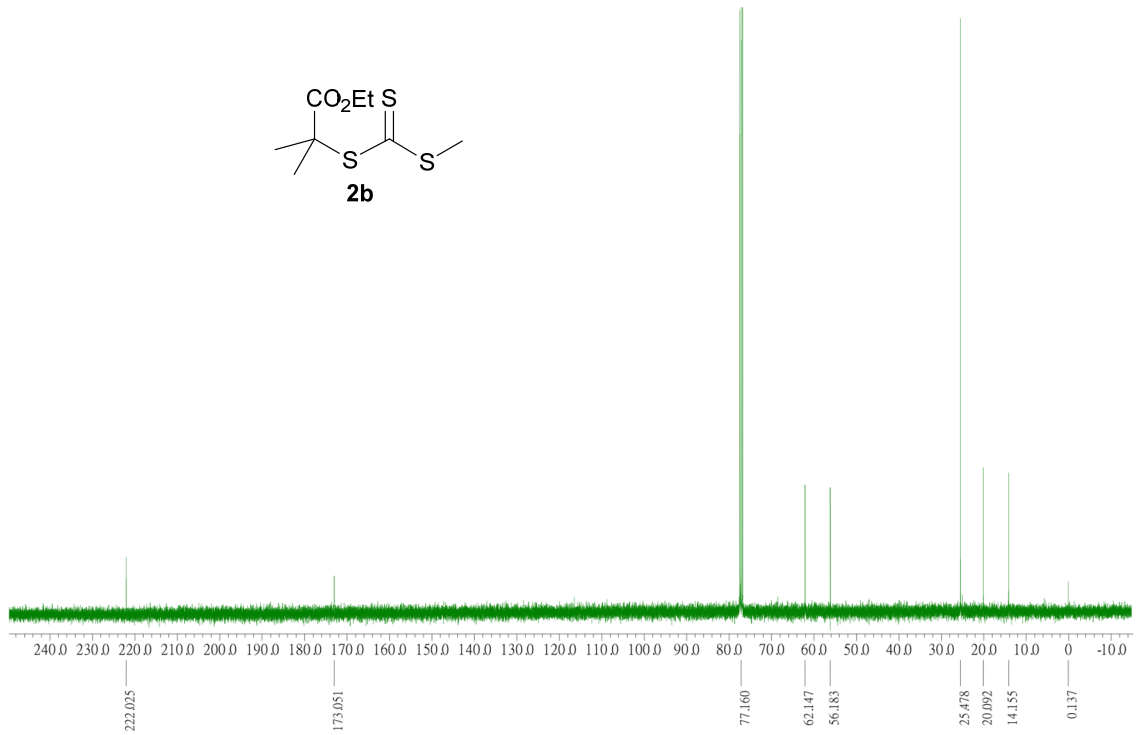


Figure S8b. ^{13}C NMR spectrum of **2b**.

[References]

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