Electronic Supplementary Material (ESI) for Polymer Chemistry.

SUPPORTING INFORMATION

Characterization of complex architecture in water-soluble copolymers using RP-HPLC

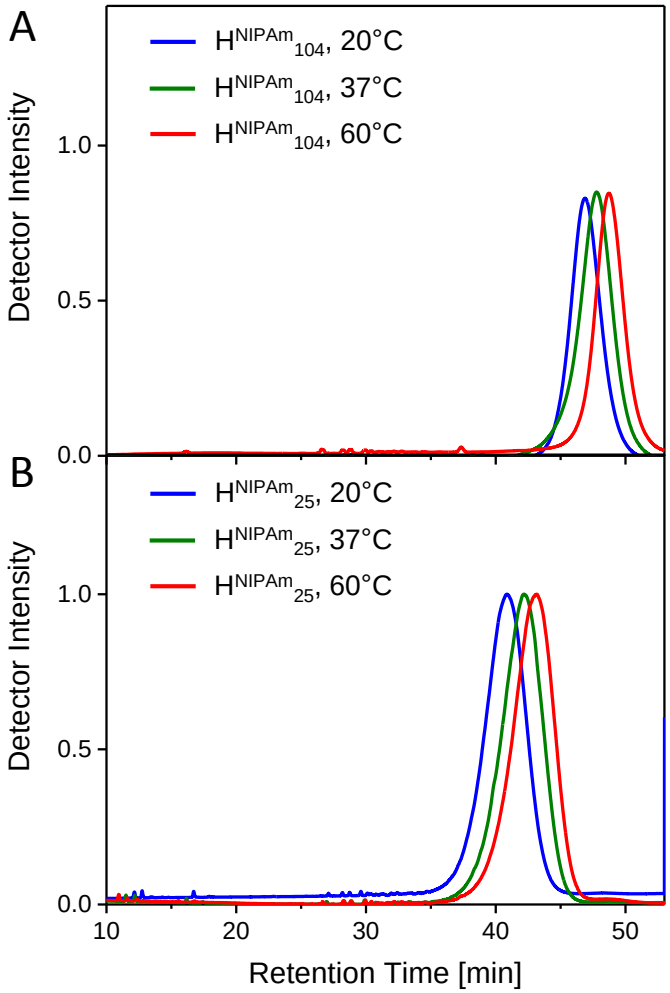

Figure S1. Influence of temperature. HPLC chromatographs of homopolymers of NIPAm A) DP = 100 or B) DP = 25 at various temperature. Solvent: water/ACN. Gradient: 1 to 95% ACN in 50 minutes. Column: C18 (4.6 mm × 150 mm)

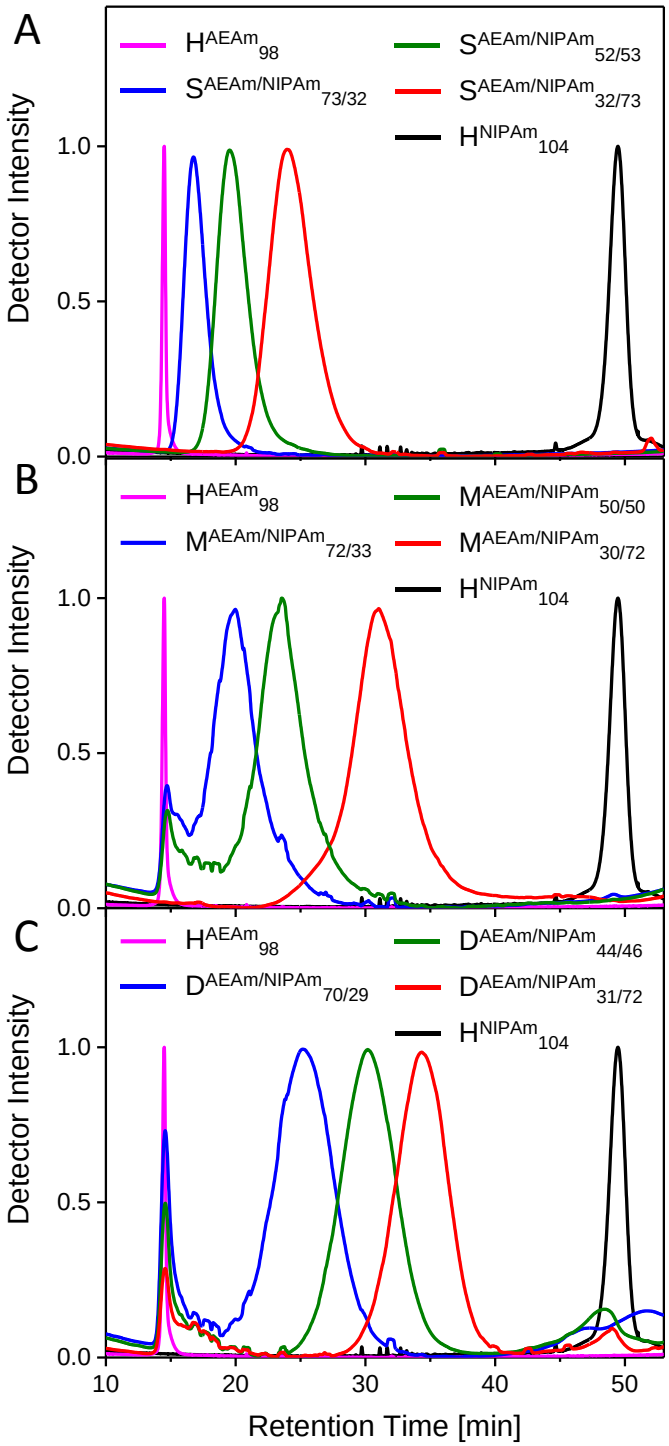

Figure S2. Influence of copolymer composition. HPLC chromatographs of copolymers with various AEAm/NIPAm ratio for A) statistical, B) multiblock, C) diblock copolymers. Homopolymers are included for references. Solvent: water/ACN. Gradient: 1 to 95% ACN in 50 minutes at 37ºC. Column: C18 (4.6 mm × 250 mm).

Table S1. Separation efficiency of copolymers AEAm/NIPAm within various composition using C18 column with a length of either 150mm or 250 mm.

Segmentation	Sample	150 mm		250 mm	
		%ACN	Δ(%ACN)	%ACN	Δ(%ACN)
Statistical copolymer	$S^{A}_{100}30$	37	8 5	45	8 6
	$S^{A}_{100}50$	29		37	
	$S^{A}_{100}70$	24		31	
Multiblock copolymer	$M^{A}_{100}30$	51	13 10	54	14 7
	$M^{A}_{100}50$	38		40	
	$M^{A}_{100}70$	28		33	
Diblock copolymer	$D^{A}_{100}30$	56	7 7	61	9 10
	$D^{A}_{100}50$	49		52	
	$D^{A}_{100}70$	42		42	

Table S2. Separation efficiency of copolymers AEAm/NIPAm within various segmentation using C18 column with a length of either 150mm or 250 mm.

% AEAm	**Δ(%ACN)**		
	Sample	**150 mm**	**250 mm**
30%	$D^{A}_{100}30$ - $M^{A}_{100}30$	5	7
	$M^{A}_{100}30$ - $S^{A}_{100}30$	14	9
50%	$D^{A}_{100}50$ - $M^{A}_{100}50$	11	12
	$M^{A}_{100}50$ - $S^{A}_{100}50$	9	3
70%	$D^{A}_{100}70$ - $M^{A}_{100}70$	14	10
	$M^{A}_{100}70$ - $S^{A}_{100}70$	4	1

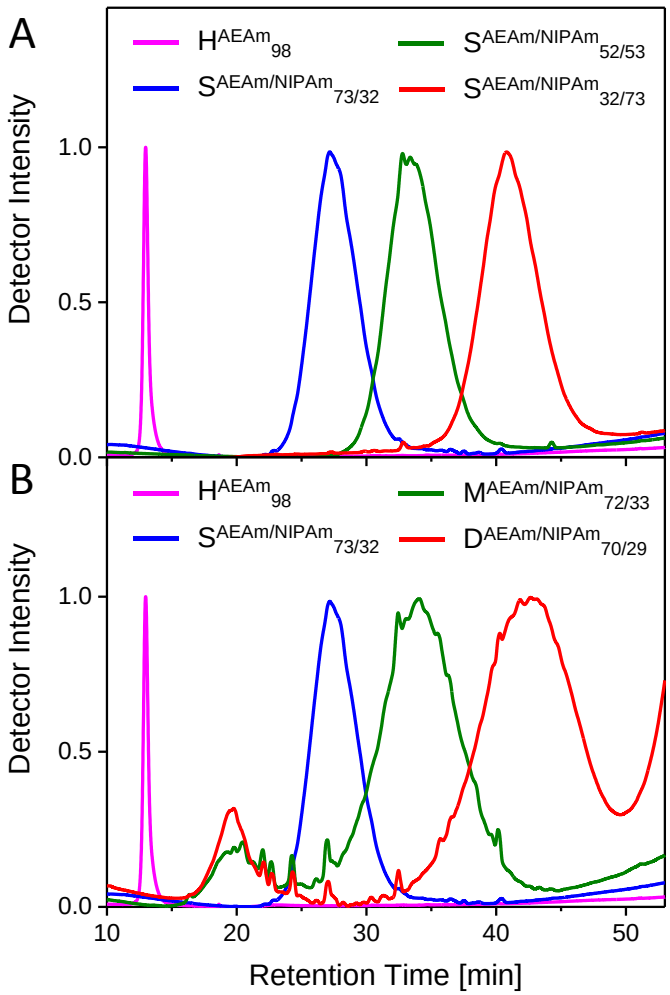

Figure S3. Influence of solvent. HPLC chromatographs of copolymers of AEAm/NIPAm (DP = 100) with A) various composition or B) various architecture. Homopolymer H^{A}_{100} included for reference. Solvent: water/MeOH. Gradient: 1 to 95% MeOH in 50 minutes at 37°C. Column: C18 (4.6 mm × 150 mm)

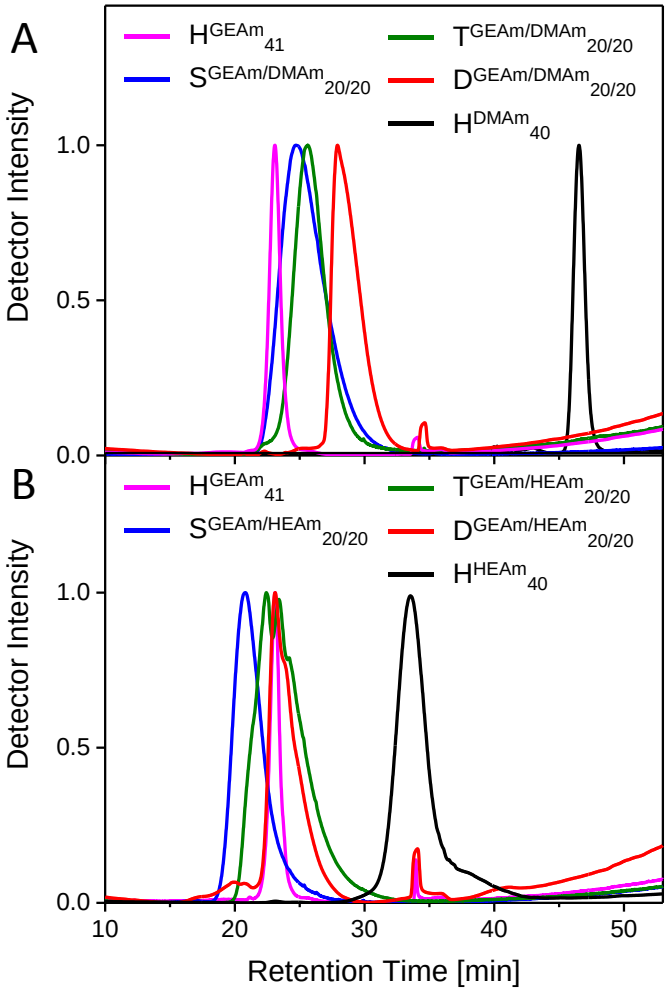

Figure S4. Influence of copolymer architecture. HPLC chromatographs of copolymers with various architecture for copolymers (DP = 40) of A) GEAm/DMAm copolymers, B) GEAm/HEAm. Homopolymers are included for references. Solvent: water/MeOH. Gradient: 5 to 90% MeOH in 50 minutes at 37ºC. Column: C18 (4.6 mm × 250 mm).

Table S3. Repeated elution characteristics of poly(HEAm-*co*-GEAm)$_{40}$ and respective homopolmers. Solvent: water/ACN. Gradient: 1 to 50% ACN in 50 minutes at 37°C. Column: C18 (4.6 mm × 250 mm).

	poly(HEAm)$_{40}$	**poly(GEAm)$_{40}$**	**50% diblock**	**50% multiblock**	**50% statistical**
rt$_1$ [min]	29.49	23.64	22.99	22.85	21.70
rt$_2$ [min]	29.62	23.55	23.40	23.06	21.72
rt$_3$ [min]	29.92	23.59	23.35	23.09	21.74
mean	29.68	23.59	23.25	23.00	21.72
SD	0.22	0.04	0.23	0.13	0.02

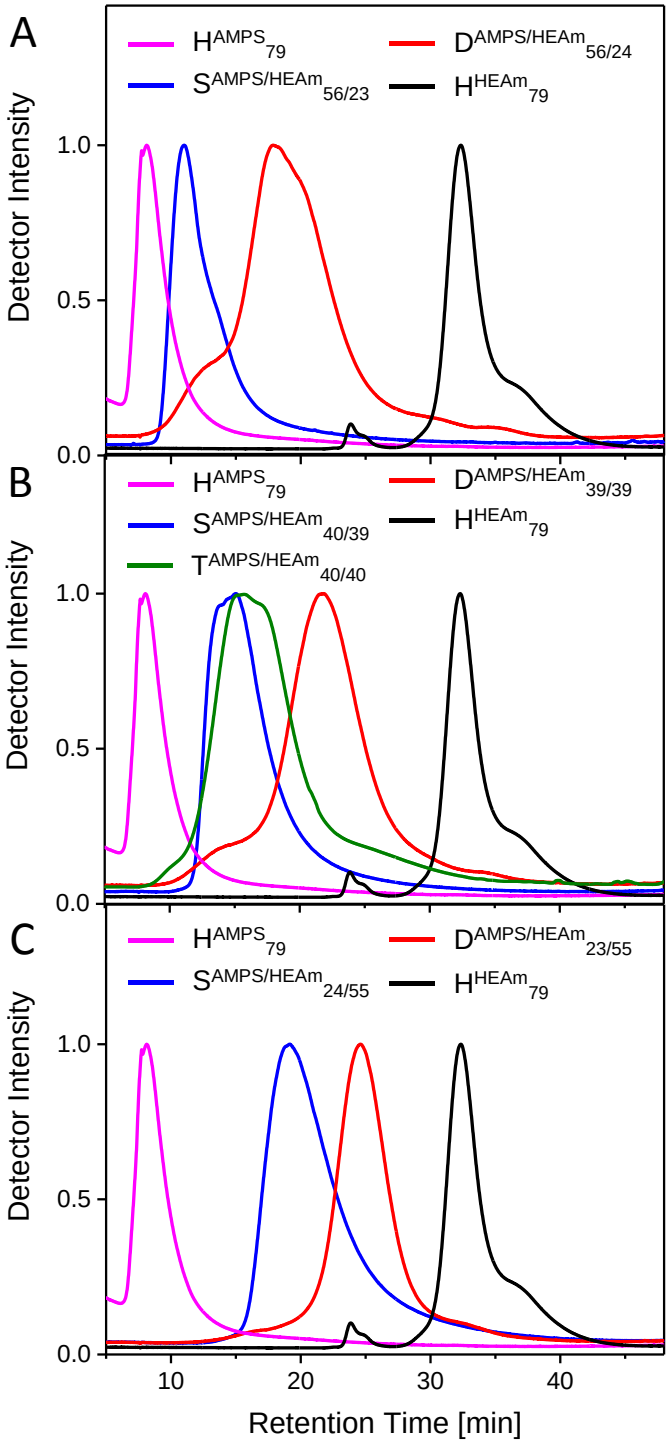

Figure S5. Influence of copolymer architecture. HPLC chromatographs of copolymers (DP = 80) with various architecture for a ratio of AMPSm/HEAm of A) 56/24, B) 40/40, C) 24/56. Homopolymers are included for references. Solvent: water/MeoH. Gradient: 10 to 80% MeOH in 50 minutes at 37ºC. Column: C18 (4.6 mm × 250 mm).

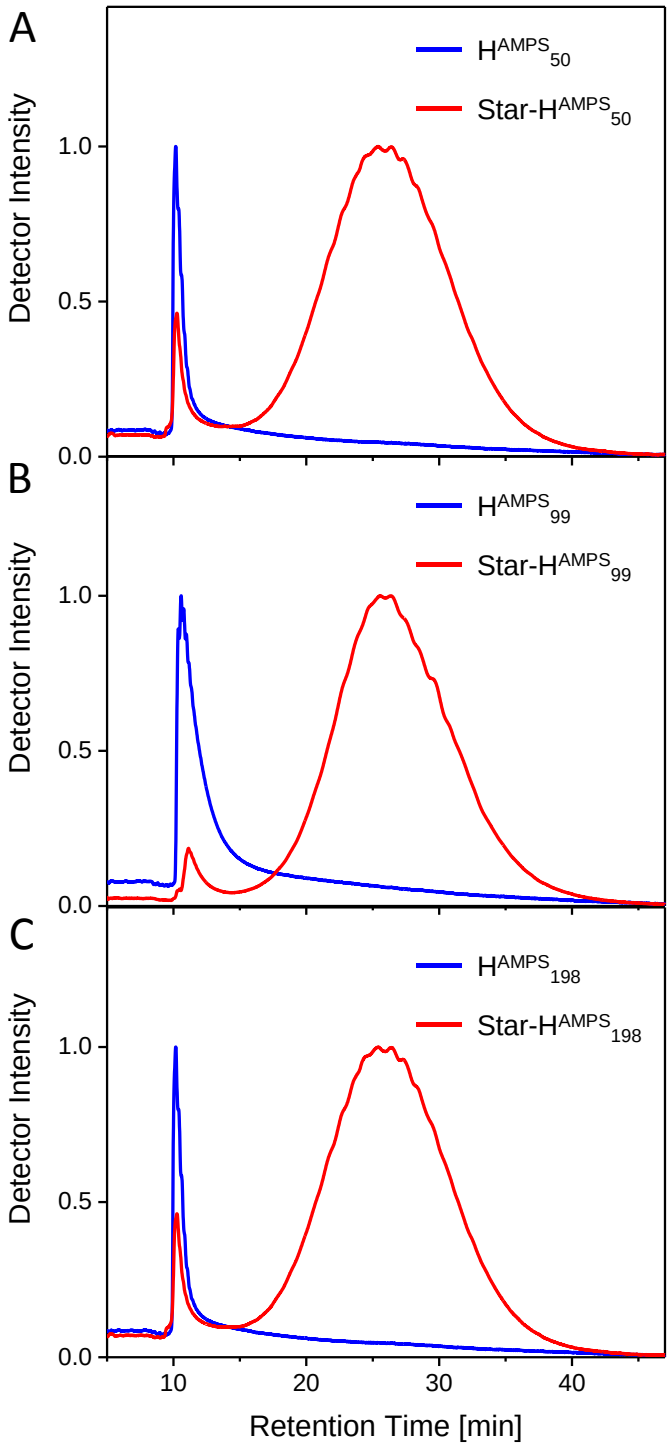

Figure S6. Homopolymer versus star-shaped homopolymers. Comparison of HPLC chromatographs of homopolymer and associated star-shaped homopolymer of a) H^{S}_{50}, b) $H^{S}_{100,}$ c) H^{S}_{200}. Solvent: water/ACN. Gradient: 1 to 50% ACN in 50 minutes at 37ºC. Column: C18 (4.6 mm × 250 mm).

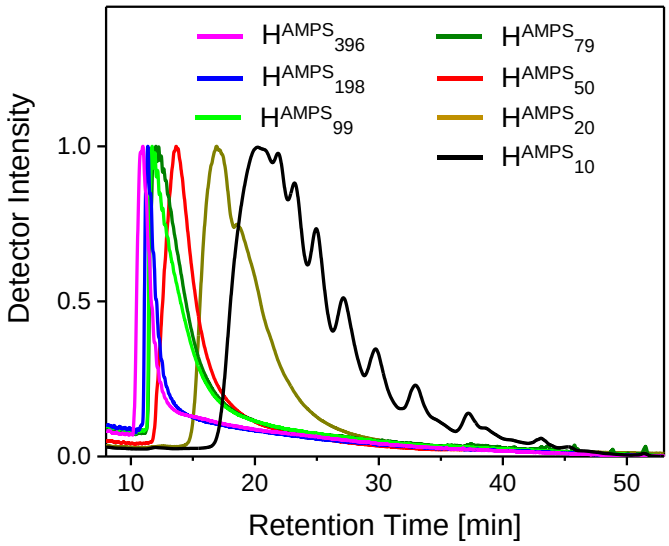

Figure S7. Influence of molecular weight. HPLC chromatographs of homopolymers of AMPSm with various DPs. Solvent: water/ACN. Gradient: 1 to 35% ACN in 50 minutes at 37ºC. Column: C18 (4.6 mm × 250 mm).