ELECTRONIC SUPPLEMENTARY INFORMATION FOR:

Avoiding compositional drift during the RAFT copolymerization of *N*-(2-hydroxypropyl)methacrylamide and *N*-acryloxysuccinimide: towards uniform platforms for post-polymerization modification

John Moraes,[1] Ioana-Maria Simionca,[1,2] Hedi Ketari[1] and Harm-Anton Klok[1,*]

[1] *École Polytechnique Fédérale de Lausanne (EPFL), Institut des Matériaux and Institut des Sciences et Ingénierie Chimiques, Laboratoire des Polymères, Bâtiment MXD, Lausanne, Switzerland.*

[2] *Current address: Center of Advanced Research in Bionanoconjugates and Biopolymers, Petru Poni Institute of Macromolecular Chemistry, 41A Grigore Ghica Voda Alley, 700487, Iasi, Romania.*

* email: harm-anton.klok@epfl.ch

Table S1: Monomer Feed and Copolymer Composition Data for the Free Radical Copolymerization of HPMA and NAS in DMSO-d_6 at 70 °C.

Expt. #	Feed composition (mol %)		Conversion by ^{1}H NMR (mol %)		M1[a] (HPMA)	M2 [a] (NAS)	m1 [a] (HPMA)	m2 [a] (NAS)	X=M1/M2	Y=m1/m2	G=X·(Y-1)/Y	F=X²/Y
	HPMAm	NAS	HPMAm	NAS								
1	95	5	1.20	4.76	0.95	0.05	0.83	0.17	19.00	4.79	15.03	75.37
2	93	7	0.61	1.60	0.93	0.07	0.84	0.16	13.29	5.07	10.66	34.85
3	91	9	0.90	3.20	0.91	0.09	0.74	0.26	10.11	2.84	6.56	35.95
4	90	10	1.51	5.00	0.90	0.10	0.73	0.27	9.00	2.72	5.69	29.80
5	85	15	1.21	4.80	0.85	0.15	0.59	0.41	5.67	1.43	1.70	22.48
6	80	20	1.15	1.98	0.80	0.20	0.70	0.30	4.00	2.32	2.28	6.89
7	75	25	1.30	5.48	0.75	0.25	0.42	0.58	3.00	0.71	-1.22	12.65
8	70	30	1.06	2.12	0.70	0.30	0.54	0.46	2.33	1.17	0.33	4.67
9	65	35	1.20	1.60	0.65	0.35	0.58	0.42	1.86	1.39	0.52	2.48
10	60	40	1.19	2.00	0.60	0.40	0.47	0.53	1.50	0.89	-0.18	2.52
11	55	45	0.89	1.58	0.55	0.45	0.41	0.59	1.22	0.69	-0.55	2.17
12	50	50	0.93	2.18	0.50	0.50	0.30	0.70	1.00	0.43	-1.34	2.34
13	45	55	0.90	2.34	0.45	0.55	0.24	0.76	0.82	0.31	-1.78	2.13
14	40	60	0.90	2.30	0.40	0.60	0.21	0.79	0.67	0.26	-1.89	1.70
15	30	70	0.91	2.23	0.30	0.70	0.15	0.85	0.43	0.17	-2.02	1.05
16	20	80	0.75	2.90	0.20	0.80	0.06	0.94	0.25	0.06	-3.62	0.97
17	15	85	1.81	3.21	0.15	0.85	0.09	0.91	0.18	0.10	-1.60	0.31
18	10	90	1.22	3.92	0.10	0.90	0.03	0.97	0.11	0.03	-3.10	0.36
19	5	95	0.60	3.85	0.05	0.95	0.01	0.99	0.05	0.01	-6.36	0.34

[a] Composition of the initial mixture (M) and composition of the copolymer (m) are expressed in molar fractions.

Table S2: Monomer Feed and Copolymer Composition Data for the RAFT Copolymerization of HPMA and NAS in DMSO-d_6 at 70 °C.

Expt. #	Feed composition (mol %)		Conversion by 1H NMR (mol %)		M1[a] (HPMA)	M2 [a] (NAS)	m1 [a] (HPMA)	m2 [a] (NAS)	X=M1/M2	Y=m1/m2	G=X•(Y-1)/Y	F=X²/Y
	HPMA	NAS	HPMA	NAS								
20	95	5	1.80	4.49	0.95	0.05	0.88	0.12	19.00	7.62	16.51	47.39
21	90	10	2.38	4.30	0.90	0.10	0.83	0.17	9.00	4.98	7.19	16.26
22	85	15	1.40	4.70	0.85	0.15	0.63	0.37	5.67	1.69	2.31	19.02
23	80	20	1.03	2.07	0.80	0.20	0.67	0.33	4.00	1.99	1.99	8.04
24	75	25	2.76	5.10	0.75	0.25	0.62	0.38	3.00	1.62	1.15	5.54
25	70	30	0.91	2.00	0.70	0.30	0.51	0.49	2.33	1.06	0.14	5.13
26	60	40	1.19	2.00	0.60	0.40	0.47	0.53	1.50	0.89	-0.18	2.52
27	50	50	0.92	2.10	0.50	0.50	0.30	0.70	1.00	0.44	-1.28	2.28
28	40	60	0.92	2.22	0.40	0.60	0.22	0.78	0.67	0.28	-1.75	1.61
29	25	75	0.91	2.13	0.25	0.75	0.12	0.88	0.33	0.14	-2.01	0.78
30	10	90	1.98	5.08	0.10	0.90	0.04	0.96	0.11	0.04	-2.45	0.29
31	5	95	1.35	4.95	0.05	0.95	0.01	0.99	0.05	0.01	-3.61	0.19

[a] Composition of the initial mixture (M) and composition of the copolymer (m) are expressed in molar fractions.

Table S3: Monomer Feed and Copolymer Composition Data for the RAFT Copolymerization of HPMA and NAS in DMF-d_7 at 70 °C.

Expt. #	Feed composition (mol %)		Conversion by 1H NMR (mol %)		M1[a] (HPMA)	M2 [a] (NAS)	m1 [a] (HPMA)	m2 [a] (NAS)	X=M1/M2	Y=m1/m2	G=X•(Y-1)/Y	F=X²/Y
	HPMA	NAS	HPMA	NAS								
32	95	5	1.53	85.71	0.95	0.05	0.25	0.75	19.00	0.34	N/A [b]	N/A [b]
33	85	15	2.16	69.44	0.85	0.15	0.15	0.85	5.67	0.18	N/A [b]	N/A [b]
34	75	25	2.42	7.14	0.75	0.25	0.50	0.50	3.00	1.02	0.04	8.87
35	65	35	3.32	7.19	0.65	0.35	0.46	0.54	1.86	0.86	-0.31	4.02
36	55	45	3.32	5.29	0.55	0.45	0.43	0.57	1.22	0.77	-0.37	1.94
37	50	50	1.81	3.88	0.50	0.50	0.32	0.68	1.00	0.47	-1.14	2.14
38	45	55	3.02	6.41	0.45	0.55	0.28	0.72	0.82	0.39	-1.30	1.74
39	35	65	2.41	2.97	0.35	0.65	0.30	0.70	0.54	0.44	-0.69	0.66
40	25	75	5.13	13.67	0.25	0.75	0.11	0.89	0.33	0.13	-2.33	0.89
41	15	85	4.33	13.99	0.15	0.85	0.05	0.95	0.18	0.05	-3.05	0.57
42	5	95	4.32	12.21	0.05	0.95	0.02	0.98	0.05	0.02	-2.77	0.15

[a] Composition of the initial mixture (M) and composition of the copolymer (m) are expressed in molar fractions.

[b] F and G vales not plotted due to the high conversions of NAS.

Table S4: Monomer conversions and NAS content of RAFT copolymerizations conducted in DMSO.

	20% NAS in DMSO			30% NAS in DMSO		
Time (mins)	**HPMA Conversion**	**NAS Conversion**	**NAS content**	**HPMA Conversion**	**NAS conversion**	**NAS content**
0	0%	0%		0%	0%	
20	6%	24%		1%	8%	
40	25%	72%	41%	26%	55%	47%
60	40%	96%	38%	38%	77%	46%
120	48%	100%	34%	59%	97%	41%
240	54%	100%	32%	66%	100%	39%
360	54%	100%	31%	72%	100%	37%
540	61%	100%	29%	76%	100%	36%

Table S5: Monomer conversions and NAS content of RAFT copolymerizations conducted in DMF.

	20% NAS in DMF			30% NAS in DMF		
Time (mins)	**HPMA Conversion**	**NAS Conversion**	**NAS content**	**HPMA Conversion**	**NAS Conversion**	**NAS content**
0	0%	0%		0%	0%	
20	0%	0%		0%	0%	
40	0%	4%		1%	2%	
60	0%	9%		3%	5%	
120	10%	35%	47%	18%	34%	44%
240	31%	65%	34%	46%	74%	41%
360	43%	84%	33%	54%	84%	40%
540	48%	92%	32%	63%	89%	38%

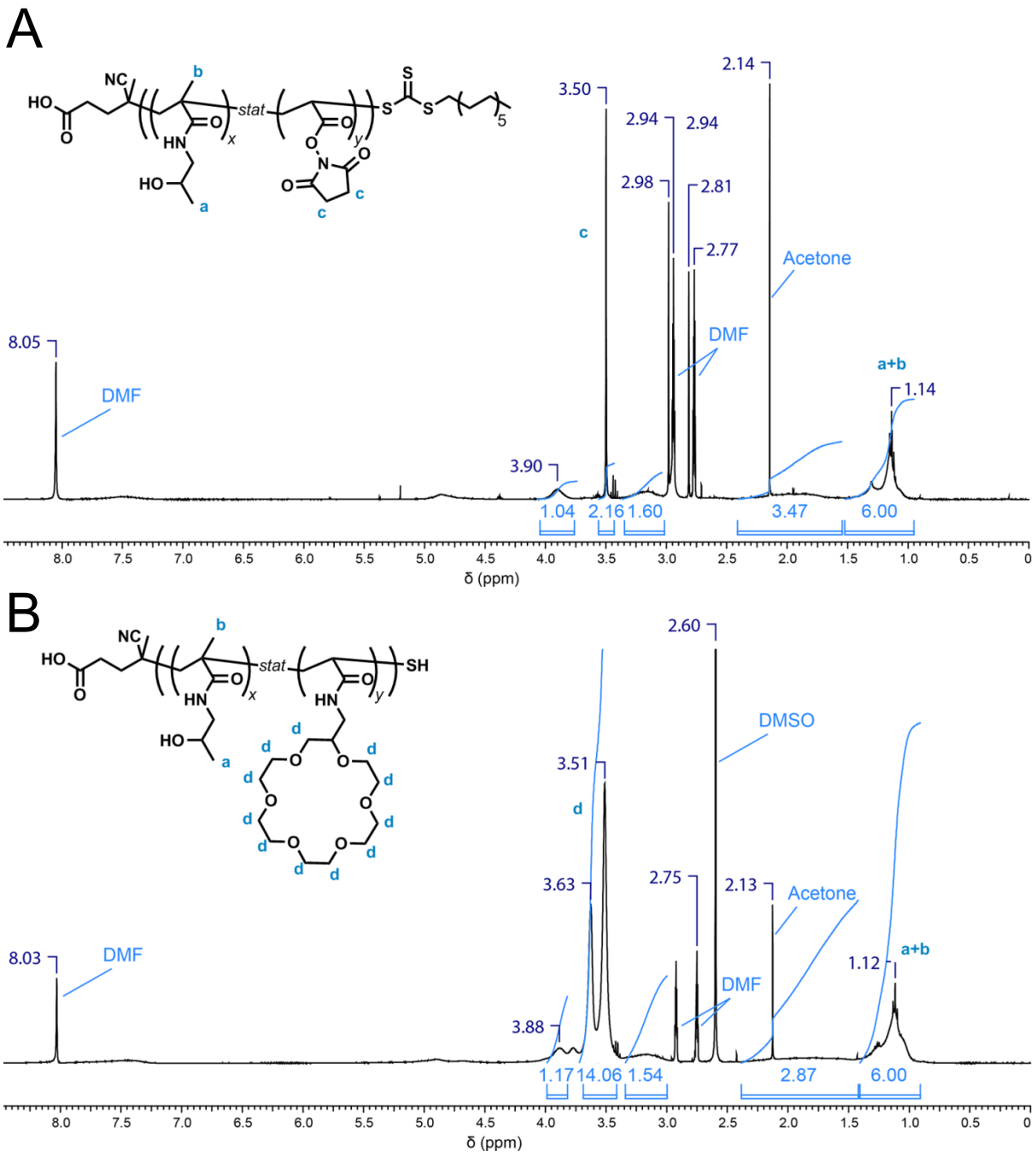

Figure S1: ^{1}H NMR spectrum of poly(HPMA-*stat*-NAS) before (A) and after (B) post-polymerization modification.

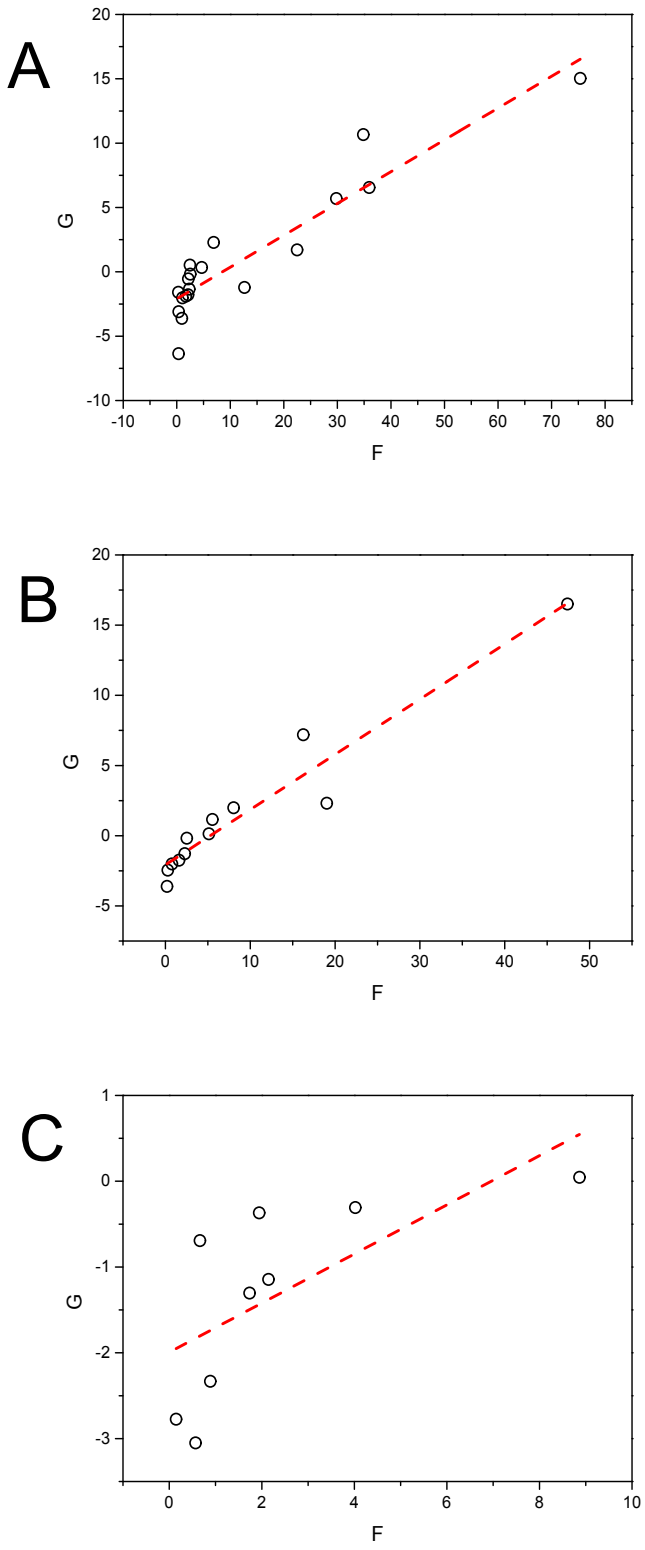

Figure S2: Fineman-Ross plots for (A) the free radical copolymerization of HPMA and NAS in DMSO, (B) the RAFT copolymerization of HPMA and NAS in DMSO and (C) the RAFT copolymerization of HPMA and NAS in DMF.

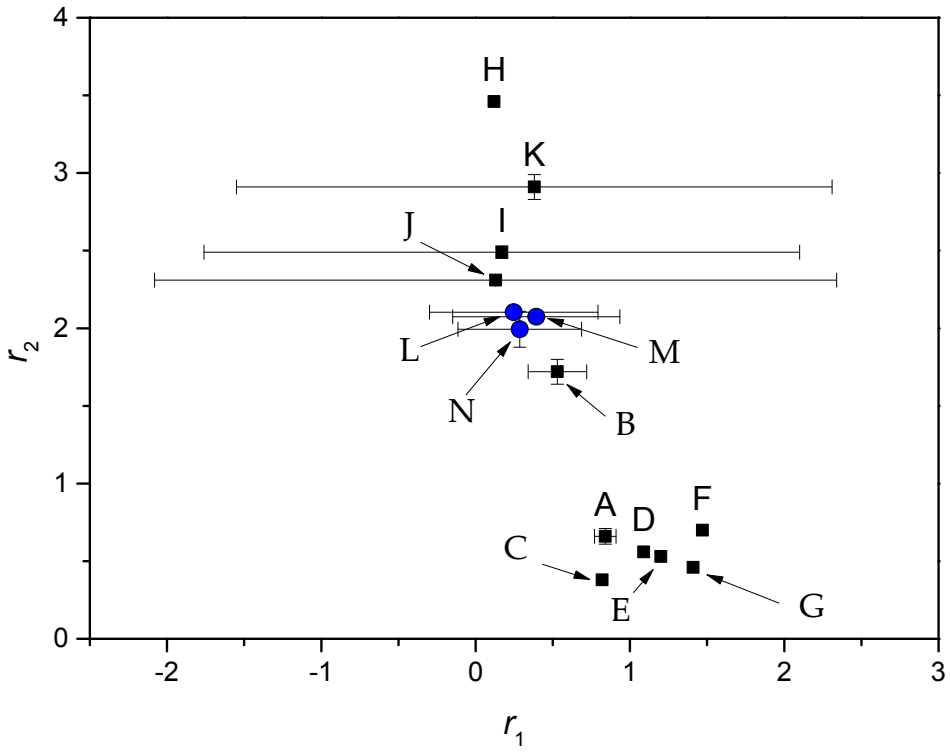

Figure S3: r_1 and r_2 values of various co-monomer systems where monomer 1 is HPMA and monomer 2 is as listed in Table 1 in the manuscript. The letters A-N refer to the different studies summarized in Table 1. (L, M and N = this work)

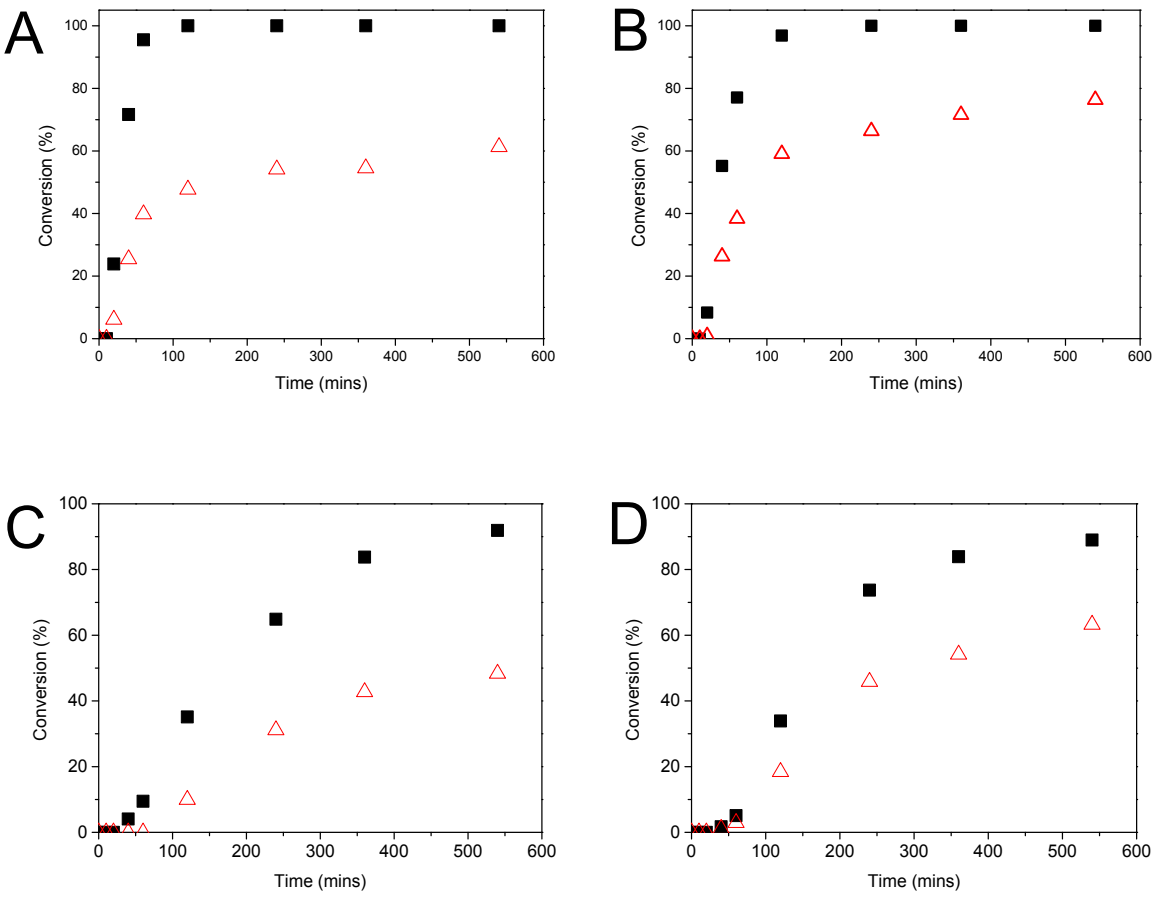

Figure S4: Conversion vs time for the RAFT-mediated polymerization of HPMA and NAS in DMSO and DMF: A) 20% NAS in DMSO; B) 30% NAS in DMSO; C) 20% NAS in DMF and D) 30% NAS in DMF where conversion of NAS is in closed squares and conversion of HPMA is open triangles.

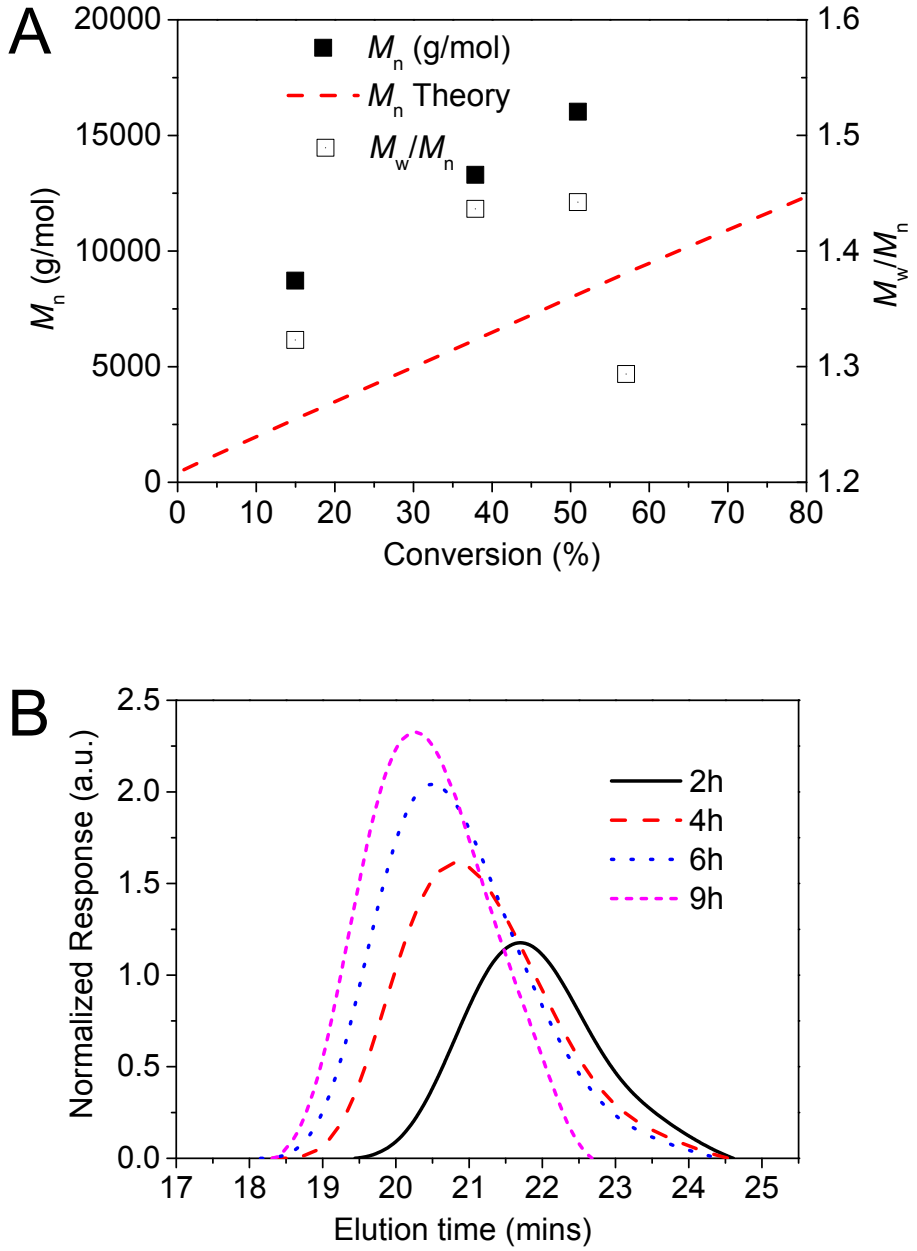

Figure S5: SEC analysis of polymers from RAFT-mediated polymerization of HPMA and NAS (20%) in DMF: A) Molecular weights (■) and dispersities (□); the line represents the theoretical M_n and B) SEC traces.

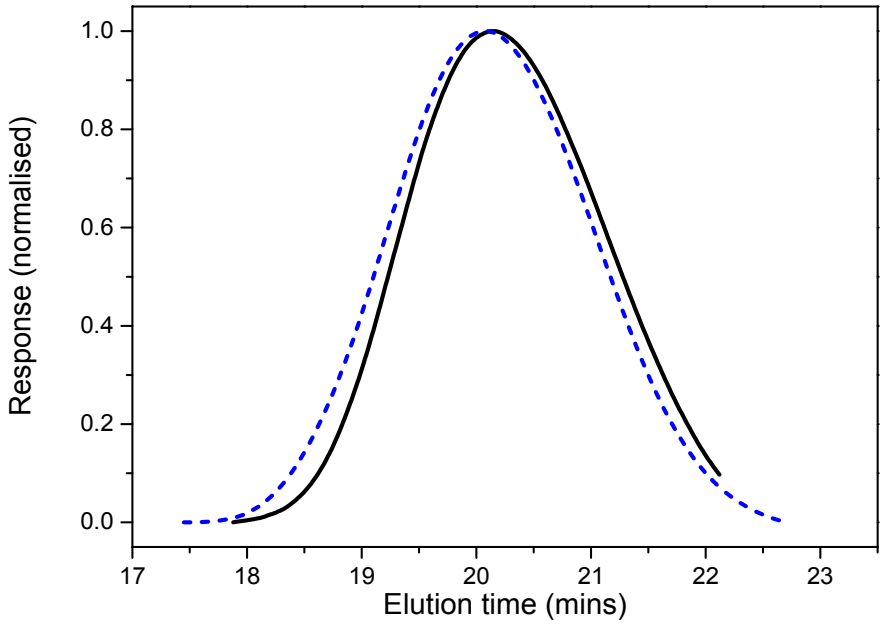

Figure S6: SEC traces of polymer from RAFT-mediated polymerization of HPMA and NAS in DMF before (—) and after (– – –) modification with 2-aminomethyl-18-crown-6.