

Supplementary Information

The Origin of Inhibition Effects in the Reversible Addition Fragmentation Chain Transfer (RAFT) Polymerization of Methyl Acrylate

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Syntheses of the various RAFT agents.

Synthesis of cumyl dithiobenzoate (CDB, 1, scheme 2)

Cumyl dithiobenzoate was synthesized using the following method. Benzyl chloride (12.6 g, 0.1 moles) was added dropwise over one hour to a round bottomed flask containing elemental sulfur (6.4 g, 0.2 moles), 30% sodium methoxide solution in methanol (36 g) and methanol (30 mL). The resulting brown solution was then heated and refluxed at 80°C overnight. After cooling to room temperature, the mixture was filtered to remove the white solid (sodium chloride) and then the methanol was removed via rotary evaporation. The resulting brown solid was then redissolved in distilled water (100 mL), and washed three times with diethyl ether (150 mL total). A final layer of ether was added to the solution and the two phase mixture was then acidified with 32% aqueous HCl until the aqueous layer lost its characteristic brown color and the top layer was deep purple. The ether layer was then dried over calcium chloride and the residual ether removed via rotary evaporation to leave the deep purple oil of dithiobenzoic acid. This acid was then dissolved in n-hexane (10 mL) and reacted with α -methylstyrene (20% excess) overnight in the presence of a small amount of acid catalyst (1%) (paratoluenesulfonic acid). The product was then isolated from residual α -methylstyrene and dithiobenzoic acid residue by column chromatography, using silica gel as the stationary phase with hexane as the eluent. The product identity was verified using $^1\text{H-NMR}$: (CDCl_3 , $\delta = 2.0\text{ppm}$ (s, 6H), $\delta = 7.2\text{-}7.6\text{ ppm}$ (m, 8H), $\delta = 7.9\text{ ppm}$ (d, 2H)). The purity of CDB was close to 98%.

Synthesis of 1-phenylethyl dithiobenzoate (1-PEDB, 2, scheme 2)

1-phenylethyl dithiobenzoate was synthesized using the following method. Benzyl chloride (12.6 g, 0.1 moles) was added dropwise over one hour to a round bottomed flask containing elemental sulfur (6.4 g, 0.2 moles), 30% sodium methoxide solution in methanol (36 g) and methanol (30 mL). The resulting brown solution was then heated and allowed to reflux at 80°C overnight. After cooling to room temperature, the mixture was filtered to remove the white solid (sodium chloride) and the methanol was subsequently removed via rotary evaporation. The resulting brown solid was then re-dissolved in distilled water (100 mL), and washed three times with diethyl ether (150 mL total). A final layer of ether was added to the solution and the two phase mixture was then acidified with 32% aqueous HCl until the aqueous layer lost its characteristic brown color and the top layer was deep purple. The etherous layer was then dried over calcium chloride and the residual ether removed via rotary evaporation to leave the deep purple oil of dithiobenzoic acid. This acid was then dissolved in n-hexane (10 mL) and reacted with styrene (20% excess) overnight in the presence of a small amount of acid catalyst (1%) (paratoluenesulfonic acid). The product was then isolated from residual styrene and dithiobenzoic acid residue by column chromatography, using silica gel as the stationary phase with hexane as the eluent. The product identity was verified using ¹H-NMR. (CDCl₃, δ = 1.8 ppm (d, 3H); δ = 5.2 ppm (q, 1H); δ = 7.2-7.6 ppm (m, 8H), δ = 7.9 ppm (d, 2H)). The purity of the RAFT agent was close to 98%.

Synthesis of 2-(2-cyanopropyl) dithiobenzoate (CPDB, 3, scheme 2)

2-(2-cyanopropyl) dithiobenzoate was synthesized using the following method. Benzyl chloride (12.6 g, 0.1 moles) was added dropwise over one hour to a round bottomed flask containing elemental sulfur (6.4 g, 0.2 moles), 25% sodium methoxide solution in methanol (40 g) and methanol (40 g). The resulting brown solution was then heated and allowed to reflux at 80°C overnight. After cooling to room temperature, the mixture was filtered to remove the white solid (sodium chloride) and the methanol was removed via rotary evaporation. The resulting brown solid was then re-dissolved in distilled water (100 mL), and washed three times with diethyl ether (3×50 mL). A final layer of ether (50 mL) was added to

the solution and the two phase mixture was then acidified with 32% aqueous HCl until the aqueous layer lost its characteristic brown color and the top layer was deep purple. The etherous layer was extracted (dithiobenzoic acid) and deionised water (120 mL) and 1.0 N NaOH (240 mL) were added to extract sodium dithiobenzoate to the aqueous layer. This washing process was repeated two more times to finally lead to a solution of sodium dithiobenzoate.

Potassium ferricyanide (13.17 g, 0.04 mol) was dissolved in deionized water (200 mL). Sodium Dithiobenzoate solution (140 mL) was transferred to a conical flask equipped with a magnetic stir bar. Potassium ferricyanide solution was added dropwise to the sodium dithiobenzoate via an addition funnel over a period of 1 h under vigorous stirring. The red precipitate was filtered and washed with deionized water until the washings became colorless. The solid was dried under vacuum at room temperature overnight. The product was recrystallized from ethanol.

A solution of AIBN (5.84 g, 0.021 mol) and bis(thiobenzoyl) disulfide (4.25 g, 0.014 mol) in ethyl acetate (80 mL) was heated at reflux for 18 h. After removal of the volatiles under vacuum the crude product was subjected to column chromatography with silica gel as the stationary phase and ethyl acetate : n-hexane (0.2:9.8) as eluent to afford 2-(2-cyanopropyl) dithiobenzoate as red liquid. The product identity was verified using $^1\text{H-NMR}$: (δ = 2.0 ppm (s, 6H); δ = 7.4 ppm (t, 2H), δ = 7.5 ppm (t, 1H), δ = 7.9 ppm (d, 2H)). The purity of CPDB was close to 97%.

Synthesis of 1-Methoxycarbonyl ethyl dithiobenzoate (1-MEDB, 4, scheme 2)

1-Methoxycarbonyl ethyl dithiobenzoate was synthesized using the following method. Phenyl magnesium bromide was prepared from bromobenzene (6.28 g, 0.04 mol) and magnesium turnings (1 g) in dry THF (30 mL). The solution was warmed to 40 °C and carbon disulfide (3.05 g, 0.04 mol) was added over 15 minutes while maintaining the reaction temperature at 40 °C. To the resultant dark brown solution was added methyl 2-bromopropionate (6 g, 0.036 mol). The reaction temperature was raised to 80 °C and maintained for 24 hours. Ice water (50 mL) was added and the organic products were extracted with diethyl ether (3 × 50 mL). The combined organic extracts were washed with water and dried over anhydrous magnesium sulfate. After removal of the volatiles under

vacuum the crude product was subjected to column chromatography with silica gel as the stationary phase and diethyl ether : n-hexane (1:9) as eluent to afford 1-methoxycarbonyl ethyl dithiobenzoate as red liquid. The product identity was verified using $^1\text{H-NMR}$: (CDCl_3 , δ = 1.8 ppm (d, 3H); δ = 3.1 ppm (q, 1H); δ = 3.7 ppm (s, 3H); δ = 7.4 ppm (t, 2H), δ = 7.5 ppm (t, 1H), δ = 7.9 ppm (d, 2H)). The purity of 1-MEDB was close to 98%.

Conversion, molecular weight and molecular weight distribution data.

Table A-1: Evolution of the monomer conversion number average molecular weight, M_n , and the polydispersity index, PDI , with time in the polymerization of methyl acrylate at 60 °C mediated by 1-PEDB in concentrations ranging from $1.9 \cdot 10^{-3} \text{ mol L}^{-1}$, $3.8 \cdot 10^{-3} \text{ mol L}^{-1}$, $7.7 \cdot 10^{-3} \text{ mol L}^{-1}$ to $17.4 \cdot 10^{-3} \text{ mol L}^{-1}$.

[RAFT]	time	Conversion	M_n	$M_{n(th)}$	PDI
(mol/L)	(h)	(%)	(g/mol)	(g/mol)	
$17.4 \cdot 10^{-3}$	2.0	0.6	-	-	-
	4.0	1.7	-	-	-
	6.0	3.5	-	-	-
	8.0	10.2	-	-	-
	10.0	12.9	-	-	-
$17.4 \cdot 10^{-3}$	2.0	0.6	-	-	-
	4.0	2.4	1,800	1,500	1.21
	6.0	6.5	5,500	3,900	1.09
	8.0	12.2	10,900	7,300	1.10
	10.0	15.9	13,300	9,500	1.11

$7.7 \cdot 10^{-3}$	1.0	0.3	-	-	-
	2.0	1.9	3,100	2,400	1.19
	3.0	6.2	11,900	7,800	1.08
	4.0	9.8	19,800	12,300	1.06
	5.0	13.6	26,100	17,000	1.08
$7.7 \cdot 10^{-3}$	1.0	0.3	-	-	-
	2.0	1.4	-	-	-
	3.0	6.7	-	-	-
	4.0	11.7	-	-	-
	5.0	12.5	-	-	-
$3.8 \cdot 10^{-3}$	0.5	0.2	-	-	-
	1.0	1.3	4,500	3,700	1.22
	1.5	4.9	20,000	14,200	1.08
	2.0	10.3	41,000	29,800	1.09
	2.5	12.2	50,700	35,100	1.08
$3.8 \cdot 10^{-3}$	1.0	2.8	-	-	-
	2.0	10.6	-	-	-
	3.0	18.8	-	-	-
	3.5	21.1	-	-	-
	4.0	24.5	-	-	-

$1.9 \cdot 10^{-3}$	0.3	0.1	-	-	-
	0.6	1.8	-	-	-
	1.0	6.2	-	-	-
	1.5	10.4	-	-	-
	2.0	15.9	-	-	-
$1.9 \cdot 10^{-3}$	0.3	0.1	-	-	-
	0.6	1.9	10,300	9,900	1.15
	1.0	6.2	37,300	31,900	1.08
	1.5	10.2	56,400	52,000	1.10
	2.0	14.9	79,000	75,800	1.11

Table A-2: Evolution of the monomer conversion number average molecular weight, M_n , and the polydispersity index, PDI , with time in the polymerization of methyl acrylate at 60 °C mediated by CPDB in concentrations ranging from $1.9 \cdot 10^{-3}$ mol L⁻¹, $3.8 \cdot 10^{-3}$ mol L⁻¹, $7.7 \cdot 10^{-3}$ mol L⁻¹ to $17.4 \cdot 10^{-3}$ mol L⁻¹.

[RAFT]	time	Conversion	M_n	$M_{n(th)}$	PDI
(mol/L)	(h)	(%)	(g/mol)	(g/mol)	
$17.4 \cdot 10^{-3}$	2.0	0.8	400	420	1.17
	4.0	3.0	2,500	1,600	1.13
	6.0	11.0	9,300	6,000	1.1
	8.0	14.4	8,900	7,800	1.09
	10.0	20.0	12,900	10,800	1.12

$17.4 \cdot 10^{-3}$	2.0	1.1	-	-	-
	4.0	4.5	-	-	-
	6.0	12.1	-	-	-
	8.0	15.2	-	-	-
	10.0	18.2	-	-	-
$7.7 \cdot 10^{-3}$	1.0	1.2	1,300	1,500	1.17
	2.0	6.8	13,000	8,500	1.09
	3.0	9.6	14,300	12,000	1.07
	4.0	15.9	18,200	19,800	1.19
	5.0	17.4	22,300	21,800	1.1
$7.7 \cdot 10^{-3}$	1.0	1.9	-	-	-
	2.0	7.3	-	-	-
	3.0	10.8	-	-	-
	4.0	14.8	-	-	-
	5.0	17.7	-	-	-
$3.8 \cdot 10^{-3}$	1.0	4.5	17,100	11,300	1.09
	2.0	13.9	32,000	34,700	1.17
	3.0	20.2	34,600	50,300	1.12
	4.0	29.8	-	-	-
	5.0	35.3	68,800	87,900	1.27

$3.8 \cdot 10^{-3}$	1.0	7.7	-	-	-
	2.0	14.0	-	-	-
	3.0	26.7	-	-	-
	4.0	31.9	-	-	-
	5.0	33.8	-	-	-
$1.9 \cdot 10^{-3}$	0.5	4.3	31,000	21,800	1.09
	1.0	11.3	69,000	57,200	1.11
	1.5	17.9	112,300	90,400	1.17
	2.0	24.5	142,200	124,100	1.18
	2.5	37.2	218,300	188,100	1.19
$1.9 \cdot 10^{-3}$	0.5	5.3	38,800	26,800	1.09
	1.0	10.9	69,600	55,200	1.11
	1.5	17.3	105,700	87,300	1.17
	2.0	22.9	150,600	115,700	1.23
	2.5	28.9	164,600	146,100	1.34

Table A-3: Evolution of the monomer conversion number average molecular weight, M_n , and the polydispersity index, PDI , with time in the polymerization of methyl acrylate at 60 °C mediated by 1-MEDB, CPDB, 1-PEDB and poly-methacryl dithiobenzoate at an initial concentration of $7.7 \cdot 10^{-3} \text{ mol L}^{-1}$.

RAFT agent	<i>time</i> (h)	<i>Conversion</i> (%)	M_n (g/mol)	$M_{n(th)}$ (g/mol)	<i>PDI</i>
PEDB	1.0	0.3	-	-	-
	2.0	1.9	3,100	2,400	1.19
	3.0	6.2	11,900	7,800	1.08
	4.0	9.8	19,800	12,300	1.06
	5.0	13.6	26,100	17,000	1.08
PEDB	1.0	0.3	-	-	-
	2.0	1.4	-	-	-
	3.0	6.7	-	-	-
	4.0	11.7	-	-	-
	5.0	12.5	-	-	-
CPDB	1.0	1.9	1,300	1,500	1.17
	2.0	7.3	13,000	8,500	1.09
	3.0	10.8	14,300	12,000	1.07
	4.0	14.8	18,200	19,800	1.19
	5.0	17.7	22,300	21,800	1.10
CPDB	1.0	1.2	-	-	-
	2.0	6.8	-	-	-
	3.0	9.6	-	-	-
	4.0	15.9	-	-	-
	5.0	17.4	-	-	-

MEDB	1.0	0.9	900	1,000	1.23
	2.0	9.6	8,000	11,200	1.18
	3.0	14.1	14,500	16,400	1.12
	4.0	16.5	21,400	19,200	1.11
	5.0	21.1	22,600	24,500	1.15
MacroRAFT	1.0	7.2	16,900	16,600	1.09
	2.0	14.7	19,400	25,500	1.11
	3.0	19.5	26,200	31,300	1.12
	4.0	25.4	35,400	38,400	1.17
	5.0	29.9	34,400	43,700	1.21

Fitting parameters.

Table B-1: Linear least squares regression parameters (equation $y = A x + B$) for Figure 1

[RAFT] (mol/L)	A	B	R²
17.4 10 ⁻³	0.0003	-0.0437	0.9209
7.7 10 ⁻³	0.0006	-0.0393	0.9633
3.8 10 ⁻³	0.0012	-0.0487	0.9847
1.9 10 ⁻³	0.0016	-0.0353	0.9900

Table B-2: Linear least squares regression parameters (equation $y = A x + B$) for**Figure 2**

[RAFT] (mol/L)	A	B	R ²
17.4 10 ⁻³	86,778	167.76	0.9963
7.7 10 ⁻³	198,419	405.96	0.9973
3.8 10 ⁻³	416,816	722.97	0.9990
1.9 10 ⁻³	527,050	1956.40	0.9955

Table B-3: Linear least squares regression parameters (equation $y = A x + B$) for**Figure 3**

[RAFT] (mol/L)	A	B	R ²
17.4 10 ⁻³	0.0004	-0.0433	0.9808
7.7 10 ⁻³	0.0007	-0.0174	0.9784
3.8 10 ⁻³	0.0012	-0.0033	0.9554
1.9 10 ⁻³	0.0020	-0.0115	0.995

Table B-4: Linear least squares regression parameters (equation $y = A x + B$) for Figure 4

[RAFT] (mol/L)	A	B	R ²
17.4 10 ⁻³	64,712	520.37	0.9602
7.7 10 ⁻³	113,330	2315.70	0.9151
3.8 10 ⁻³	166,372	7284.80	0.9624
1.9 10 ⁻³	563,630	8453.20	0.9919

Table B-5: Linear least squares regression parameters (equation $y = A x + B$) for Figure 7

RAFT agent	A	B	R ²
1-PEDB	0.0006	-0.0432	0.9620
CPDB	0.0007	-0.0232	0.9818
1-MEDB	0.0009	-0.0246	0.9612
Poly(methyl acrylate) macroRAFT agent	0.0012	0.0112	0.9970