Electronic Supplementary Material (ESI) for Polymer Chemistry.

Direct synthesis via RAFT of amphiphilic diblock polyelectrolytes facilitated by the use of a polymerizable ionic liquid as monomer

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Supporting Information

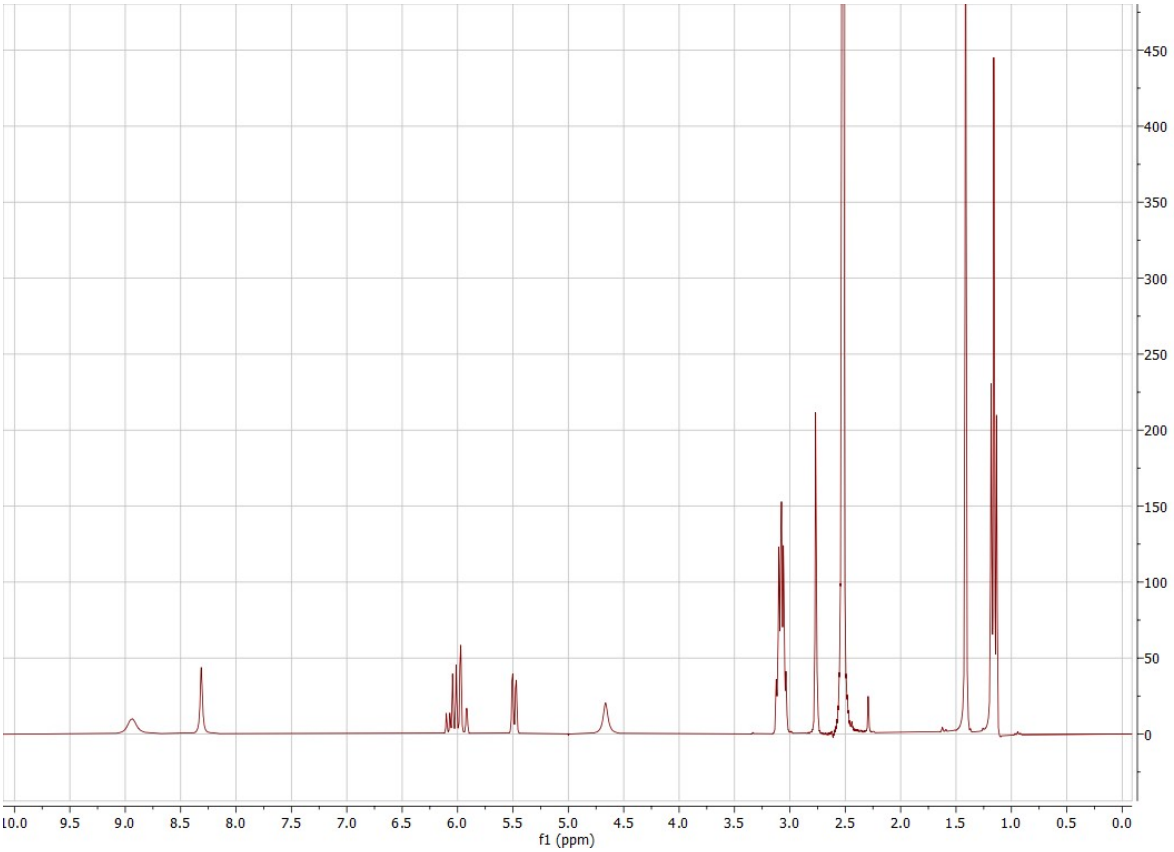

Figure S1. ^{1}H NMR spectrum (recorded in d_6-DMSO) of a DMSO solution of the Et_3N-AMPS polymerizable ionic liquid monomer.

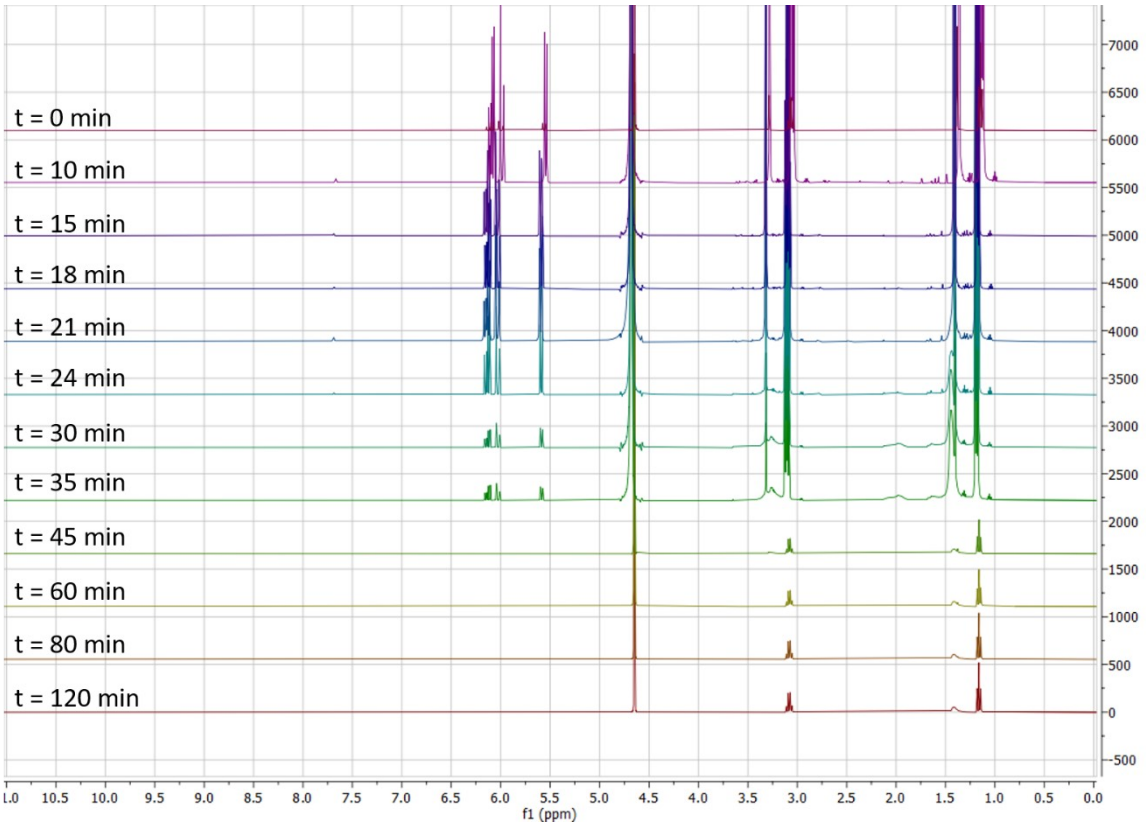

Figure S2. ^{1}H NMR spectra of Et_3N-AMPS RAFT polymerization mixture at various time points. The spectra were used to calculate monomer conversions reported in Figure 1A.

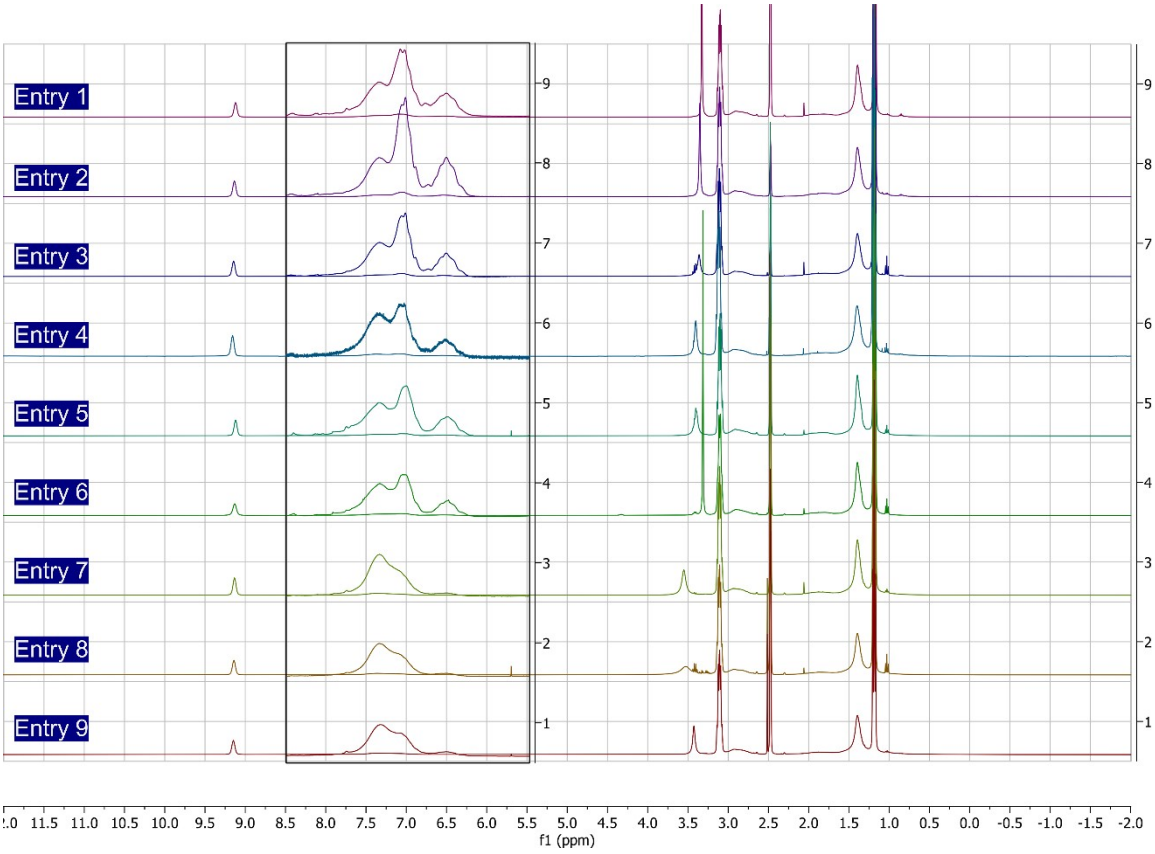

Figure S3. ^{1}H NMR spectra of poly(Et_3N-AMPS)-*block*-polystyrene copolymers from Table 2, recorded in d_6-DMSO. The inset shows a close-up of the 8.5 – 5.5 ppm range.

Table S1. Results of elemental analysis on the sample in Table 2 entry 9.

	nitrogen wt %	carbon wt %	hydrogen wt %	sulfur wt %
homopolymer	5.37	32.55	6.04	12.03
diblock	5.22	34.08	6.065	13.56

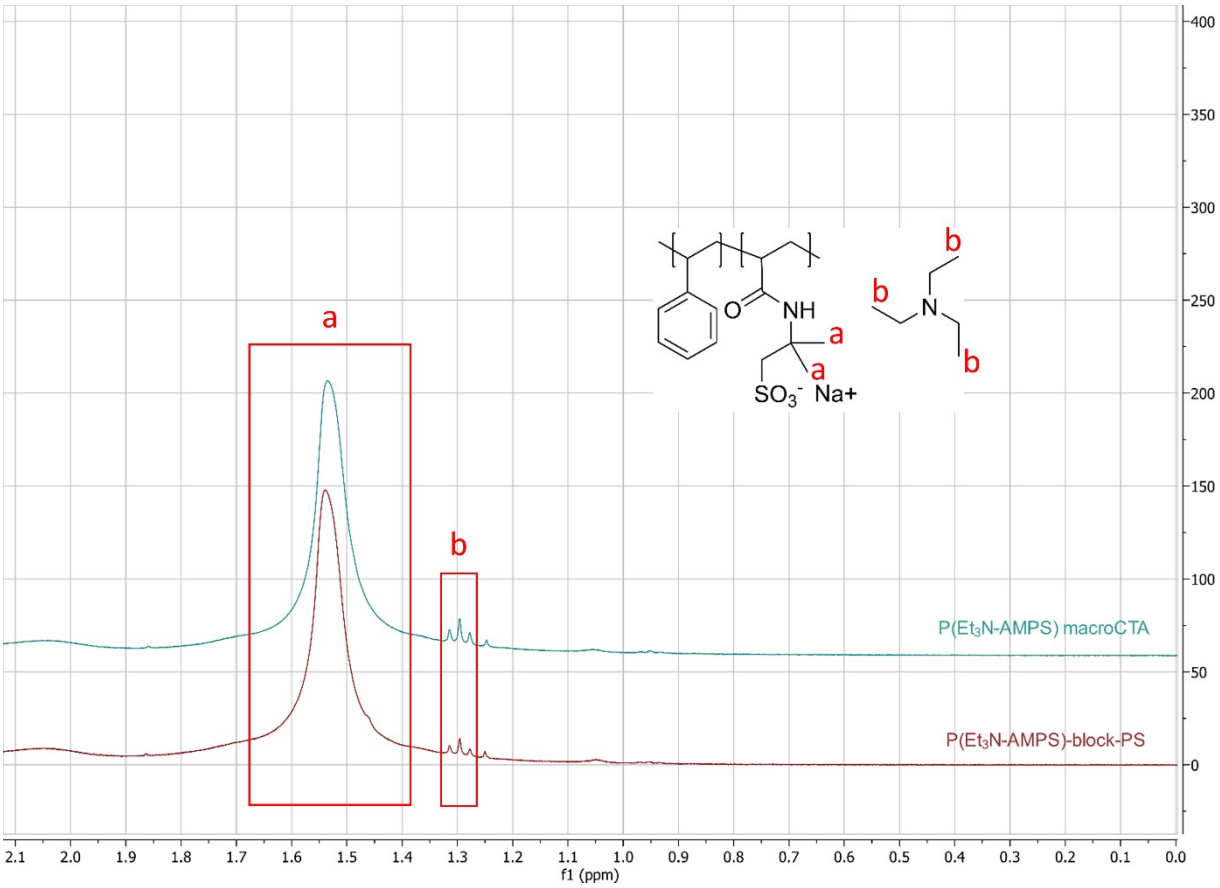

Figure S4. NMR spectra (in D_2O) of the macroCTA and diblock sample from Table 2 entry 9 after treatment with NaOH. The residual peak of Et_3N (b) from both polymer samples integrates for less than 1 % of peak (a) .

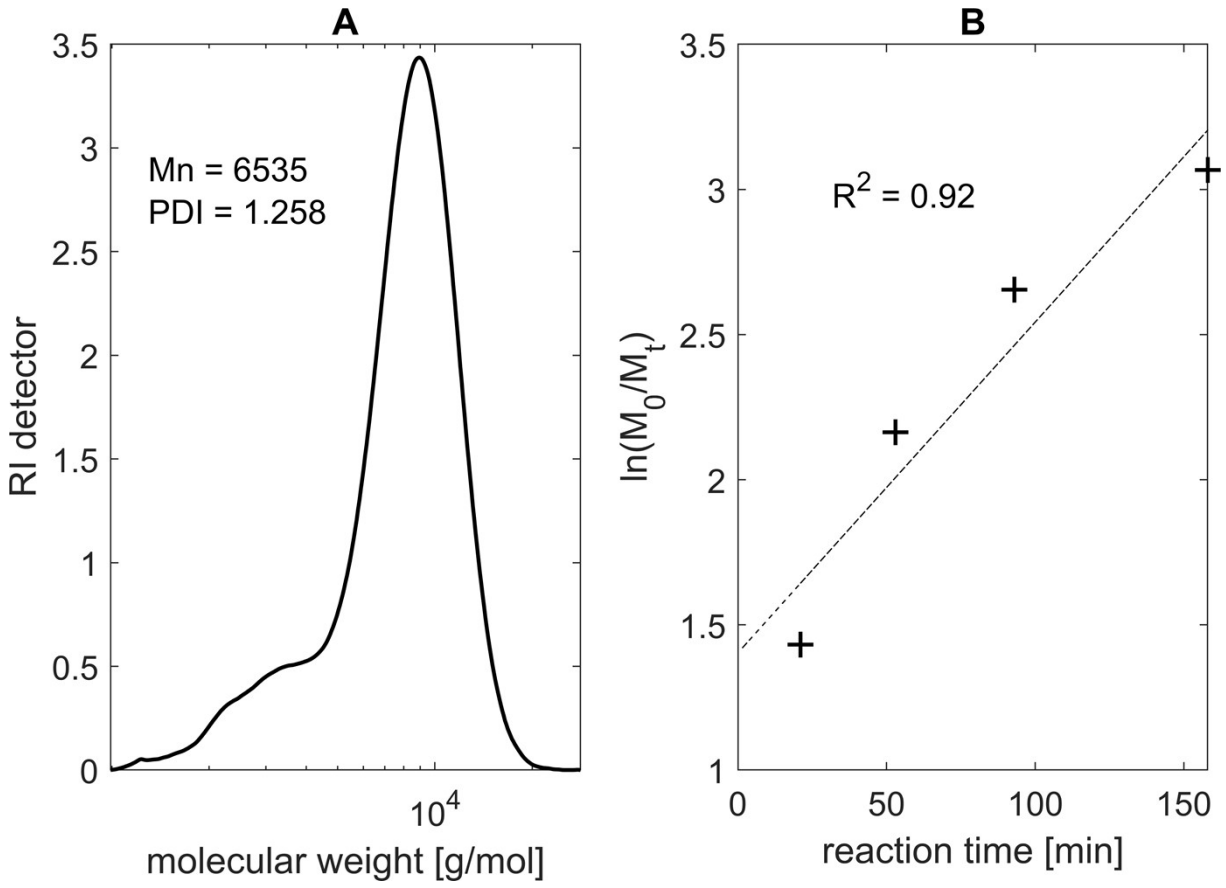

Figure S5. Investigation of the Et_3N-AMPS RAFT homopolymerization conducted in ethanol. **A** – aqueous SEC trace of the product after purification by precipitation, **B** – NMR kinetic study of the polymerization showing pseudo-1st order behavior

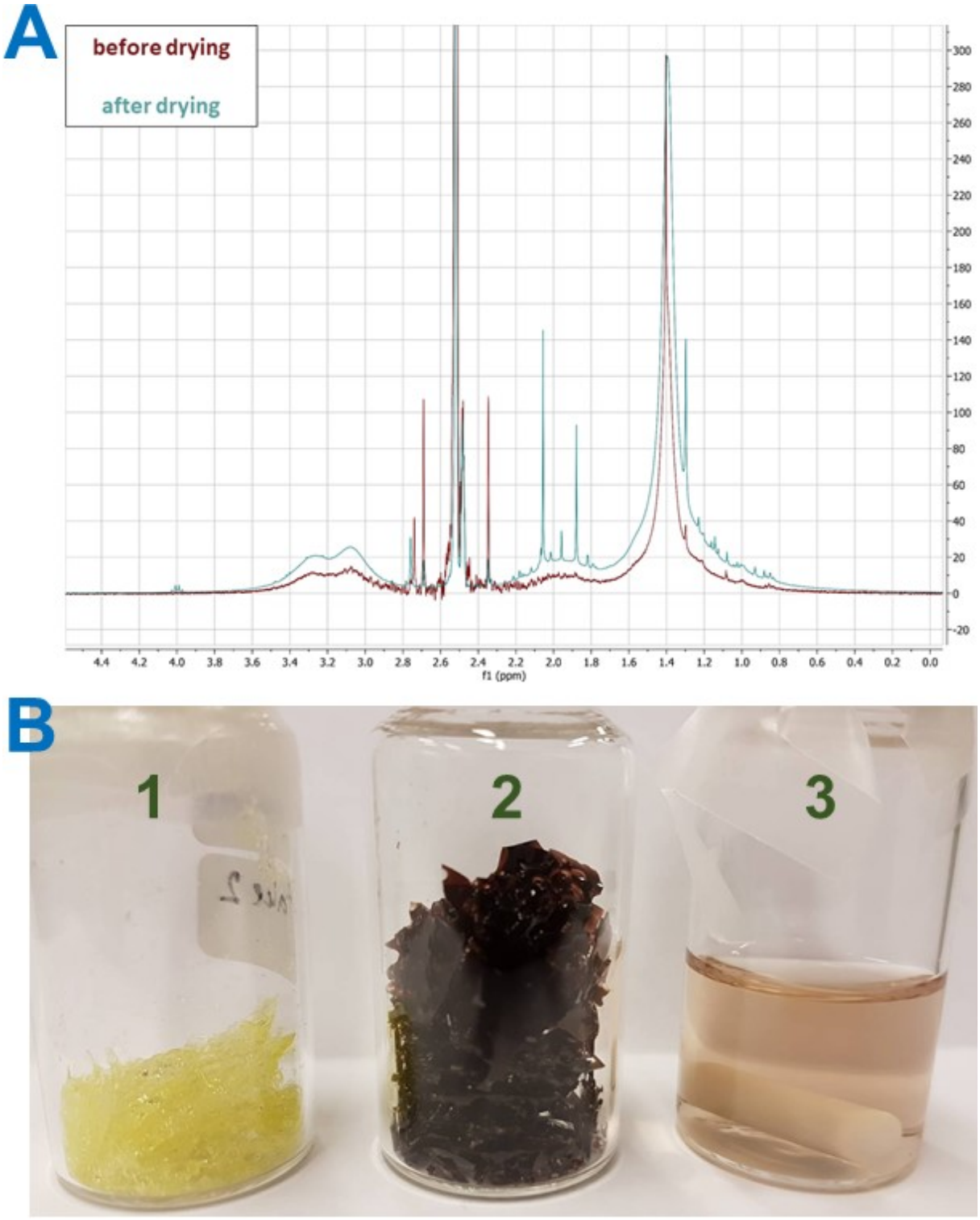

Figure S6. A: comparison of NMR spectra of the product of polymerization of non-neutralized H-AMPS in DMSO before and after oven drying at 80 °C. The appearance of new peaks after drying may be a sign of decomposition **B:** Appearance of PAMPS-RAFT macroCTA synthesized by the method involving Et_3N **(B1)**, and by polymerizing H-AMPS acid in DMSO **(B2)**. The change in color from yellow to dark red/brown was a consequence of drying the polymer in an oven. Et_3N-AMPS polymer was processed in the same way and did not change its appearance. The discolored product is soluble in water **(B3)**, the solution being characterized by a foul smell.

Table S2. Measured DLS values for all samples in Table 2 and Figure 5

Sample		Number-average diameter [nm]		Z-average diameter [nm]		polydispersity index	
		value	std. dev	value	std. dev	value	std. dev
Entry 1	**macroCTA**	-	-	-	-	-	-
	diblock in MilliQ	14.640	0.651	30.840	8.156	0.361	0.105
	diblock in 0.5M NaCl	15.370	0.727	22.900	0.514	0.201	0.059
Entry 2	**macroCTA**	-	-	-	-	-	-
	diblock in MilliQ	26.360	1.375	51.630	2.032	0.409	0.036
	diblock in 0.5M NaCl	23.110	1.634	41.610	2.941	0.300	0.036
Entry 3	**macroCTA**	-	-	-	-	-	-
	diblock in MilliQ	35.570	2.756	65.850	0.520	0.218	0.011
	diblock in 0.5M NaCl	29.140	1.610	49.240	0.288	0.148	0.010
Entry 4	**macroCTA**	-	-	-	-	-	
	diblock in MilliQ	60.260	7.401	117.600	2.202	0.264	0.024
	diblock in 0.5M NaCl	34.120	1.552	58.360	0.658	0.179	0.010
Entry 5	**macroCTA**	0.804	0.056	307.300	157.300	0.414	0.077
	diblock in MilliQ	39.170	1.118	58.160	0.769	0.108	0.014
	diblock in 0.5M NaCl	30.400	2.497	47.550	0.612	0.142	0.032
Entry 6	**macroCTA**	1.153	0.605	984.500	492.700	0.731	0.260
	diblock in MilliQ	32.150	1.860	49.510	0.835	0.115	0.013
	diblock in 0.5M NaCl	22.080	1.603	37.710	0.612	0.171	0.010
Entry 7	**macroCTA**	0.833	0.027	338.000	127.900	0.421	0.088
	diblock in MilliQ	57.770	1.880	94.13	2.415	0.2942	0.047
	diblock in 0.5M NaCl	6.004	0.738	35.380	1.287	0.476	0.070
Entry 8	**macroCTA**	0.806	0.033	41.950	47.470	0.299	0.129
	diblock in MilliQ	114.400	8.179	155.700	0.535	0.144	0.015
	diblock in 0.5M NaCl	20.050	13.370	67.990	2.911	0.433	0.031
Entry 9	**macroCTA**	0.909	0.071	355.300	140.800	0.610	0.198
	diblock in MilliQ	226.600	25.190	386.100	7.676	0.311	0.027
	diblock in 0.5M NaCl	46.830	7.256	107.300	2.242	0.398	0.014

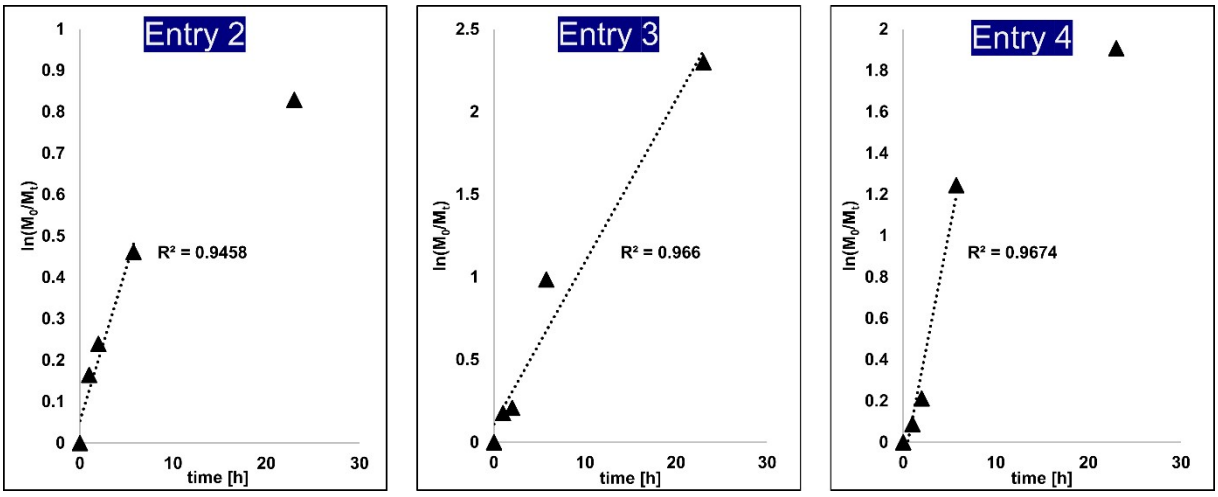

Figure S7. Kinetic plots measured with ^{1}H NMR for "PS-first" reactions in Table 2 Entry 2,3,4

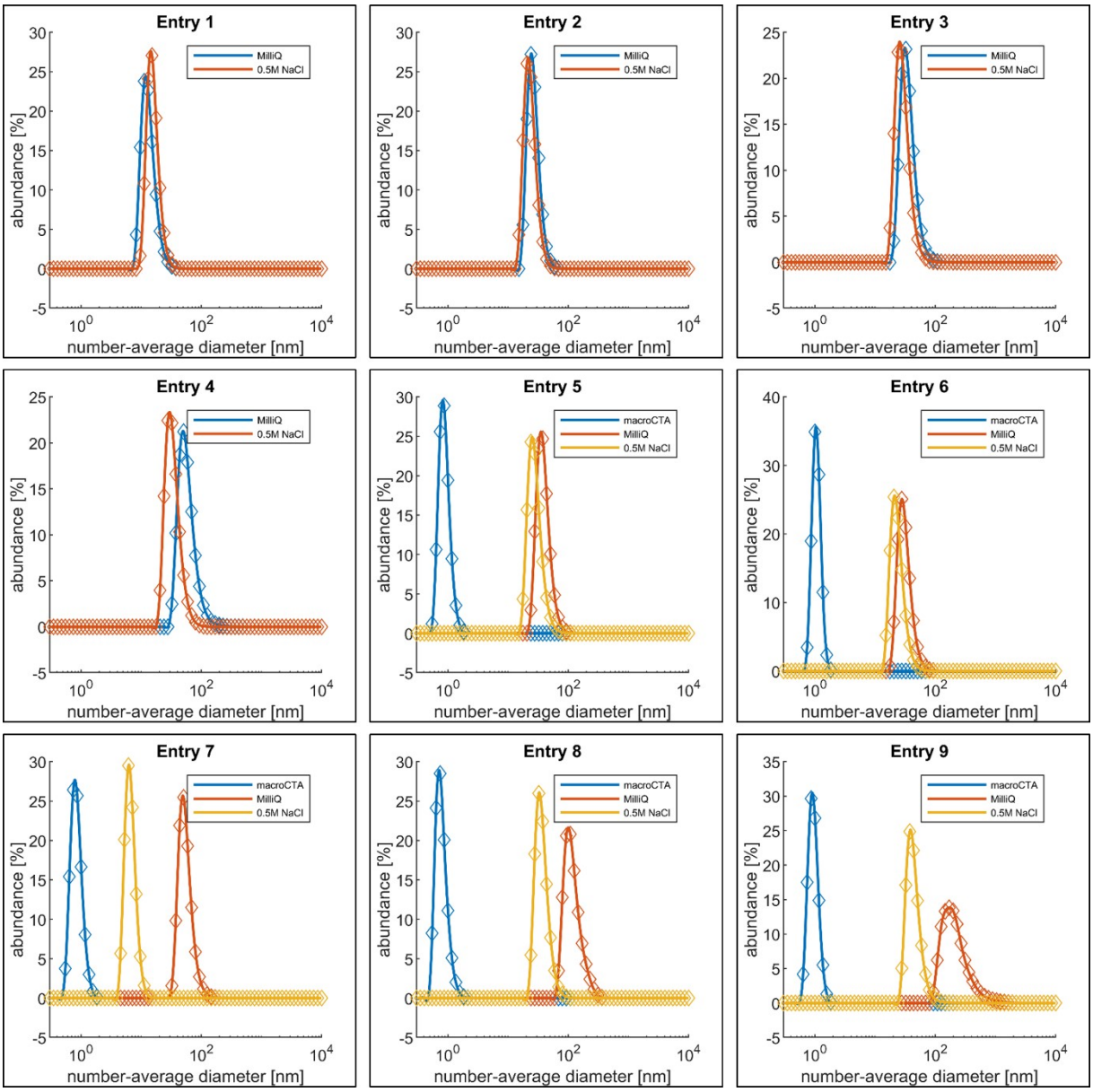

Figure S8. DLS number distributions of hydrodynamic diameter for each sample presented on the bargraph in Figure 5.

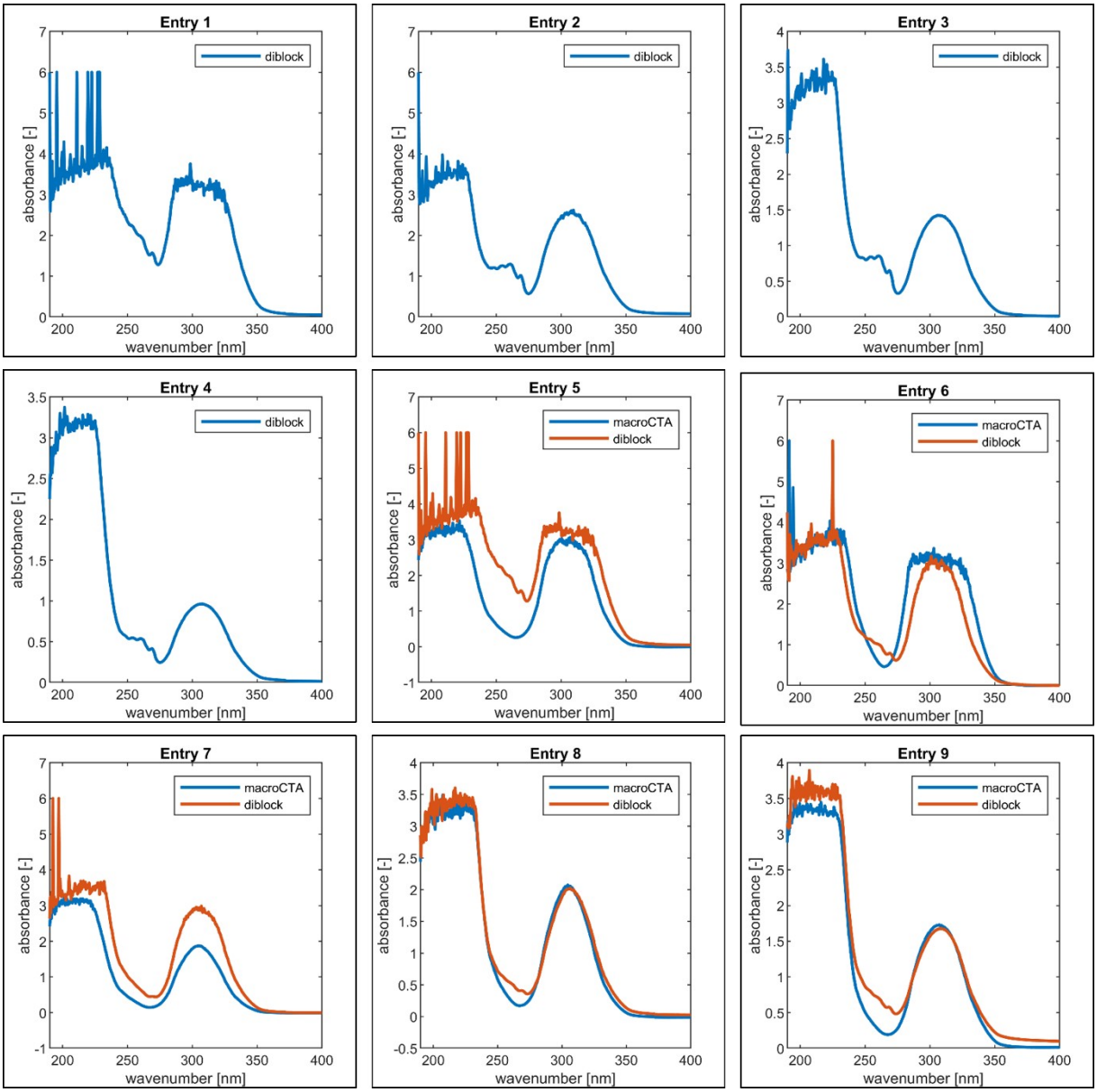

Figure S9. UV-VIS spectra recorded in water for all samples in Table 2 and for their corresponding macroCTAs (where applicable)

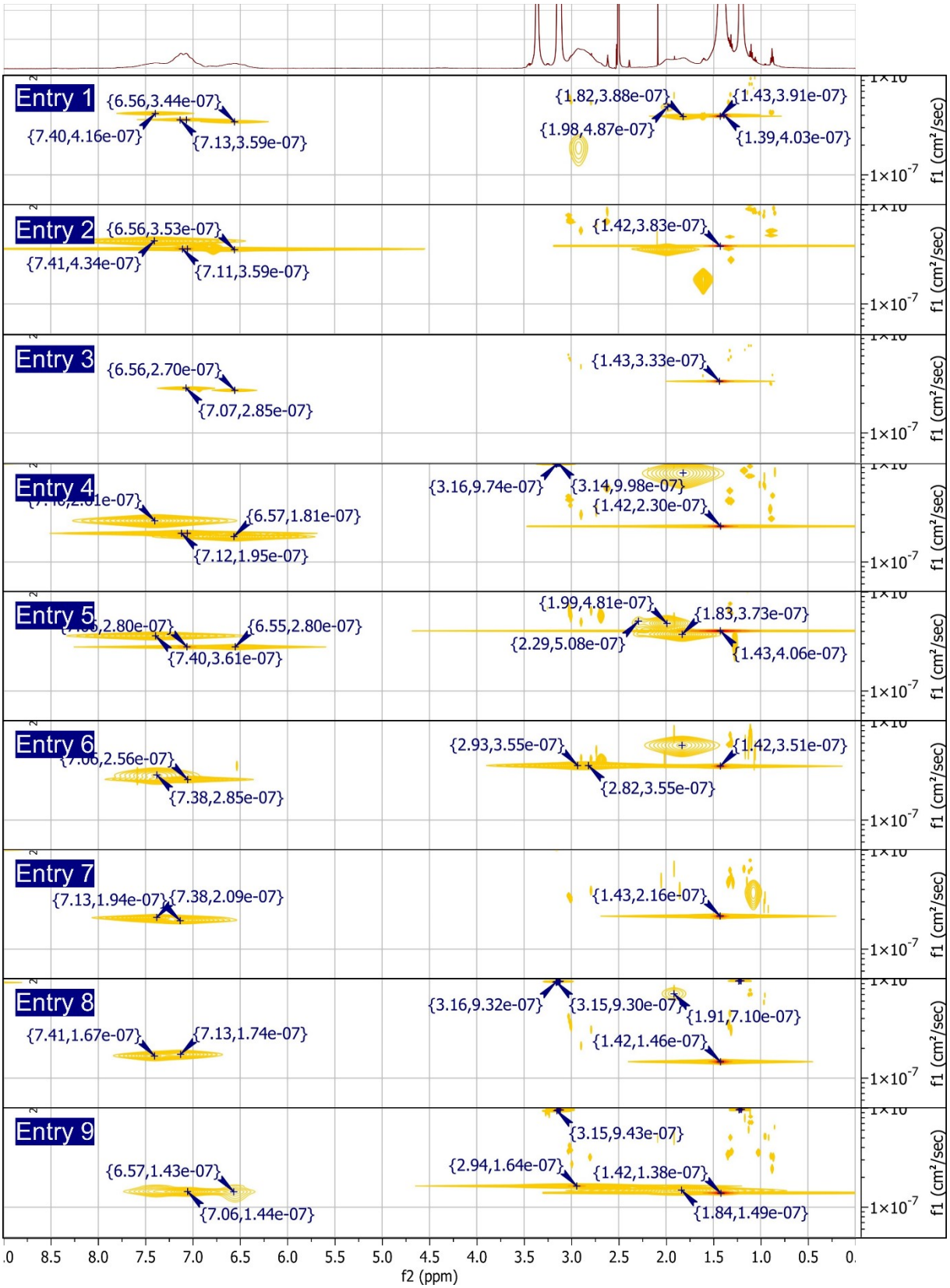

Figure S10. DOSY-NMR spectra recorded in d6-DMSO for all diblock samples in Table 2. The 1H-NMR spectrum at the top belongs to the sample in Entry 1, but is representative of all the samples (also see Figure S3).

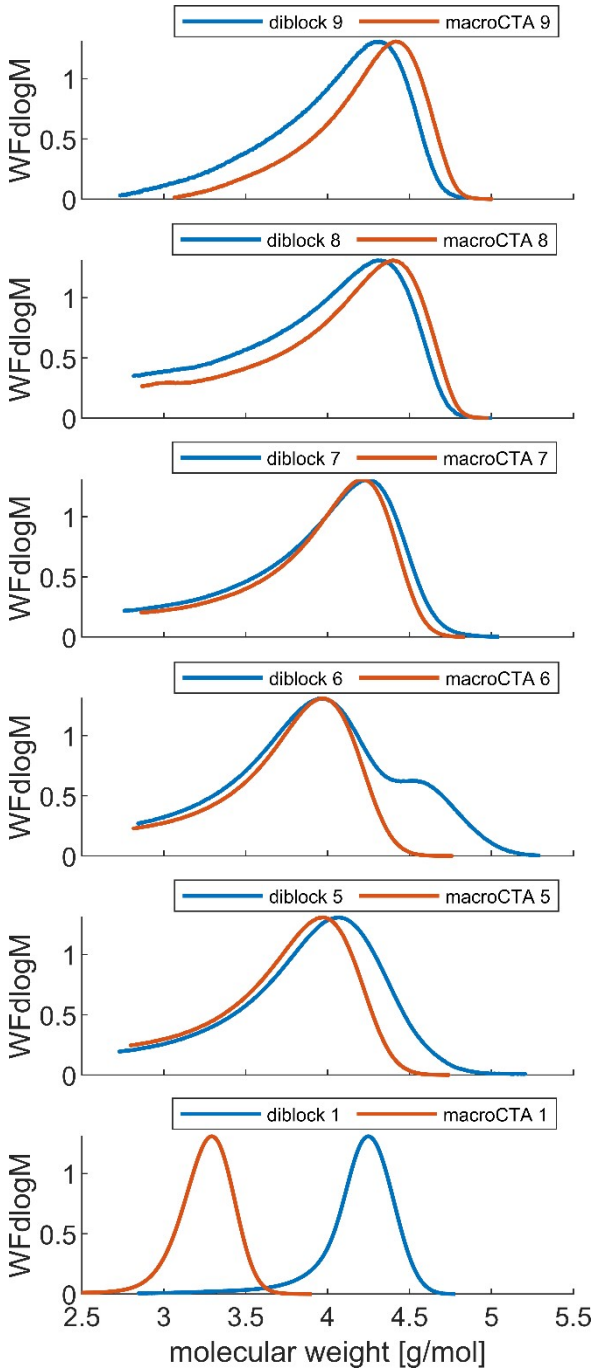

Figure S11. DMF SEC traces for diblock samples from Table 2 and their corresponding macroCTAs. The results have been recorded using a different SEC apparatus than that used in Figure 3.

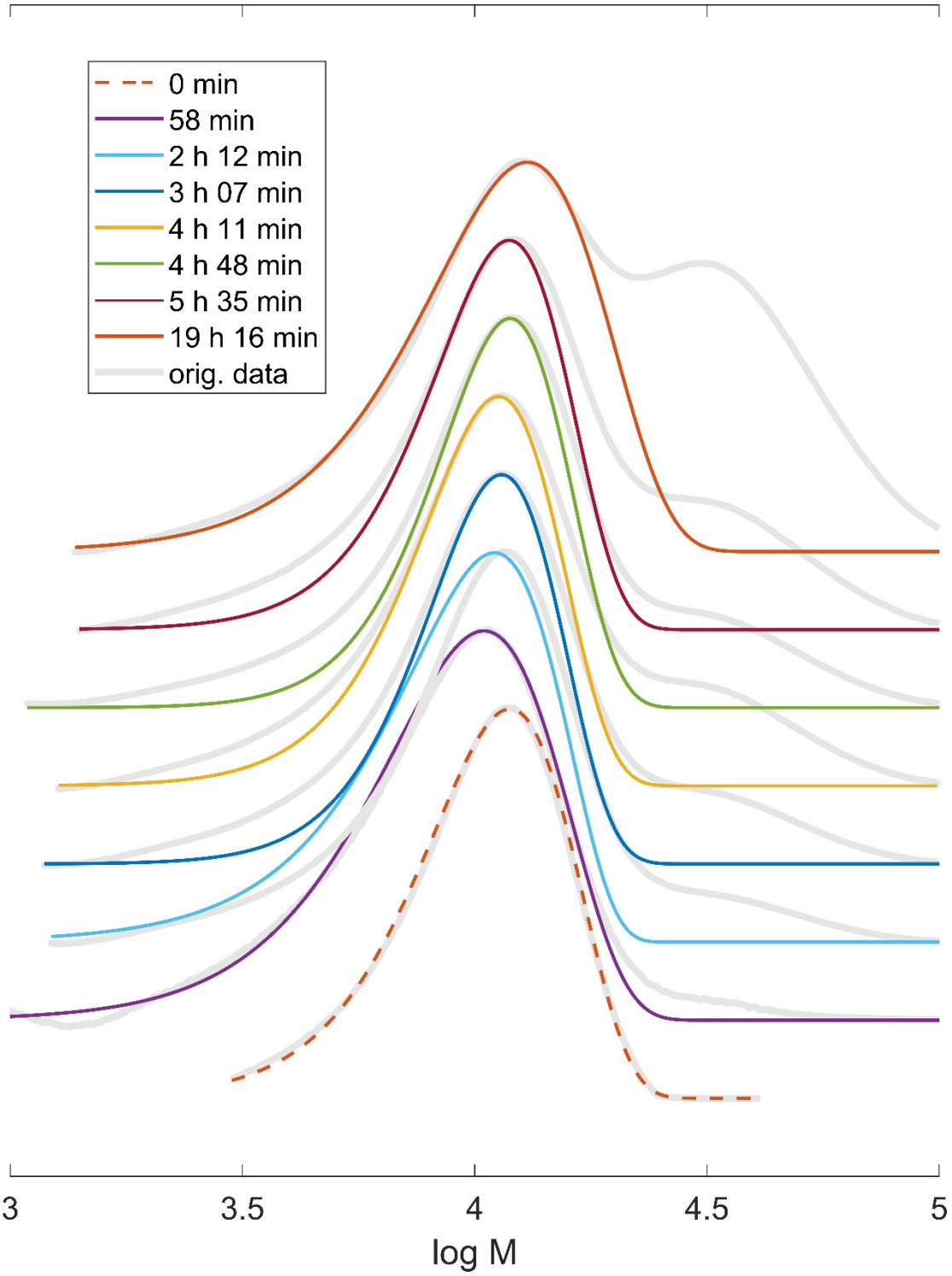

Figure S12. DMF SEC traces recorded for polymerization of styrene in the presence of $(Et_3N\text{-AMPS})_{50}$-BDMAT macroCTA. Parameters of the reaction: [M]/[CTA] = 200, [CTA]/[I] = 10, [M]/[I] = 2000, $[M]_0$ = 1 mol/dm^3, solvent: DMF, temperature: 70 °C. Coloured traces are lognormal distributions fitted to the original data.