Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary material for:

A RAFT Copolymerization of NIPAM and HPMA and Evaluation of Thermo-responsive Properties of Poly(NIPAM-*co*-HPMA)

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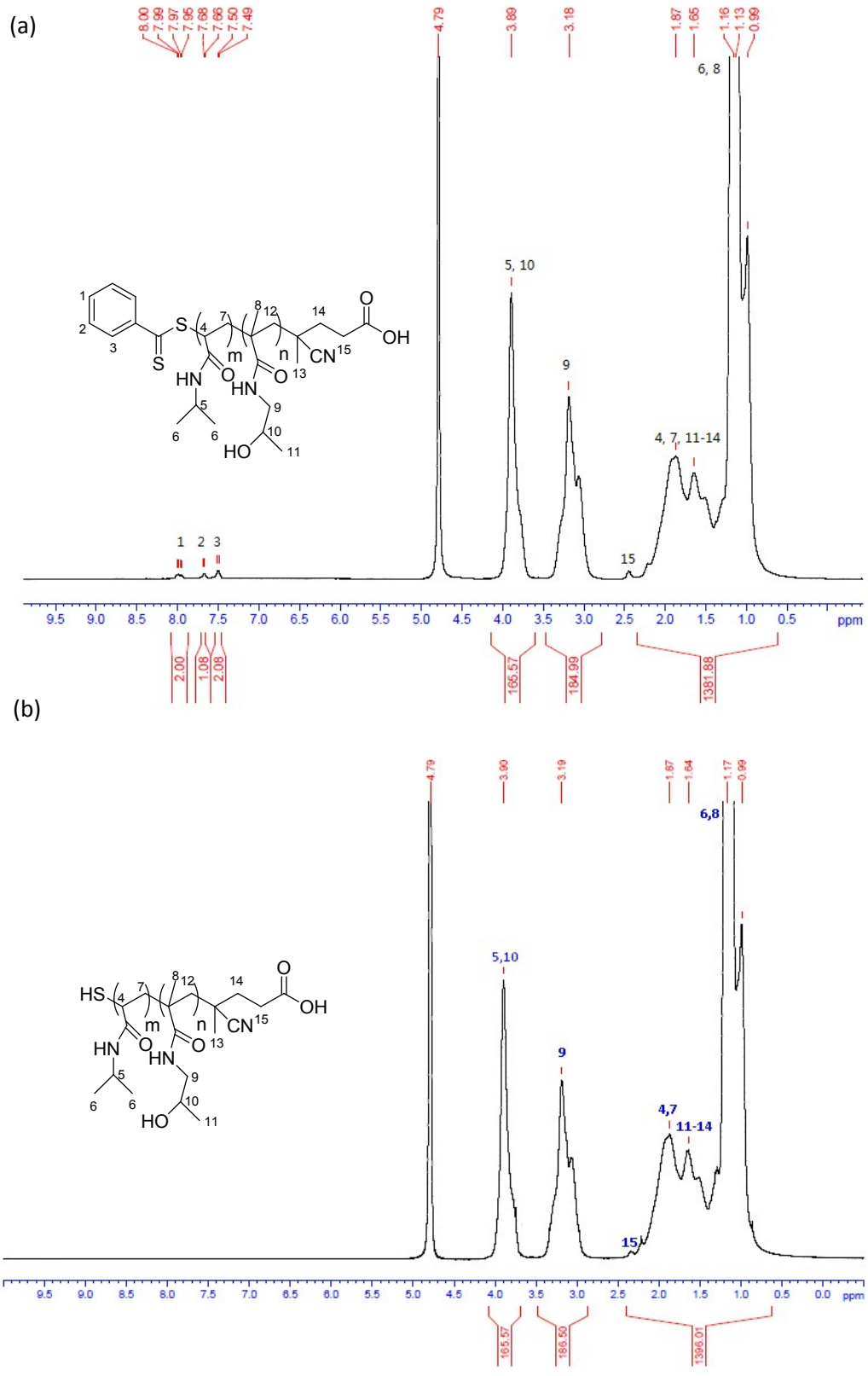
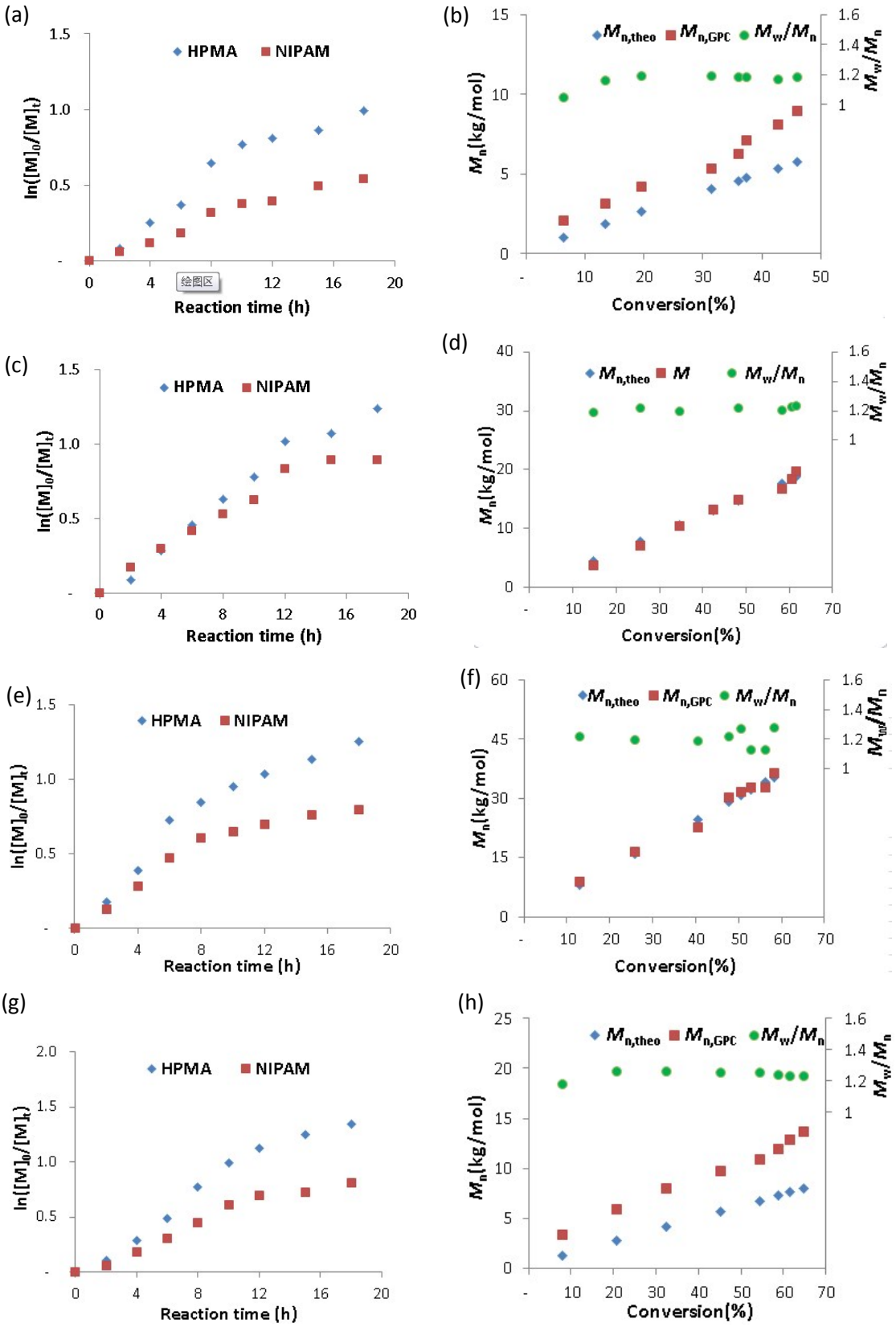


Figure S1. ^{1}H NMR spectra of the NIPAM-*co*-HPMA (F_{HPMA} = 0.56; DP_{NMR} = 165): (a) **P_B-10** (b) **$P_{B,SH}$-10**.


(a)
HPMA
NIPAM
ln([M]0/[M]t)
Reaction time (h)
(b)
Mn,theo
Mn,GPC
Mw/Mn
Mn(kg/mol)
Conversion(%)
(c)
HPMA
NIPAM
ln([M]0/[M]t)
Reaction time (h)
(d)
Mn,theo
M
Mw/Mn
Mn(kg/mol)
Conversion(%)
(e)
HPMA
NIPAM
ln([M]0/[M]t)
Reaction time (h)
(f)
Mn,theo
Mn,GPC
Mw/Mn
Mn(kg/mol)
Conversion(%)
(g)
HPMA
NIPAM
ln([M]0/[M]t)
Reaction time (h)
(h)
Mn,theo
Mn,GPC
Mw/Mn
Mn(kg/mol)
Conversion(%)

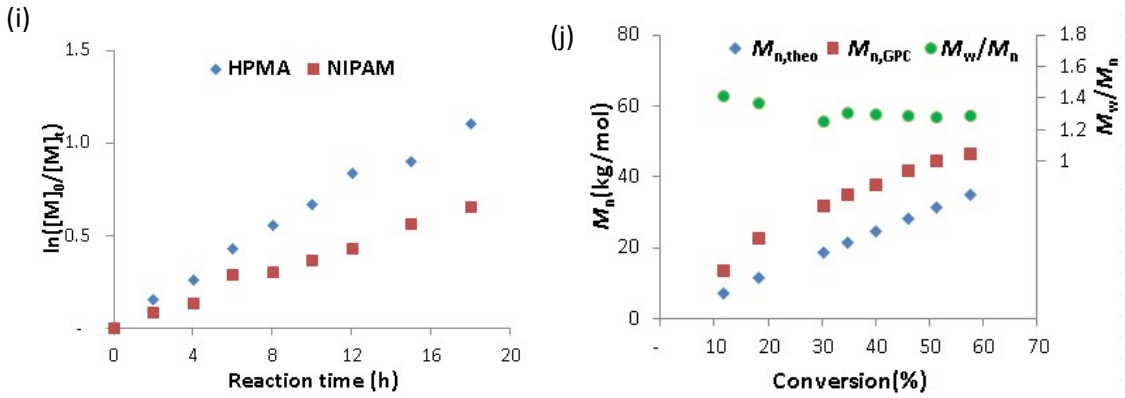


Figure S2. Kinetic plots of $\ln([M]_0/[M]_t)$ *vs.* time in the RAFT copolymerization of NIPAM and HPMA: (a) 20 mol% HPMA, target MW 12k; (c) 20 mol% HPMA, target MW 30k; (e) 20 mol% HPMA, target MW 60k; (g) 50 mol% HPMA, target MW 12k; (i) 50 mol% HPMA, target MW 60k; plots of the theoretical number-average molecular weight ($M_{n,theo}$), the experimental number-average molecular weight ($M_{n,GPC}$) and PDI (M_w/M_n) *vs.* total monomer conversions in the RAFT copolymerization of NIPAM and HPMA: (b) 20 mol% HPMA, target MW 12k; (d) 20 mol% HPMA, target MW 30k; (f) 20 mol% HPMA, target MW 60k; (h) 50 mol% HPMA, target MW 12k; (j) 50 mol% HPMA, target MW 60k.

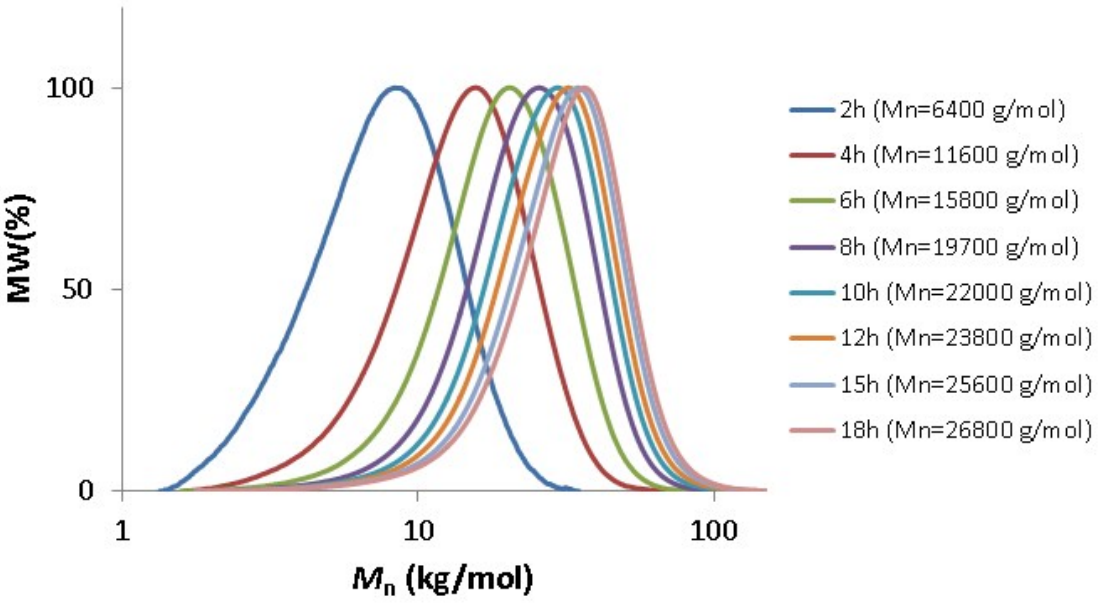


Figure S3. GPC traces of NIPAM-co-HPMA copolymers from the kinetic study of the copolymerization of NIPAM and HPMA with 50 mol % HPMA in dioxane/water, target MW 30k.

Table S1. Results of kinetic studies for RAFT copolymerization of NIPAM and HPMA.

Entry	Time (h)	f(NIPAM /HPMA)[a]	Conv.(%)[b] NIPAM	Conv.(%)[b] HPMA	*F*(HPMA)[c] (%)	$M_{n,theo}$[d] (g/mol)	M_n[e]	M_w/M_n[e]
target M_n 12k	2	4/1	6	8	26	1000	2100	1.05
	4		11	23	34	1900	3200	1.16
	6		17	31	32	2600	4200	1.19
	8		27	48	30	4100	5300	1.19
	10		32	54	30	4600	6300	1.18
	12		33	56	30	4800	7100	1.18
	15		39	58	27	5400	8100	1.17
	18		42	63	27	5800	8900	1.18
	2	1/1	5	10	66	1200	3400	1.18
	4		17	25	60	2700	5900	1.26
	6		26	38	59	4200	8000	1.26
	8		36	54	60	5700	9700	1.25
	10		46	63	58	6800	10900	1.25
	12		50	68	57	7300	12000	1.24
	15		52	71	58	7600	12900	1.23
	18		56	74	57	8000	13700	1.23
target M_n 30k	2	4/1	16	9	12	4500	3600	1.18
	4		26	25	19	7800	7000	1.21
	6		34	37	21	10600	10300	1.19
	8		41	47	22	13000	13000	1.19
	10		47	54	23	14700	14800	1.21
	12		57	64	22	17700	16500	1.2
	15		59	66	22	18300	18200	1.22
	18		59	71	23	18700	19600	1.23
	2	1/1	8	2	22	1700	6400	1.32
	4		18	12	39	4700	11600	1.31
	6		28	29	51	8800	15800	1.28
	8		34	40	54	11500	19700	1.26
	10		41	52	56	14400	22000	1.26
	12		46	56	55	15700	23800	1.26
	15		54	64	54	17900	25600	1.26
	18		58	72	55	19900	26800	1.27
target M_n 60k	2	4/1	12	16	25	8000	8800	1.22
	4		24	32	25	15900	16500	1.2
	6		38	52	26	24700	22700	1.19
	8		45	57	24	29100	30300	1.22
	10		48	61	24	30800	31600	1.27
	12		50	64	24	32300	32800	1.13
	15		53	68	24	34100	32800	1.13
	18		55	71	25	35400	36600	1.28
	2	1/1	9	15	63	7400	13600	1.41

	4		13	23	64	11400	22600	1.37
	6		25	35	58	18600	32000	1.25
	8	1/1	27	43	62	21600	34900	1.31
	10		31	49	61	24700	38000	1.3
	12		35	57	62	28500	41800	1.29
	15		43	59	58	31400	44800	1.28
	18		48	67	58	35200	46500	1.29

[a] Monomer feed molar ratio at time zero.

[b] Determined by ^{1}H NMR spectroscopy.

[c] Determined by the formula:

F(HPMA) = [f(HPMA/NIPAM)*Conv.(HPMA)]/[f(HPMA/NIPAM)*Conv.(HPMA) + Conv.(NIPAM)].

[d] Determined by the formula: $M_{n,theo}$=[([M]$_{NIPAM}$/[CPADB] × Conv.$_{NIPAM}$ × M$_{NIPAM}$) + ([M]$_{HPMA}$/[CPADB] × Conv.$_{HPMA}$ × M$_{HPMA}$) + (M$_{CPADB}$)].

[e] Molar mass (in PMMA equivalents) and dispersity obtained by DMAc GPC using PMMA standard.

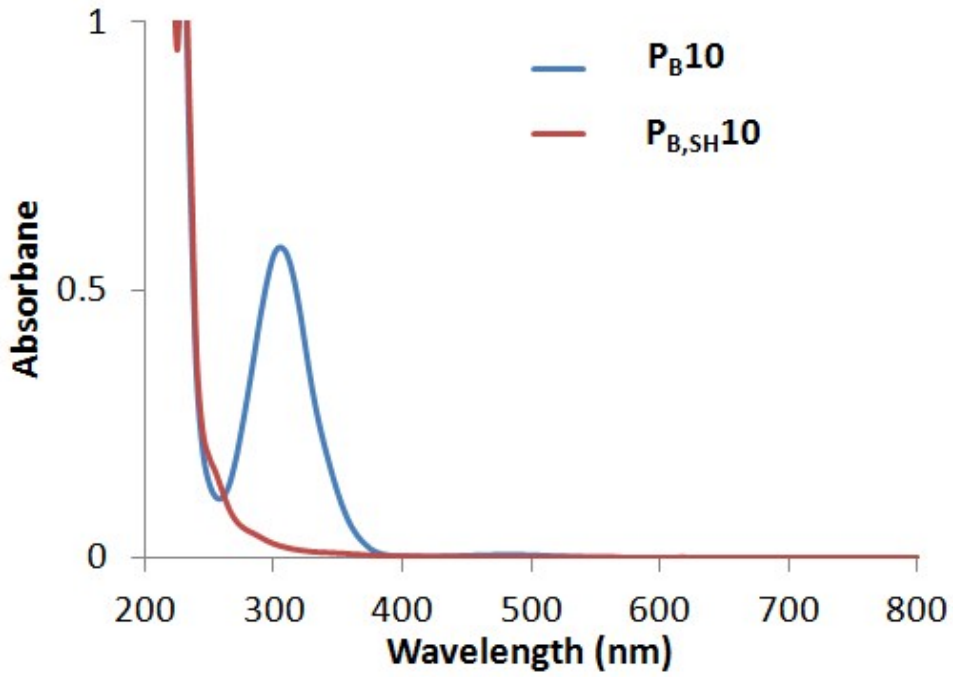


Figure S4. UV-visible absorbance spectra of RAFT polymer with RAFT agent end-group **P$_B$10** (blue line) and thiol end group **P$_{B,SH}$10** (red line), measured at concentration of 2 mg/mL in deionized water.

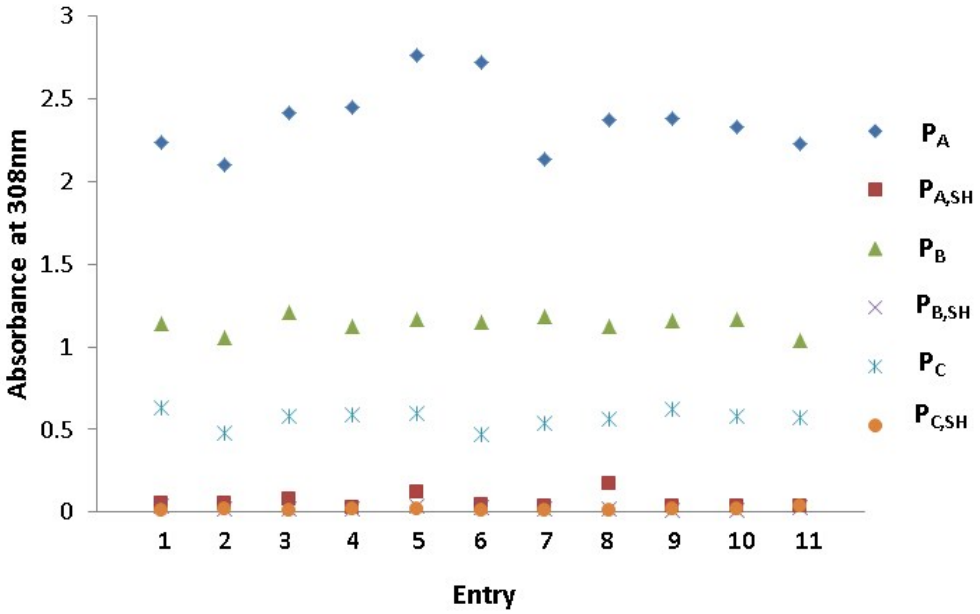


Figure S5. UV-visible absorbance of RAFT polymers with RAFT end group ($\mathbf{P_A}$, $\mathbf{P_B}$, **and** $\mathbf{P_c}$) and thiol end group ($\mathbf{P_{A,SH}}$, $\mathbf{P_{B,SH}}$, **and** $\mathbf{P_{c,SH}}$), measured at wavelength of 308 nm and at a concentration of 2 mg/mL in deionized water.

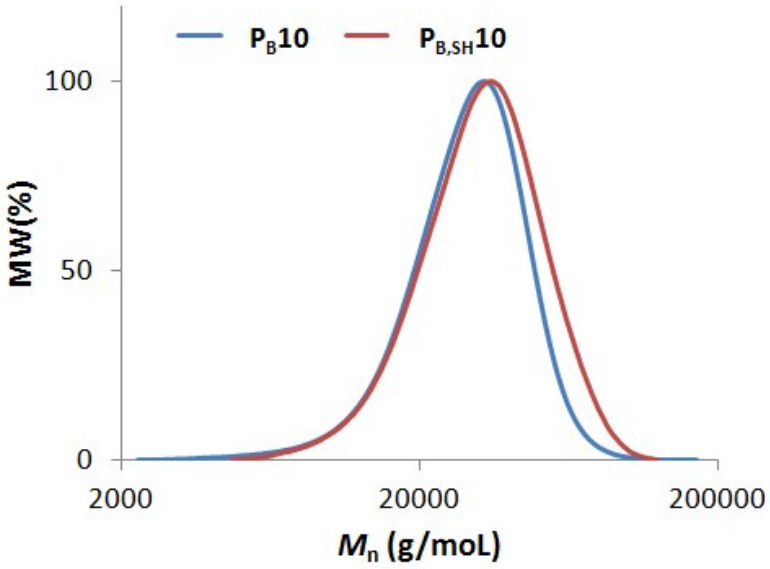
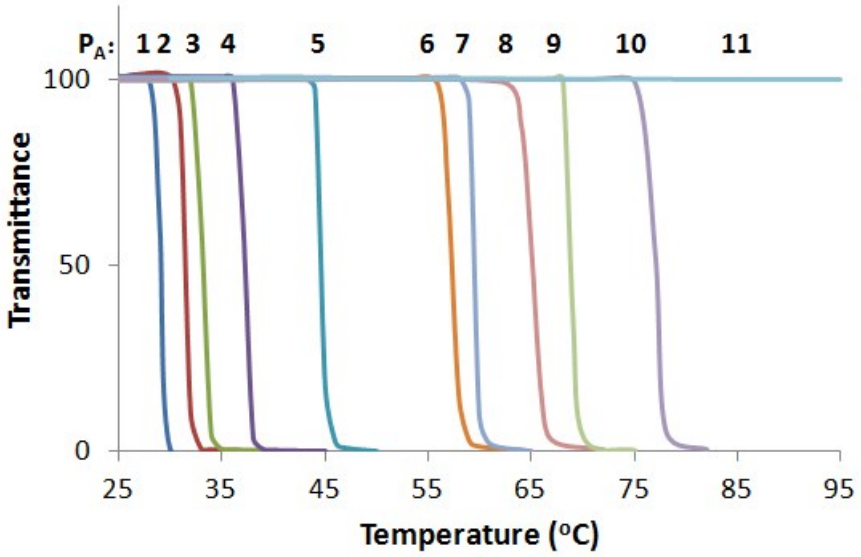
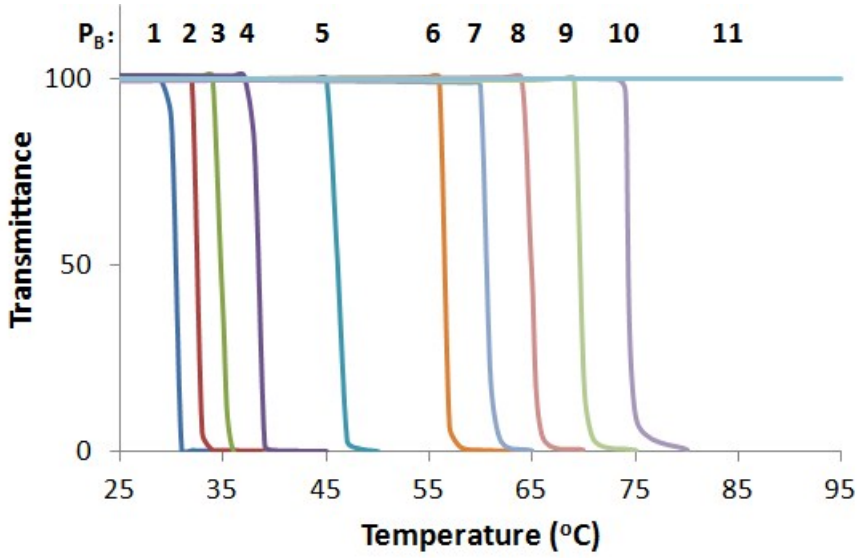
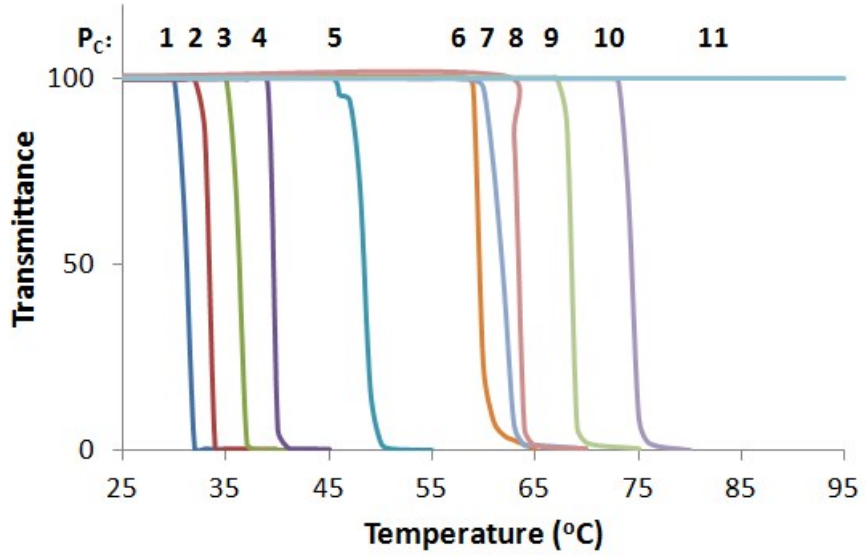
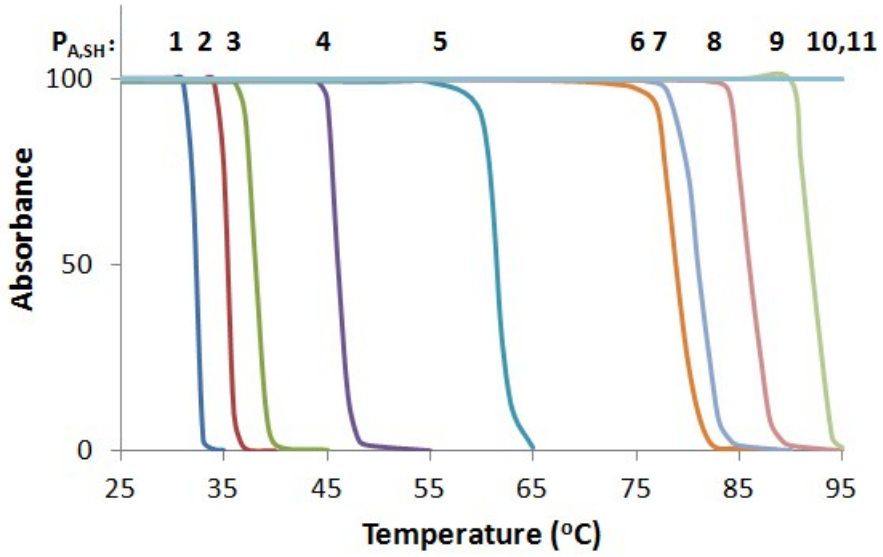


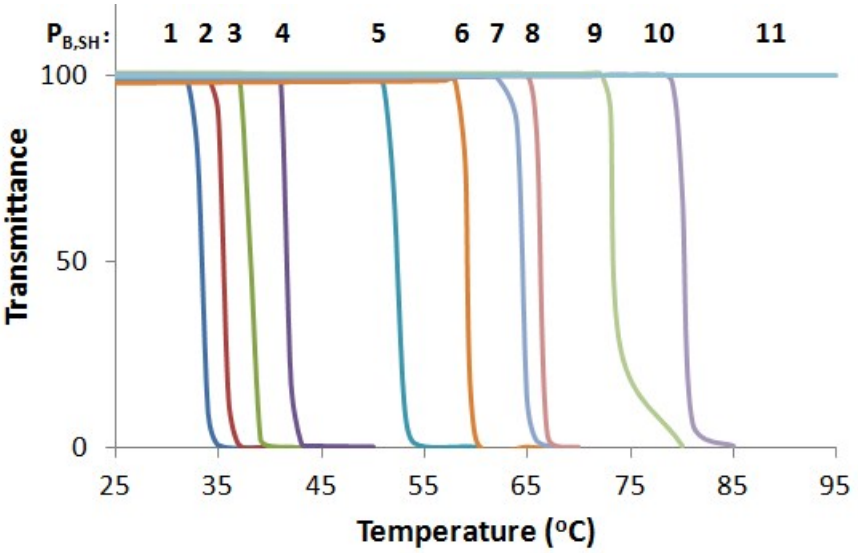
Figure S6. GPC traces of the NIPAM-*co*-HPMA (F_{HPMA} = 0.56) before ($\mathbf{P_B10}$, M_n=24900, M_w/M_n =1.24) and after aminolysis with hexylamine ($\mathbf{P_{B,SH}10}$, M_n=27500, M_w/M_n=1.25).


P_A: 1 2 3 4 5 6 7 8 9 10 11
100
50
0
Transmittance
25 35 45 55 65 75 85 95
Temperature (°C)


P_B: 1 2 3 4 5 6 7 8 9 10 11
100
50
0
Transmittance
25 35 45 55 65 75 85 95
Temperature (°C)


P_C: 1 2 3 4 5 6 7 8 9 10 11
100
50
0
Transmittance
25 35 45 55 65 75 85 95
Temperature (°C)


P A,SH :
1 2 3 4 5 6 7 8 9 10,11
100
50
0
Absorbance
25 35 45 55 65 75 85 95
Temperature (°C)


P B,SH :
1 2 3 4 5 6 7 8 9 10 11
100
50
0
Transmittance
25 35 45 55 65 75 85 95
Temperature (°C)

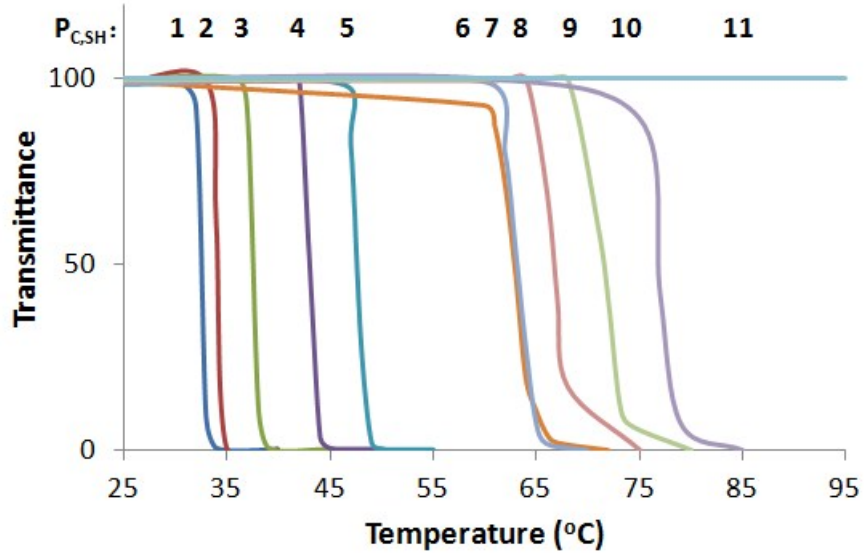

P C,SH :
1 2 3 4 5 6 7 8 9 10 11
100
50
0
Transmittance
25 35 45 55 65 75 85 95
Temperature (°C)

Figure S7. Transmittance of the (co)polymers as a function of temperature determined in deionized water with a polymer concentration of c = 5 mg/mL: (a) $\mathbf{P_A}$, (b) $\mathbf{P_B}$, (c) $\mathbf{P_C}$, (d) $\mathbf{P_{A,SH}}$, (e) $\mathbf{P_{B,SH}}$, and (f) $\mathbf{P_{C,SH}}$.