

## **SUPPORTING INFORMATION**

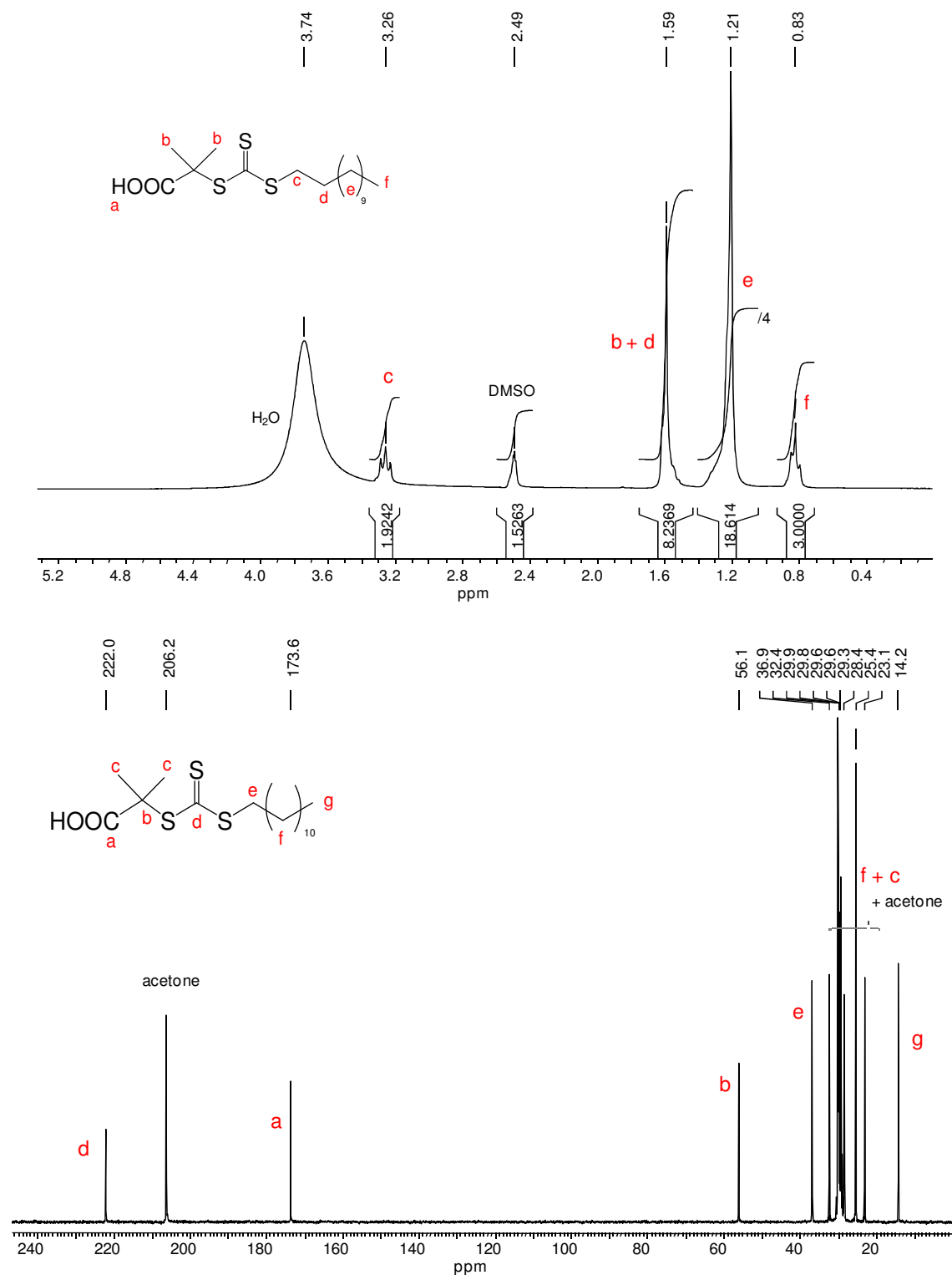
### **Surfactant-free RAFT emulsion polymerization using poly(*N,N*-dimethyl acrylamide) trithiocarbonate macromolecular chain transfer agents.**

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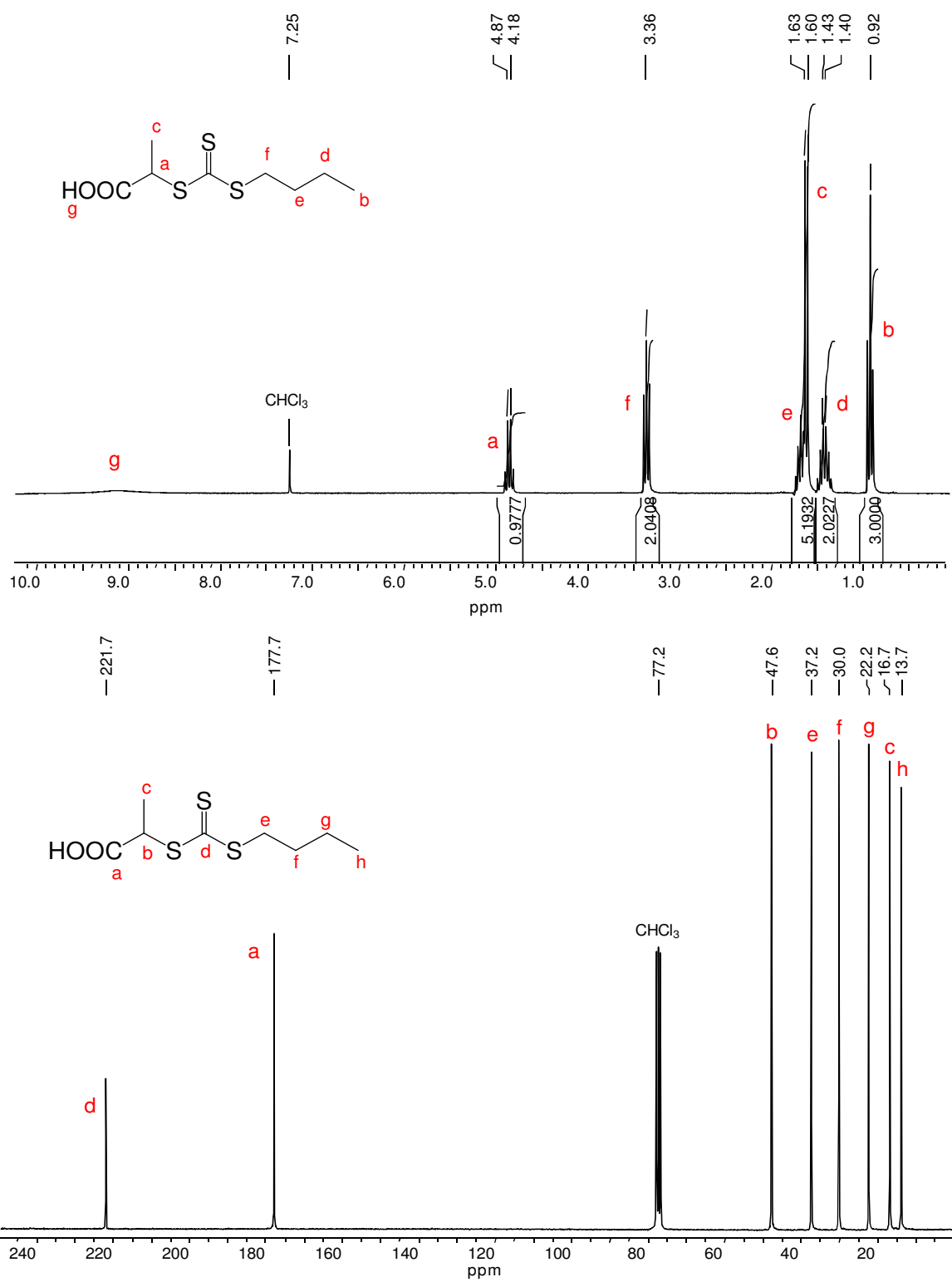
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# **A- NMR characterization of the RAFT agents TTCA-12, TTCA-4 and ATTCA**



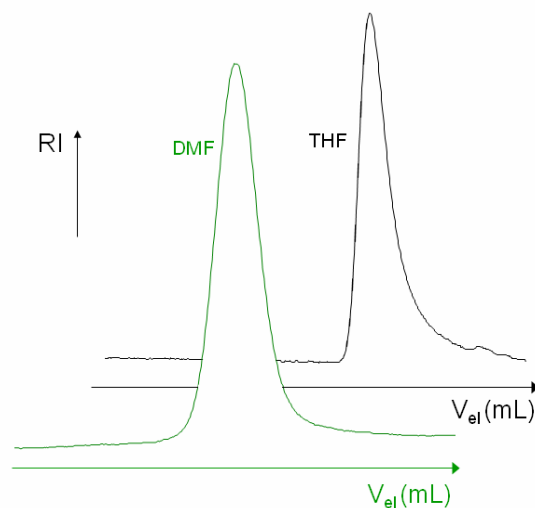
**Figure SI-1.** 250 MHz <sup>1</sup>H NMR spectrum of TTCA-12 in DMSO-d<sub>6</sub> and 63 MHz <sup>13</sup>C NMR spectrum in acetone-d<sub>6</sub>.



**Figure SI-2.** 250 MHz <sup>1</sup>H NMR and 63 MHz <sup>13</sup>C NMR spectra of TTCA-4 in CDCl<sub>3</sub>.



## **B- SEC characterization of the PDMAAm macroRAFT agents**



**Figure SI-4.** SEC chromatograms for the PDMAAm macroRAFT agent **B3** in THF and in DMF (see Table 1 in the article).

## **C- Solution polymerization of *n*-butyl acrylate and styrene in the presence of the PDMAAm macroRAFT agents and characterization of the formed diblock copolymers**

### **Solution polymerization of *n*-butyl acrylate (*n*BA)**

For the synthesis of PDMAAm-*Pn*BA block copolymers, polymerizations of *n*BA were performed in 1,4-dioxane at 70°C with ACPA as an initiator, in the presence of the different macromolecular RAFT agents (see Table SI-1 for detailed polymerization conditions). In a typical experiment (Table SI-1, entry **A2-S1**), the polymerization of 1.5 g *n*BA (4.0 mol.L<sup>-1</sup>) was carried out with 126 mg PDMAAm-TTC-12, **A2**, ( $M_n = 7300$  g.mol<sup>-1</sup>;  $5.8 \times 10^{-3}$  mol.L<sup>-1</sup>) in 1.3 mL of 1,4-dioxane with 1.1 mg ACPA (0.5 mL of a stock solution at 2.2 g.L<sup>-1</sup>). The solution was placed in a septum-sealed flask, purged for 30 min with nitrogen in an ice bath and heated to 70°C in a thermostated oil bath under stirring. Sampling was performed at regular time intervals, and the polymerization was stopped by immersion of the flask in iced water. The monomer conversion was determined by gravimetry.

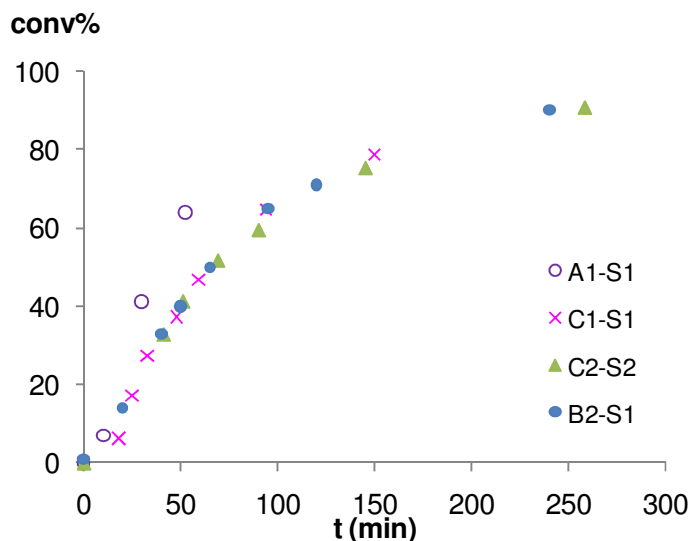
### **Solution polymerization of styrene (S)**

For the synthesis of PDMAAm-PS block copolymers, polymerizations of S were performed in 1,4-dioxane at 80°C with ACPA as an initiator, in the presence of the different macromolecular RAFT agents (see Table SI-2 for detailed polymerization conditions). In a typical experiment (Table SI-2, entry **A3-SS1**), the polymerization of 1.51 g S (2.0 mol.L<sup>-1</sup>) was carried out with 211 mg PDMAAm-TTC-12, **A3**, ( $M_n = 10700$  g.mol<sup>-1</sup>;  $2.7 \times 10^{-3}$  mol.L<sup>-1</sup>) in 5.6 mL of 1,4-dioxane with 1.3 mg ACPA (0.5 mL of a stock solution at 2.6 g.L<sup>-1</sup>). The solution was placed in a septum-sealed flask, purged for 30 min with nitrogen in an ice bath and heated to 80°C in a thermostated oil bath under stirring. The monomer conversion was determined by gravimetry.

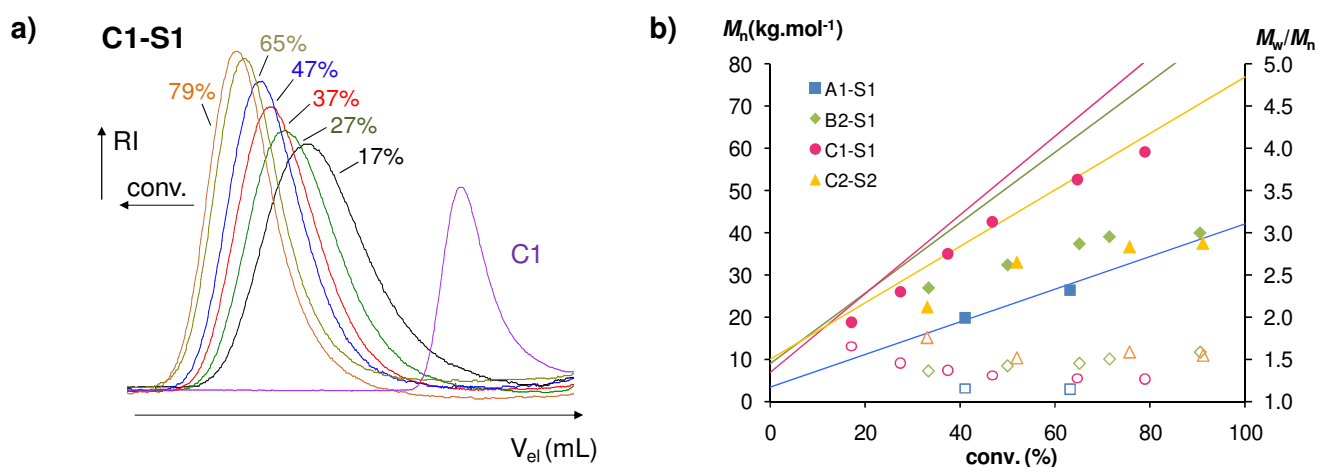
**Table SI-1.** Experimental conditions and results for the solution polymerizations of *n*BA in 1,4-dioxane at 70 °C in the presence of different PDMAAm-TTC macroRAFT agents.

Entry	Macro-RAFT		$[nBA]_0$ (mol.L <sup>-1</sup> )	$[Macro-RAFT]_0$ (mmol.L <sup>-1</sup> )	$[ACPA]_0$ (mmol.L <sup>-1</sup> )	DP <sub>n,th</sub> <sup>b</sup> <i>Pn</i> BA block	<i>t</i> (min)	conv. (%) <sup>c</sup>	$M_{n,th}$ <sup>b</sup> (kg.mol <sup>-1</sup> )	$M_{n,exp}$ <sup>d</sup> (kg.mol <sup>-1</sup> )	$M_w/M_n$ <sup>d</sup>
	#	$M_n$ <sup>a</sup>									
<b>A1-S1</b>	<b>A1</b>	3.2	4.0	13	2.7	300	30	42	19.1	19.9	1.15
							52	64	27.7	26.3	1.14
<b>A2-S1</b>	<b>A2</b>	7.3	4.0	5.8	1.4	690	25	25	35.4	42.5	1.27
							90	35	43.3	48.7	1.22
<b>A2-S2<sup>e</sup></b>	<b>A2</b>	7.3	bulk	8.9	0.9 <sup>d</sup>	790	160	70	78.0	77.9	1.16
<b>B1-S1</b>	<b>B1</b>	4.2	2.0	2.8	0.7	710	100	43	43.2	28.4	1.36
							190	73	70.3	38.5	1.46
							270	87	83.0	42.0	1.50
<b>B2-S1</b>	<b>B2</b>	8.7	2.0	3.1	0.7	650	40	33	36.4	26.7	1.36
							65	50	50.6	32.2	1.42
							240	90	84.1	39.8	1.58
<b>B3-S1</b>	<b>B3</b>	12.4	4.0	6.6	1.4	600	43	66	63.4	50.7	1.28
<b>C1-S1</b>	<b>C1</b>	6.6	4.0	5.5	1.3	730	48	37	41.7	35.1	1.35
							94	65	67.6	52.6	1.27
							150	79	80.7	59.0	1.26
<b>C2-S1</b>	<b>C2</b>	9.8	4.0	6.5	1.3	620	31	19	24.9	15.7	1.81
							51	33	35.9	23.8	1.56
<b>C2-S2</b>	<b>C2</b>	9.8	2.0	3.8	0.8	520	41	33	31.9	22.3	1.75
							69	52	44.7	33.0	1.51
							145	76	60.8	36.7	1.52
							258	91	70.9	37.5	1.54

<sup>a</sup>  $M_n$  determined by SEC in DMF by light scattering (LS) ( $dn/dc = 0.081 \text{ mL.g}^{-1}$ ); <sup>b</sup> theoretical number-average molar mass,  $M_{n,th}$ , and number-average degree of polymerization,  $DP_n$ , calculated using conversion<sup>c</sup>; <sup>c</sup> Monomer conversion determined by gravimetry; <sup>d</sup>  $M_n$  and  $M_w/M_n$  determined by SEC in THF with a PS calibration; <sup>e</sup> Experiment **A2-S2** was performed in bulk with 2,2'-azobis(isobutyronitrile) (AIBN) as initiator.



**Figure SI-5.** Evolution of the monomer conversion with time for the solution polymerization of *n*BA in the presence of different PDMAAm macroRAFT agents ( $[nBA]_0 = 2 \text{ mol.L}^{-1}$  (**B2-S1**, **C2-S2**) or  $4 \text{ mol.L}^{-1}$  (**A1-S1**, **C1-S1**),  $[ACPA]_0 = 0.7 \text{ mmol.L}^{-1}$  (**B2-S1**),  $0.8 \text{ mmol.L}^{-1}$  (**C2-S2**),  $1.3 \text{ mmol.L}^{-1}$  (**C1-S1**) or  $2.7 \text{ mmol.L}^{-1}$  (**A1-S1**\*). \*The higher initiator concentration being responsible for the faster kinetics.

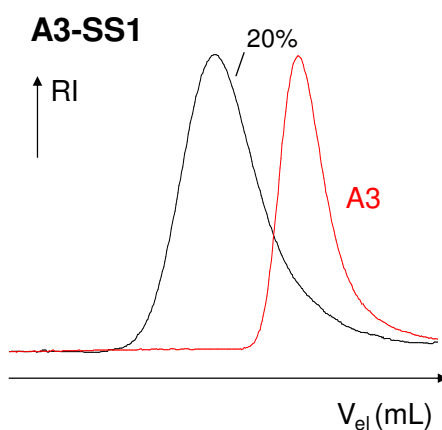


**Figure SI-6.** Solution polymerization of *n*BA in 1,4-dioxane in the presence of different PDMAAm macroRAFT agents (**A1**, **B2**, **C1** and **C2**): a) an example of the evolution of the size exclusion chromatograms with monomer conversion (Experiment **C1-S1**); b) evolution of the number average molar mass,  $M_n$ , (full symbols) and polydispersity index ( $M_w/M_n$ ) (open symbols) with time (determined by SEC in THF and calculated with a PS calibration curve). The straight lines correspond to the theoretical  $M_n$  vs. conversion.

**Table SI-2.** Experimental conditions and results for the solution polymerizations of styrene (S) in 1,4-dioxane at 80 °C in the presence of PDMAAm-TTC-12, **A1** and **A3**.<sup>a</sup>

Entry	MacroRAFT		DP <sub>n</sub> <sup>c</sup> (S)	[RAFT] <sub>0</sub> (mmol.L <sup>-1</sup> )	[ACPA] <sub>0</sub> (mmol.L <sup>-1</sup> )	t (h)	conv. <sup>b</sup> (%) <sup>a</sup>	M <sub>n,th</sub> <sup>c</sup> (kg.mol <sup>-1</sup> )	M <sub>n,exp</sub> <sup>d</sup> (kg.mol <sup>-1</sup> )	M <sub>w</sub> /M <sub>n</sub> <sup>d</sup>
	#	M <sub>n</sub> (kg.mol <sup>-1</sup> )								
<b>A1-SS1</b>	A1	3.2	620	3.2	0.6	20	19	15.5	12.4	1.44
<b>A3-SS1</b>	A3	10.7	736	2.7	0.6	20	20	25.6	14.3	1.46

<sup>a</sup> [S]<sub>0</sub> = 2 M; <sup>b</sup> Monomer conversion by gravimetry; <sup>c</sup> Theoretical number-average molar mass, M<sub>n,th</sub>, and number-average degree of polymerization, DP<sub>n</sub>, calculated using conversion<sup>b</sup>; <sup>d</sup> M<sub>n</sub> and M<sub>w</sub>/M<sub>n</sub> determined by SEC in THF with a PS calibration.



**Figure SI-7.** SEC chromatograms in THF for sample **A3-SS1** prepared by polymerization of styrene in 1,4-dioxane at 80 °C with macroRAFT agent **A3**.