

Controlled Homopolymerization of Multi-vinyl Monomers: From ATRA to Dendritic Polymers

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Electronic Supplementary Information (ESI)

Experimental details

Materials: Acryloyl chloride ($\geq 97\%$) and 2-hydroxyethyl disulfide (90%) were purchased from Sigma-Aldrich. The bis(2-acryloyl)oxyethyl disulfide (disulfide-based diacrylate, DSDA, $\geq 95\%$) was synthesized according to literature. Styrene ($\geq 95\%$), ethylene glycol dimethacrylate (EGDMA, 98%), divinylbenzene (DVB 80%) was purchased from Sigma-Aldrich. Monomers were passed through a column to remove inhibitors. The chloroform (CHCl_3 , $\geq 99\%$, Aldrich) and 1,1'-azobis(cyclohexanecarbonitrile) (ACHN, 98%, Aldrich) were used as the initiator. Pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich), triethylamine (TEA, 99%, Aldrich), copper (I) chloride (CuCl , 99%, Aldrich), copper (II) chloride (CuCl_2 , 99%, Aldrich), L-ascorbic acid (AA, 99%, Aldrich), tributylphosphine (Bu_3P 97% Aldrich), d-chloroform (99.8%, Aldrich), 2-butanone (HPLC grade, Aldrich), toluene (HPLC grade, Aldrich), tetrahydrofuran (THF, HPLC grade, Aldrich), n-hexane (ACS reagent grade, Aldrich), diethyl ether (ACS reagent grade, Aldrich) and dichloromethane (DCM, ACS reagent grade, Aldrich) were used as received.

FRP of styrene: Styrene (25 mmol, 1 equiv), CHCl_3 (25 mmol, 1 equiv) and toluene (5.2 ml) were added into the flask and oxygen was removed by bubbling argon through the solutions for 20 min at room temperature. ACHN (0.1 mmol, 0.004 equiv) was carefully transferred into the flask under an argon blanket. The solution was stirred at 800 rpm and the polymerization was conducted at 60 °C in an oil bath for the desired reaction time.

ARGET of styrene: Styrene (25 mmol, 1 equiv), CHCl_3 (25 mmol, 1 equiv), CuBr_2 (0.1 mmol, 0.004 equiv), PMDETA (0.1 mmol, 0.004 equiv) and toluene (5.2 ml) were added into the flask and oxygen was removed by bubbling argon through the solutions for 20 min at room temperature. AA (0.1 mmol, 0.004 equiv, 100% of CuCl_2) was carefully transferred into the flask under an argon blanket. The solution was stirred at 800 rpm and the polymerization was conducted at 60 °C in an oil bath for the desired reaction time.

ATRA1 of styrene: Styrene (25 mmol, 1 equiv), CHCl_3 (25 mmol, 1 equiv) and toluene (5.2 ml) were added into the flask and oxygen was removed by bubbling argon through the solutions for 20 min at room temperature. CuCl (0.1 mmol, 0.004 equiv) was carefully transferred into the flask under an argon blanket. The solution was stirred at 800 rpm and the polymerization was conducted at 60 °C in an oil bath for the desired reaction time.

FRP of methyl methacrylate (MMA): MMA (25 mmol, 1 equiv), CHCl_3 (25 mmol, 1 equiv) and 2-butanone (5.4 ml) were added into the flask and oxygen was removed by bubbling argon through the solutions for 20 min at room temperature. ACHN (0.1 mmol, 0.004 equiv) was carefully transferred into the flask under an argon blanket. The solution was stirred at 800 rpm and the polymerization was conducted at 60 °C in an oil bath for the desired reaction time.

ATRA1 of MMA: MMA (25 mmol, 1 equiv), CHCl_3 (25 mmol, 1 equiv), PMDETA (0.1 mmol, 0.004 equiv) and 2-butanone (5.4 ml) were added into the flask and oxygen was removed by bubbling

argon through the solutions for 20 min at room temperature. CuCl (0.1 mmol, 0.004 equiv) was carefully transferred into the flask under an argon blanket. The solution was stirred at 800 rpm and the polymerization was conducted at 60 °C in an oil bath for the desired reaction time.

ATRA2 of MMA: MMA (25 mmol, 1 equiv), CHCl₃ (25 mmol, 1 equiv), PMDETA (0.2 mmol, 0.008 equiv) and 2-butanone (5.4 ml) were added into the flask and oxygen was removed by bubbling argon through the solutions for 20 min at room temperature. CuCl (0.2 mmol, 0.008 equiv) was carefully transferred into the flask under an argon blanket. The solution was stirred at 800 rpm and the polymerization was conducted at 60 °C in an oil bath for the desired reaction time.

In situ ATRA of MMA: MMA (25 mmol, 1 equiv), CHCl₃ (25 mmol, 1 equiv), CuCl₂ (0.625 mmol, 0.025 equiv), PMDETA (0.625 mmol, 0.025 equiv) and 2-butanone (5.4 ml) were added into the flask and oxygen was removed by bubbling argon through the solutions for 20 min at room temperature. AA (0.047 mmol, 0.00188 equiv, 7.5% of CuCl₂) was carefully transferred into the flask under an argon blanket. The solution was stirred at 800 rpm and the polymerization was conducted at 60 °C in an oil bath for the desired reaction time.

Preparation of hyperbranched polyDVB: DVB (25 mmol, 1 equiv), CHCl₃ (12.5 mmol, 0.5 equiv), PMDETA (0.1 mmol, 0.004 equiv) and toluene (4.7 ml) were added into the flask and oxygen was removed by bubbling argon through the solutions for 20 min at room temperature. CuCl (0.1 mmol, 0.004 equiv) was carefully transferred into the flask under an argon blanket. The solution was stirred at 800 rpm and the polymerization was conducted at 60 °C in an oil bath for the desired reaction time.

Preparation of hyperbranched polyEGDMA: Ethylene glycol dimethacrylate (EGDMA, 20 mmol, 1 equiv), 2-butanone (8.1 ml), CHCl₃ (10 mmol, 0.5 equiv), CuCl₂ (0.5 mmol, 0.025 equiv) and PMDETA (0.5 mmol, 0.025 equiv) were added into the flask and oxygen was removed by bubbling argon through the solutions for 20 min at room temperature. AA (0.0375 mmol, 0.00188 equiv, 7.5% of CuCl₂) was carefully transferred into the flask under an argon blanket. The solution was stirred at 800 rpm and the polymerization was conducted at 60 °C in an oil bath for the desired reaction time.

Preparation of hyperbranched polyDSDA: Bis(2-acryloyl)oxyethyl disulfide (disulfide-based diacrylate, DSDA, 20 mmol, 1 equiv), 2-butanone (8.2 ml), CHCl₃ (10 mmol, 0.5 equiv), CuCl₂ (0.5 mmol, 0.025 equiv) and PMDETA (0.5 mmol, 0.025 equiv) were added into the flask and oxygen was removed by bubbling argon through the solutions for 20 min at room temperature. AA (0.0375 mmol, 0.00375 equiv, 7.5% of CuCl₂) was carefully transferred into the flask under an argon blanket. The solution was stirred at 800 rpm and the polymerization was conducted at 60 °C in an oil bath for the desired reaction time.

Size exclusion chromatography (SEC) characterizations: Weight average molecular weight (M_w), number average molecular weight (M_n) and polydispersity (M_w/M_n) were obtained by SEC (Varian 920-LC) equipped with an RI and an LS detector. The columns (30 cm PLgel Mixed-C, two in series) were eluted using tetrahydrofuran (THF) and calibrated using a series of 12 near-monodisperse PMMA standards (M_p from 690 to 1,944,000 gmol⁻¹). The polymers were analyzed in THF at a concentration of 5.0 mg/ml. All calibrations and analysis were performed at 40 °C and a flow rate of 1 ml/min.

¹H NMR characterizations: ¹H NMR analysis was carried out on a S4 300 MHz Bruker NMR with JEOL Delta v5.0.1 processing software. The chemical shifts were referenced to the lock chloroform (7.26 ppm).

Scheme S1 Scheme depicting the dependence of mono-adduct formation on the Cu(I) to Cu(II) ratio.

Table S1 Detailed information of polyDVB via ATRA1 reaction and polyEGDMA via *in situ* ATRA reaction.

Reaction	Time (hrs)	RI		LS		Conv (%)	Branch ratio (%)
		M _w (KDa)	PDI	M _w (KDa)	PDI		
ATRA1 DVB	1	0.7	1.2	0.9	1.1	4	-
	10	3.3	1.6	4.7	1.4	37	-
	24	4.8	2.7	6.2	2.0	63	-
	purified	10.1	1.8	12.1	1.6	-	23%
<i>In situ</i> ATRA EGDMA	0.25	0.8	1.1	0.9	1.1	3.3	-
	0.5	1.2	1.3	1.7	1.2	14	-
	1	3.6	1.8	4.3	1.6	42	-
	2	22.2	5.4	30	3.3	72	-
	purified	34	1.7	41	1.5	-	28%

Table S2. Reaction and degradation results for *in situ* ATRA of polyDSDA.

Time (hrs)	M _w (KDa)	PDI	Vinyl conv (%)	Branch ratio (%)
0.5	1.8	1.1	10	20
3	4.5	1.6	45	26
6.5	7.4	2	64	34
Purified ^[a]	8.2	1.6	-	-
Degraded	0.7	1.7	-	-

[a] Purified from 6.5 hrs sample

Figure S1. SEC for FRP of styrene (entry 1, Table 1)

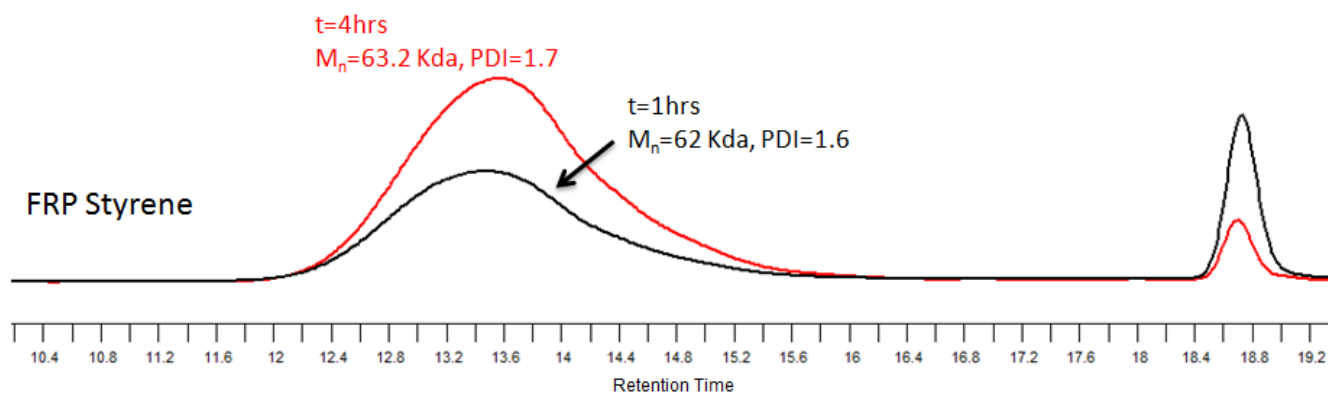


Figure S2. SEC for ARGET styrene (entry 2, Table 1)

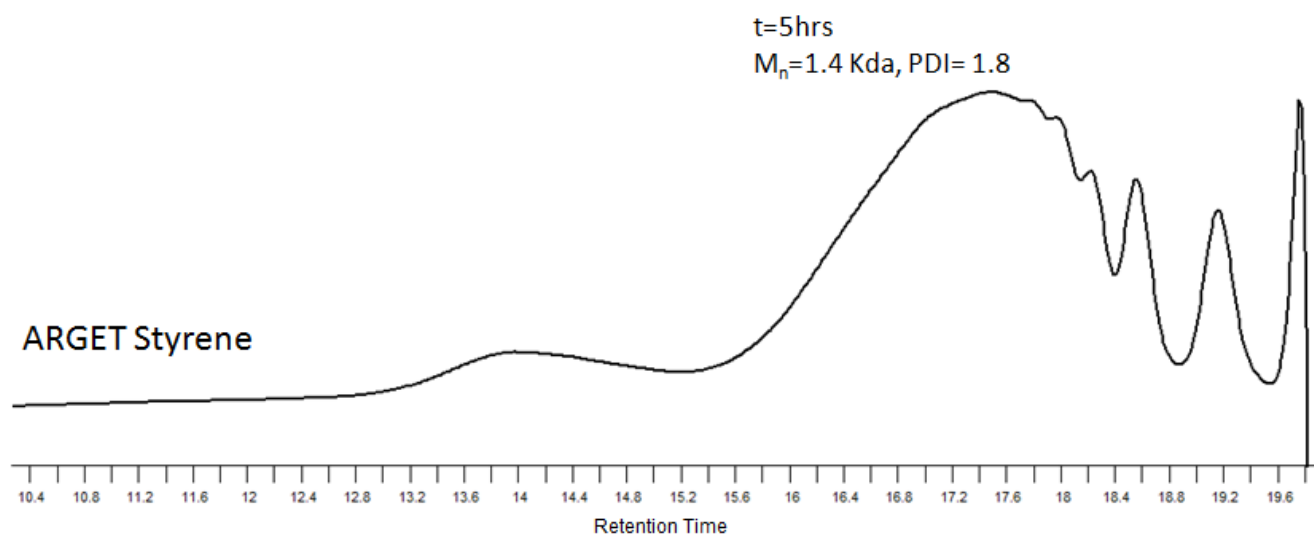


Figure S3. SEC for FRP MMA (entry 4, Table 1)

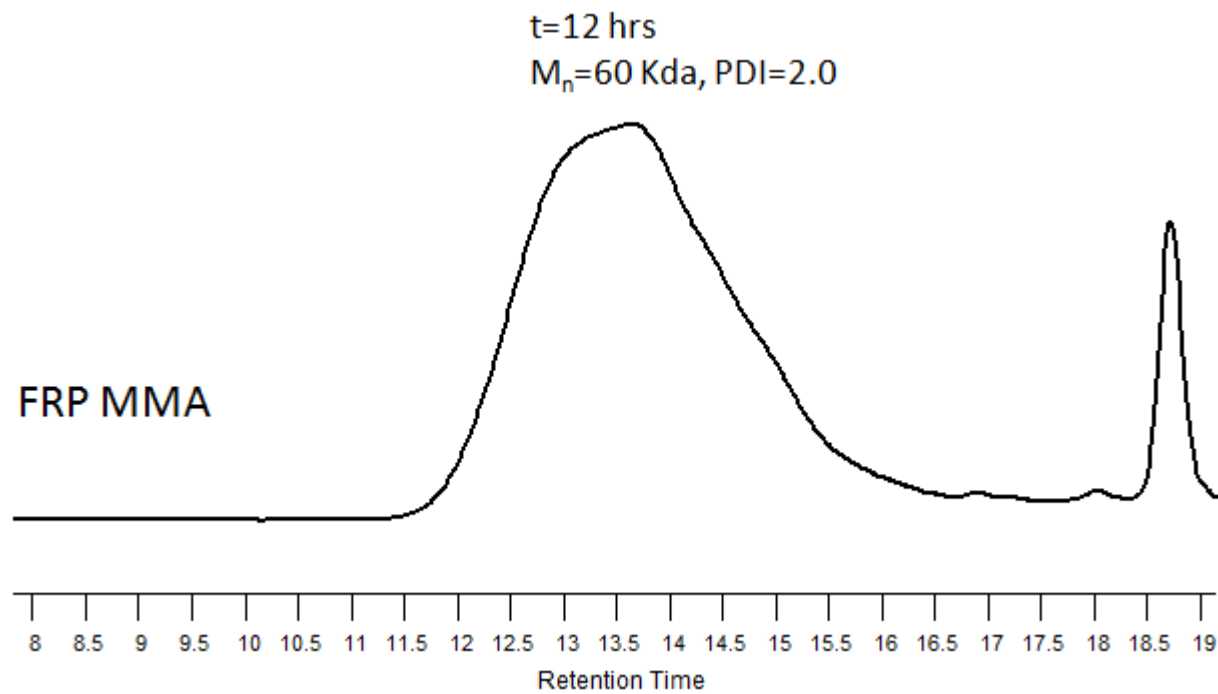


Figure S4. SEC for ATRA1 MMA (entry 5, Table 1)

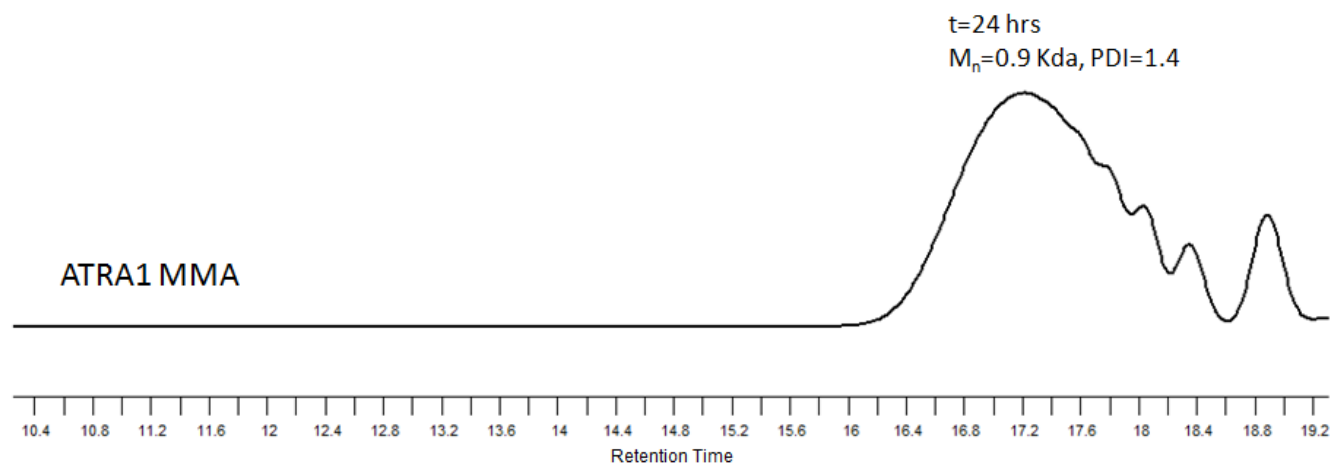


Figure S5. SEC for ATRA2 MMA (entry 6, Table 1)

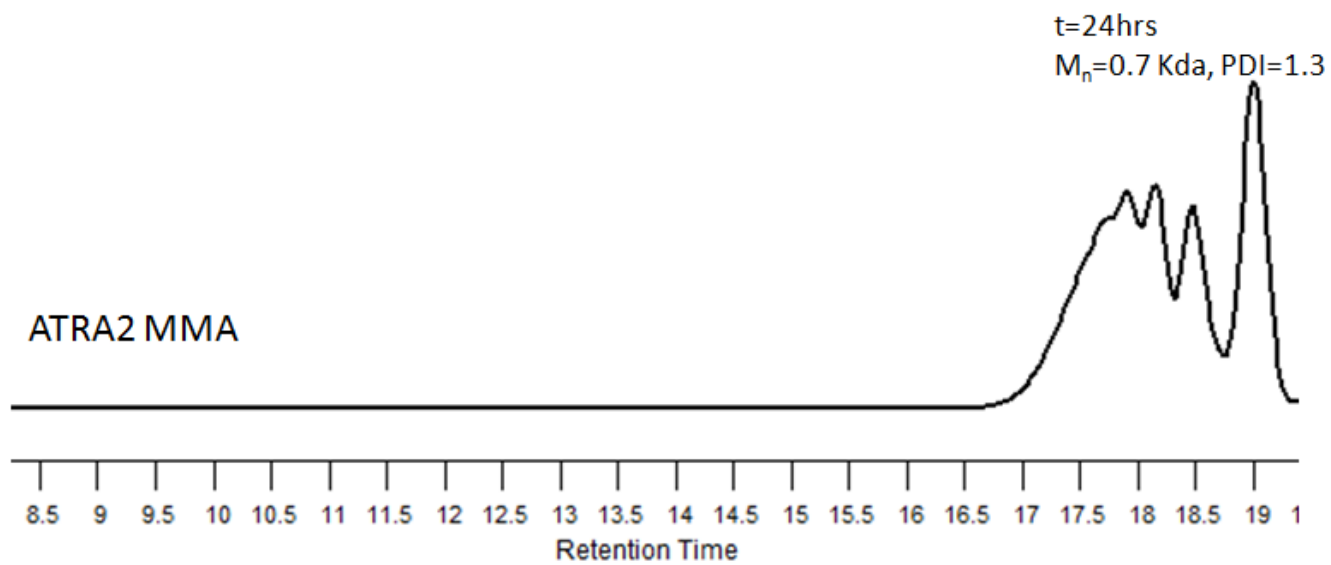


Figure S6. SEC for *in situ* ATRA of EGDMA (entry 7, Table 1)

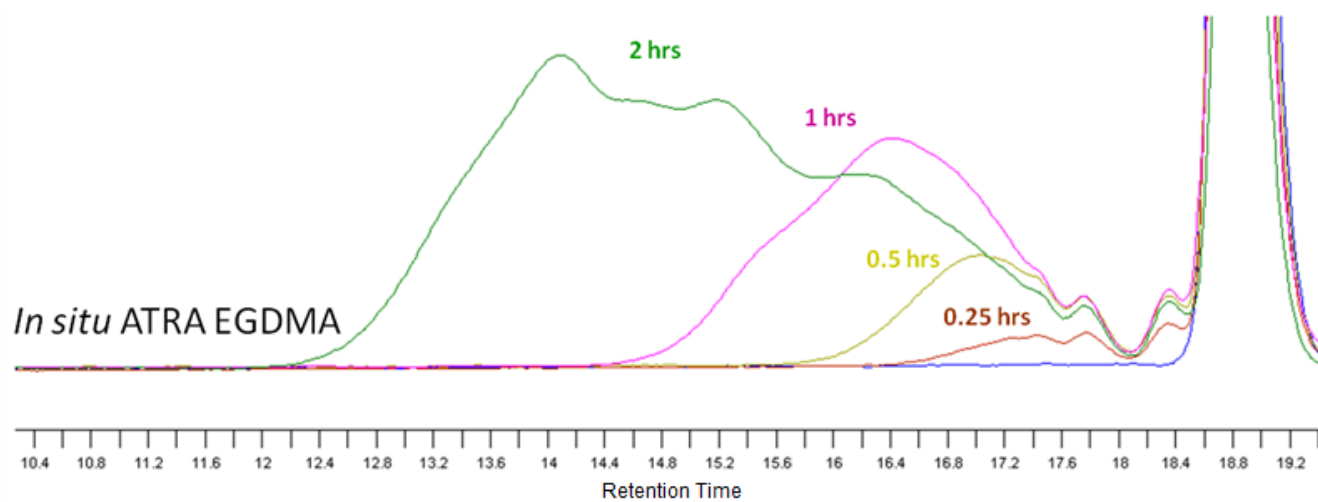


Figure S7. Kinetic study for *in situ* ATRA of EGDMA (entry 7, Table 1)

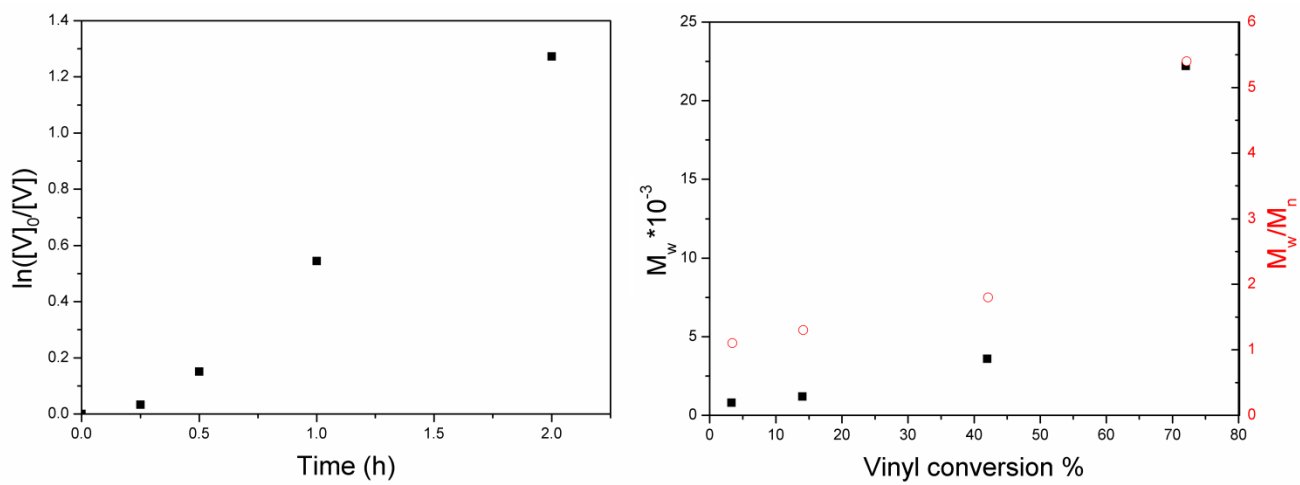


Figure S8. Scheme of *in situ* ATRA of EGDMA and ¹H NMR results for the final product, the results indicate the purified polyEGDMA contain 28% branched EGDMA unit.

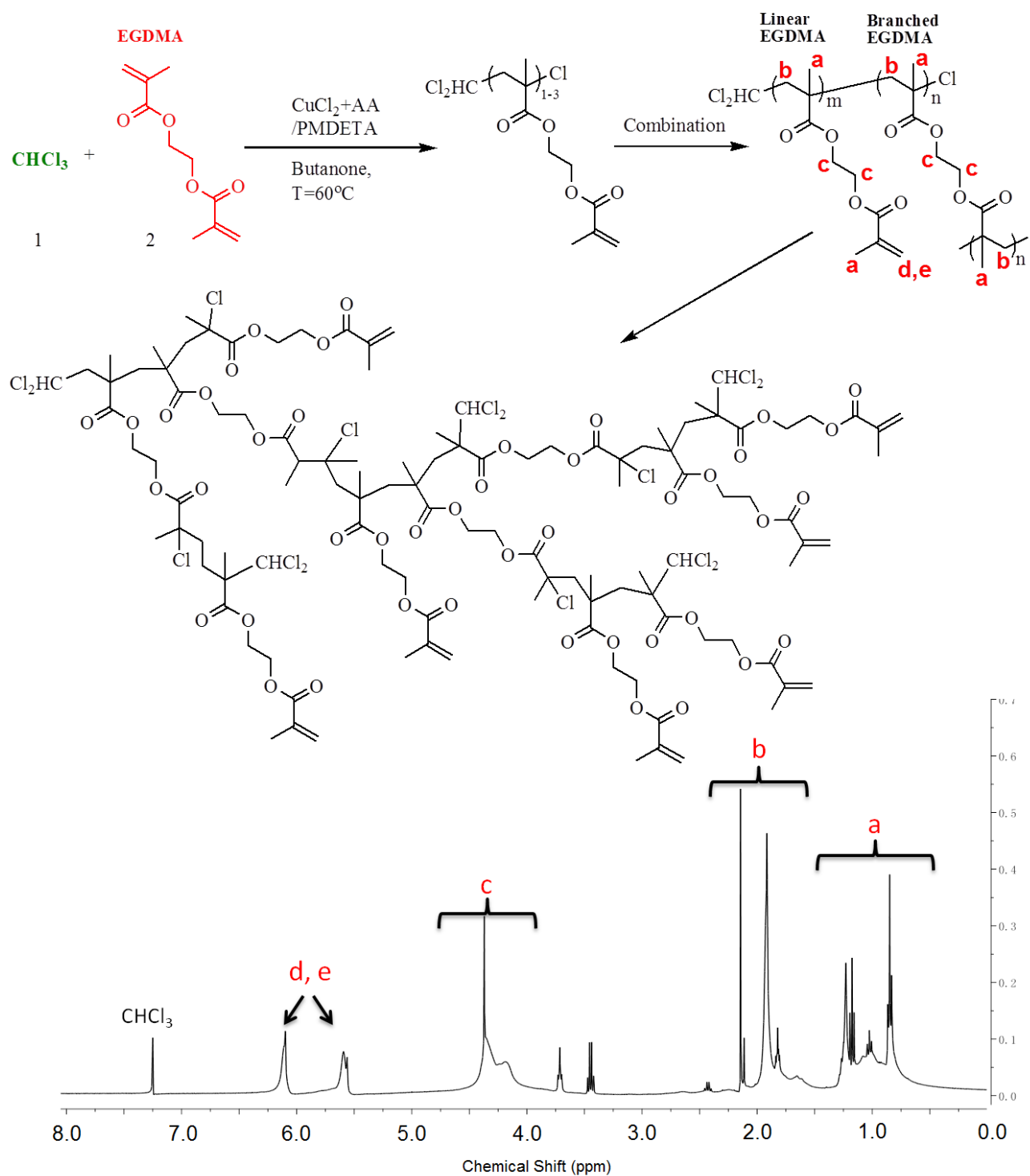
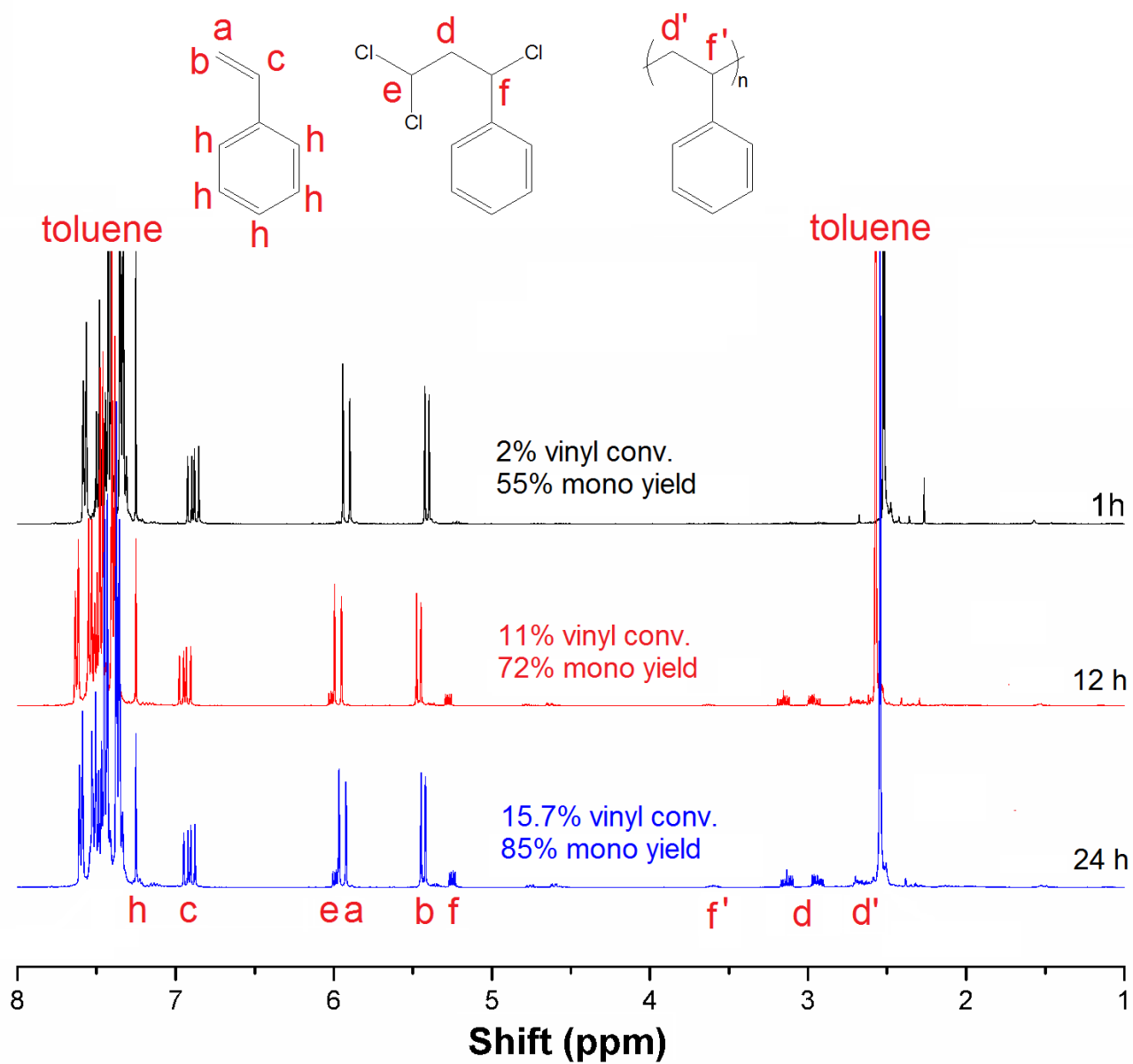


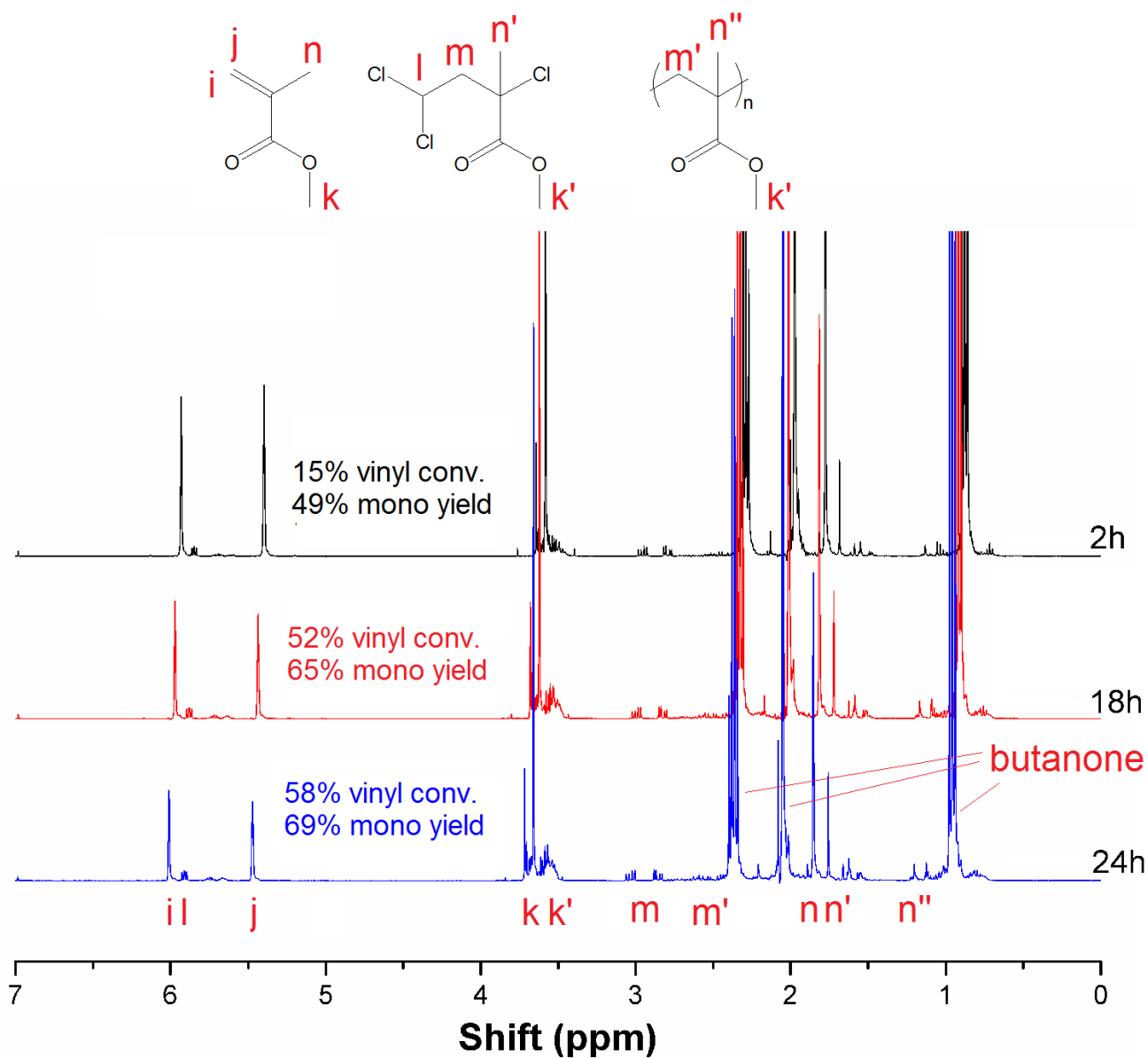
Figure S9 ^1H NMR spectra of ATRA1 reaction of styrene (entry 3, Table 1).



$$\text{Equation. S1 Vinyl conversion} = \frac{(\text{Integral of } f) + (\text{Integral of } f')}{(\text{Integral of } c) + (\text{Integral of } f) + (\text{Integral of } f')}$$

$$\text{Equation. S2 Mono yield} = \frac{(\text{Integral of } f)}{(\text{Integral of } f) + (\text{Integral of } f')}$$

Figure S10 ^1H NMR spectra of *in situ* ATRA reaction of MMA (entry 7, Table 1).



$$\text{Equation. S3 Vinyl conversion} = \frac{(\text{Integral of } k')}{(\text{Integral of } k) + (\text{Integral of } k')}$$

$$\text{Equation. S4 Mono yield} = \frac{(\text{Integral of } m)}{(\text{Integral of } m) + (\text{Integral of } m')}$$

Figure S11. SEC for ATRA1 of DVB (entry 8, Table 1)

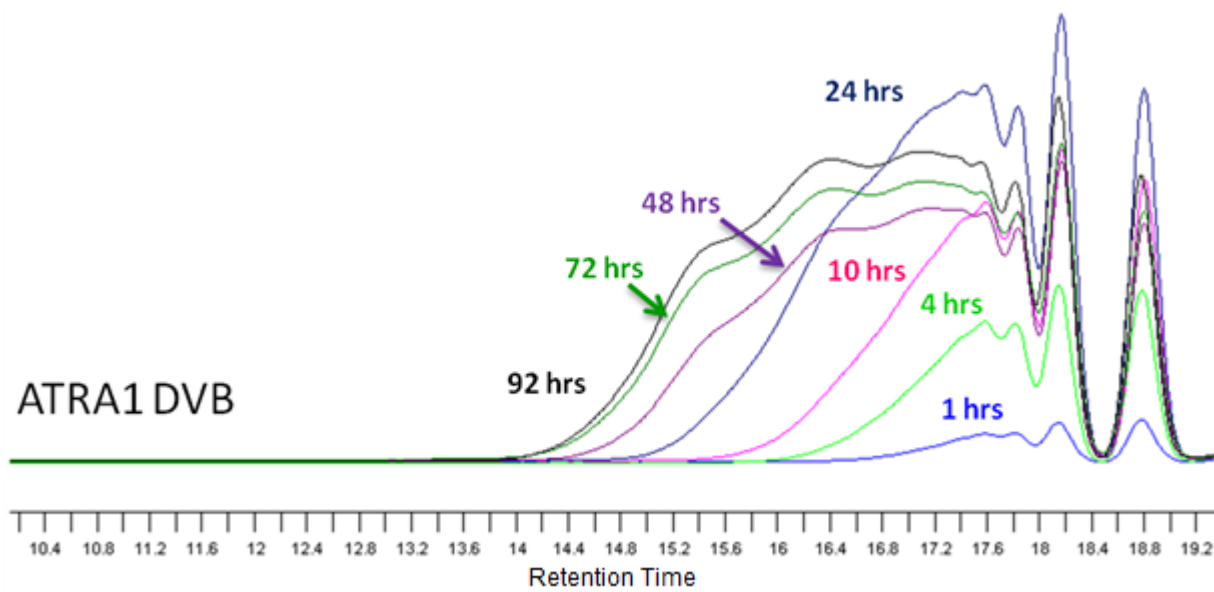


Figure S12. The plot of the gyration radius versus Log MW of ATRA1 DVB (Figure S11) using GPC equipped with light scattering detector.

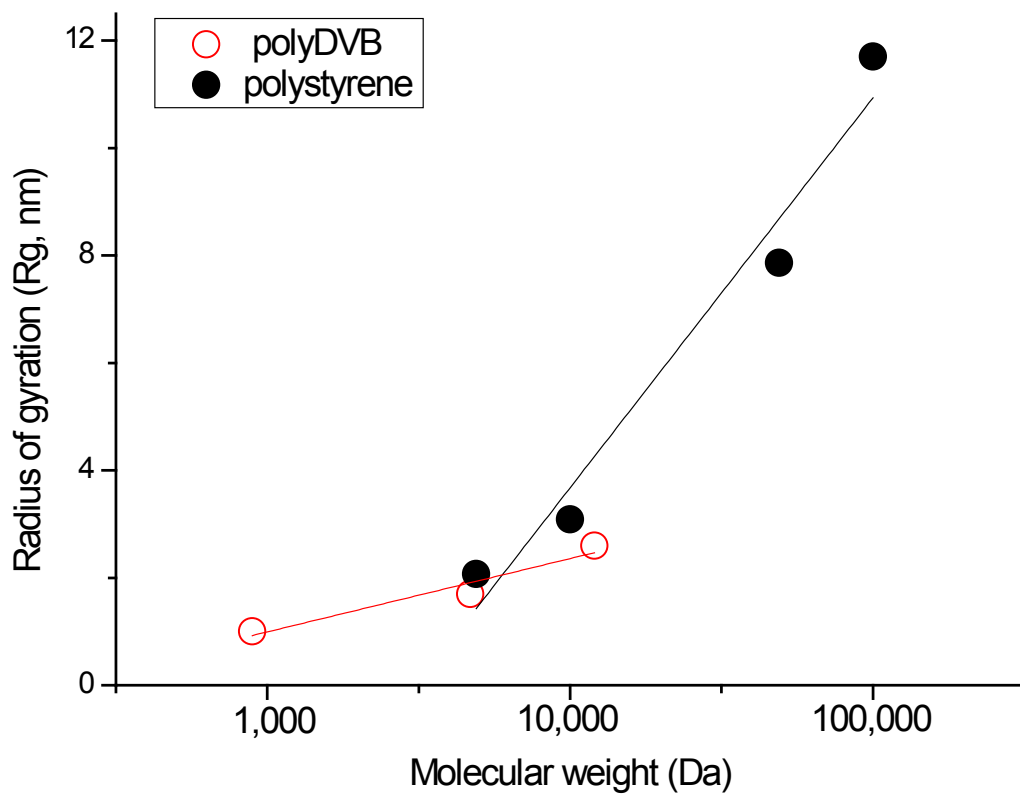


Figure S13. SEC for DSDA

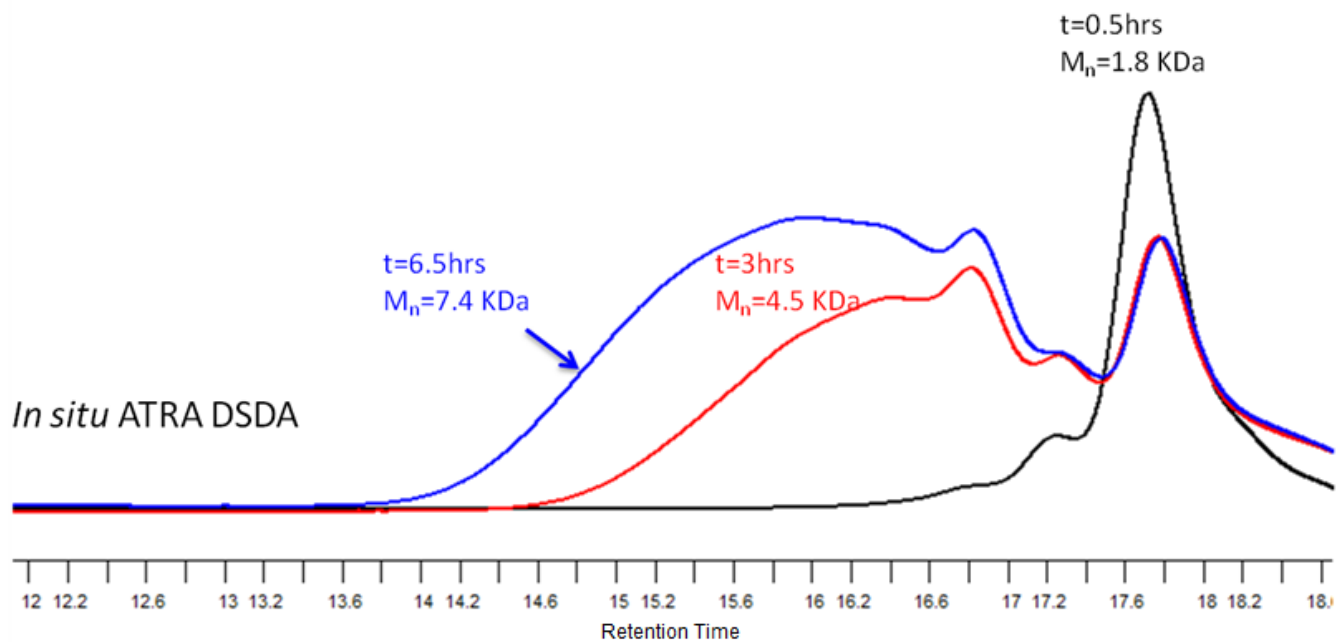


Figure S14. Schematic representation and proof of the short primary chain length via the degradation of the polybis(2-acryloyl)oxyethyl disulfide (polyDSDA): (a) Schematic representation of the degradation that would occur from the disulfide polymer to linear primary chains by disulfide bond cleavage using reduction of tributylphosphine (Bu_3P). (b) The SEC trace before and after cleavage of the hyperbranched polyDSDA synthesized by *in situ* ATRA strategy (purified 6.5 h product in Table S2 and Supplementary Figure S13).

