Supporting Information

Tuning the aggregation behaviour of pH responsive micelles by copolymerization

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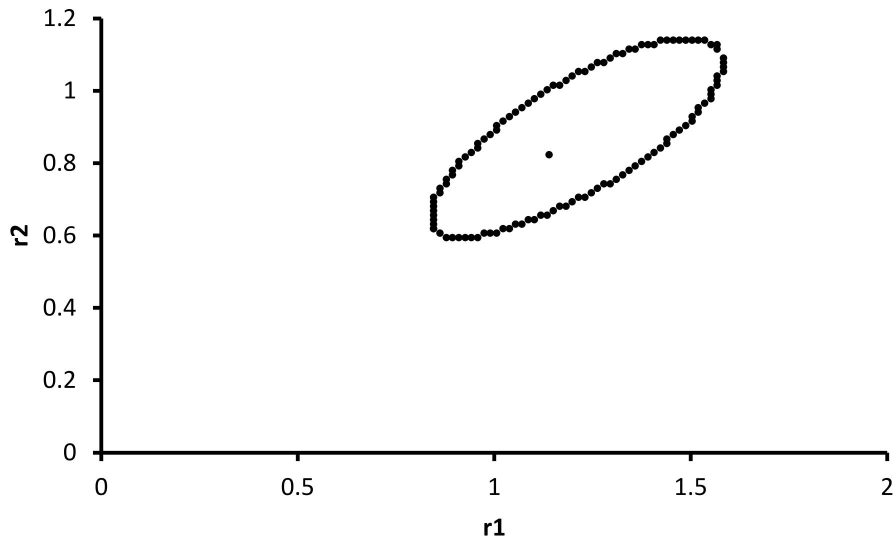

Figure S1. 95% joint confidence intervals of the r_1 and r_2 values for the DMAEMA/DEAEMA copolymerization determined using a nonlinear least-squares fitting method, developed by van Herk. [1]

Table S1. f1 and F1 values for the copolymerization of DMAEMA(f1) and DEAEMA(f2).

Experiment	Mol fraction in initial feed (f1)	Mol fraction in copolymer (F1)
1	0.09	0.09
2	0.25	0.32
3	0.32	0.35
4	0.37	0.41
5	0.54	0.55
6	0.60	0.63
7	0.71	0.76
8	0.83	0.86

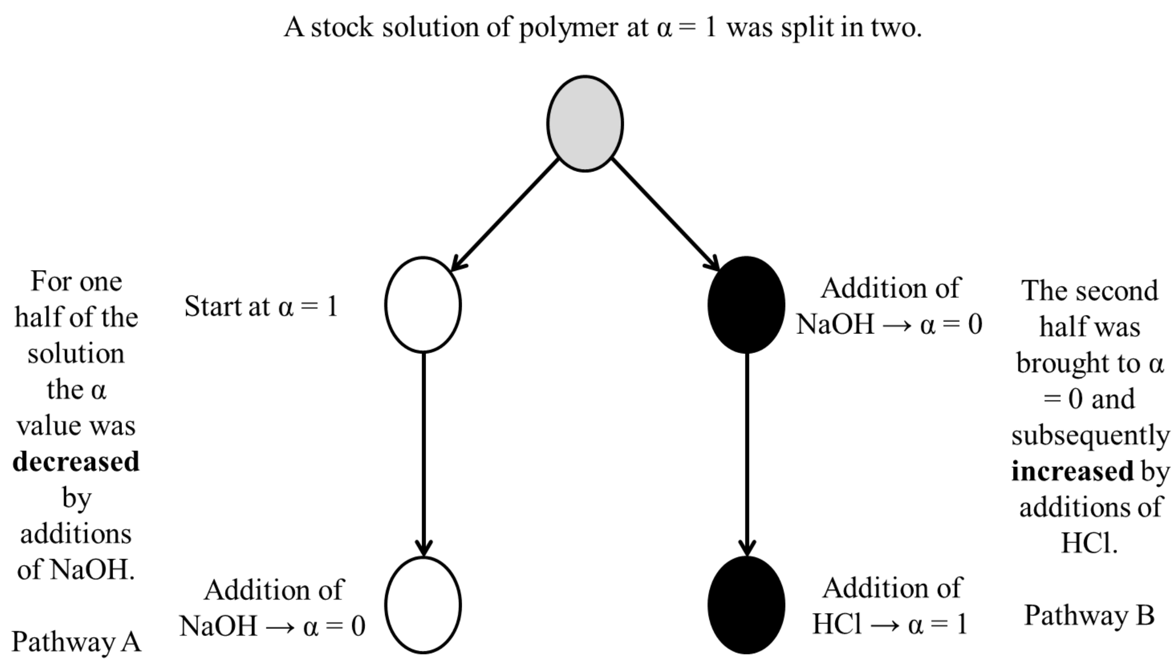

Figure S2. Schematic showing the 2 pathways (A and B) used for the reversibility testing in sample preparation Method 2.

Table S2. Effect of ionization on the characteristics of polymer **1**.

α	M_w **(kg.mol^{-1})** [a]	N_{agg} [a]	R_h **(nm)** [b]
0	13	1.2	3.0
0.1	12	1.1	2.5
0.25	13	1.3	2.7
0.5	12	1	3.0
0.8	13	1.5	2.9
1	13	1.4	2.5

[a] Determined by SLS, M_w is the weight-average molecular weight of the scatterers. [b] Determined from DLS.

$\alpha = 0$

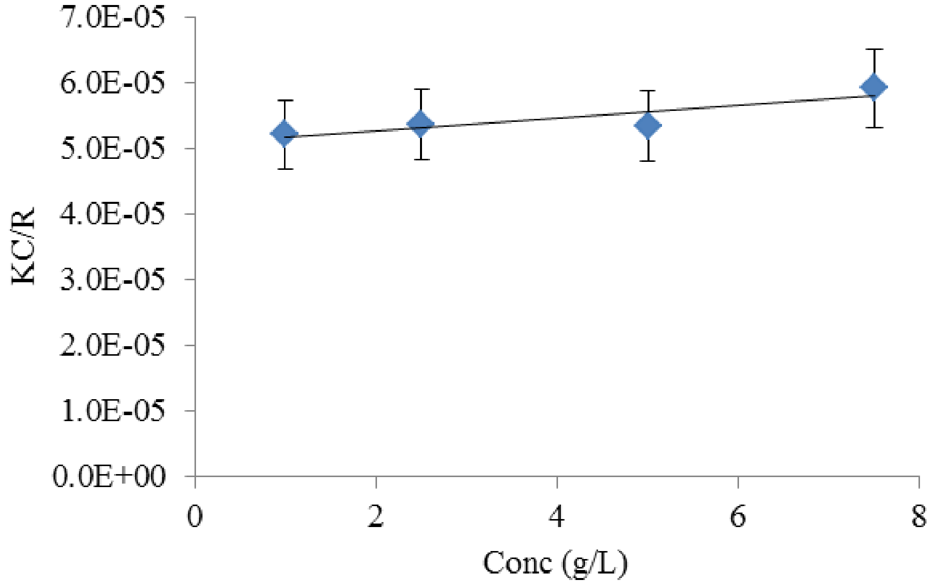

Figure S3. Example SLS data plotted as Kc/RΘ versus concentration for **1** at α = 0.

Table S3. Effect of ionization on the characteristics of polymer **2**.

α	**M_w (kg.mol^{-1})** [a]	**N_{agg}** [a]	**R_h** [b] **(nm)**	**R_c** [c] **(nm)**	**Corona Stretching (%)** [d]
0	256	21	9.5	3.9	64
0.1	58	5	3.1	[e]	[e]
0.25	21	2	2.4	[e]	[e]
0.5	25	2	2.5	[e]	[e]
0.8	25	2	3.2	[e]	[e]
1	20	2	2.8	[e]	[e]

[a] From SLS, M_w is the weight-average molecular weight of the scatterers. [b] Determined from DLS. [c] Calculated from equation 7 assuming a core density of 1. [d] (R_{hDLS}-R_{cSLS})/$L_{contour,DMAEMA}$. [e]For polymers above α = 0 the model of "core-corona" is no longer applicable.

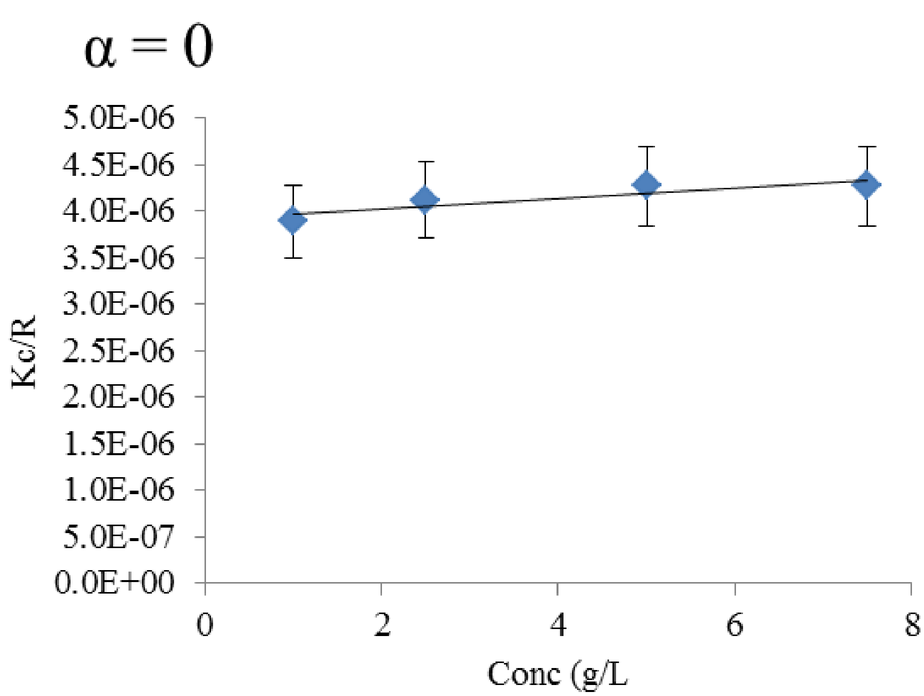

Figure S4. Example SLS data plotted as Kc/RΘ versus concentration for **3** at α = 0.

Table S4. Effect of ionization on the characteristics of polymer 3.

α	M_w (kg.mol^{-1}) [a]	N_{agg} [a]	R_h [b](nm)	R_g [c](nm)	R_c [c](nm)	R_c [f](nm)	Corona Stretching (%)[h]
0	556	46	10.5	8.5[d]	4.9	4.6	70
0.1	556	46	11.5	-	-	4.6	81
0.25	200	16	6.1	7.5[d]	5.3	3.2	34
0.5	18	1	2.6	-	-	[h]	[h]
0.8	18	1	2.9	3.7[e]	-	[h]	[h]
1	14	1	2.5	3.5[e]	-	[h]	[h]

[a] From SLS, M_w is the weight-average molecular weight of the scatterers. [b] Determined from DLS. [c] From SAXS at a concentrations of 2.5 gL^{-1} using method1. [d] Determined with the Guinier-Porod model. [e] Determined with the Debye model.[f] Calculated from equation 7 assuming a core density of 1. [g] (R_{hDLS}-R_{cSLS})/$L_{contour,DMAEMA}$. [h]For polymers above α = 0.25 the model of "core-corona" is no longer applicable.

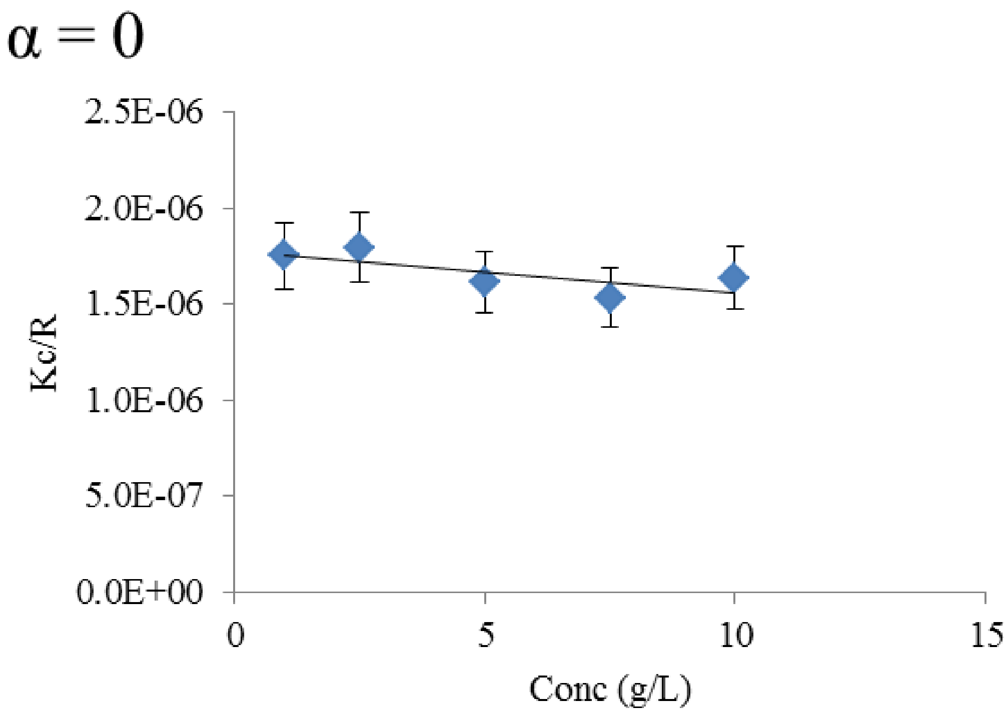

Figure S5. Example SLS data plotted as Kc/RΘ versus concentration for **3** at α = 0.

Table S5. Effect of ionization on the characteristics of **4**.

α	**M_w (kg.mol^{-1}) [a]**	**N_{agg} [a]**	**R_h [b] (nm)**	**R_c [c] (nm)**	**Corona Stretching (%) [d]**
0	1086	80	10.1	5.6	56
0.1	915	68	9.7	5.3	55
0.25	209	15	5.3	3.2	26
0.5	86	6	4.5	[e]	[e]
0.8	16	1	3.2	[e]	[e]
1	16	1	2.9	[e]	[e]

[a] From SLS at concentrations, M_w is the weight-average molecular weight of the scatterers. [b] Determined from DLS. [c] Calculated from equation 7 assuming a core density of 1. [d] (R_{hDLS}-R_{cSLS})/$L_{contour,DMAEMA}$. [e] For polymers above α = 0.25 the model of "core-corona" is no longer applicable.

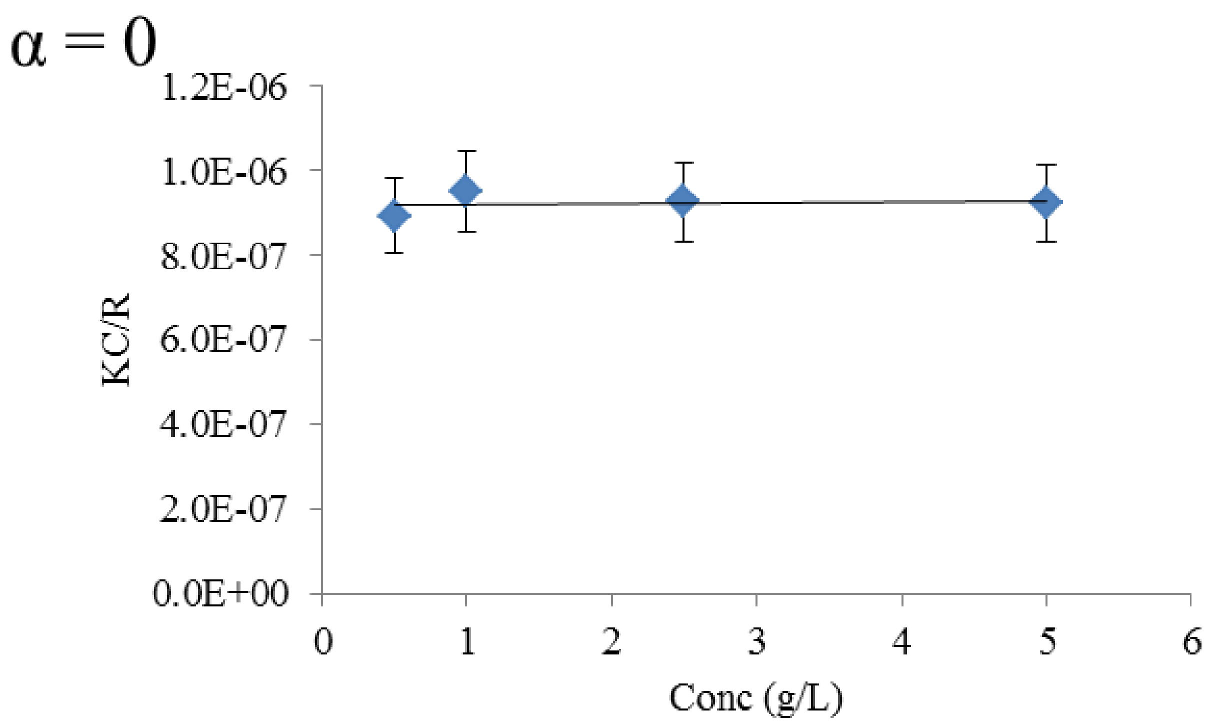

Figure S6. Example SLS data plotted as Kc/RΘ versus concentration for **4** at α = 0.

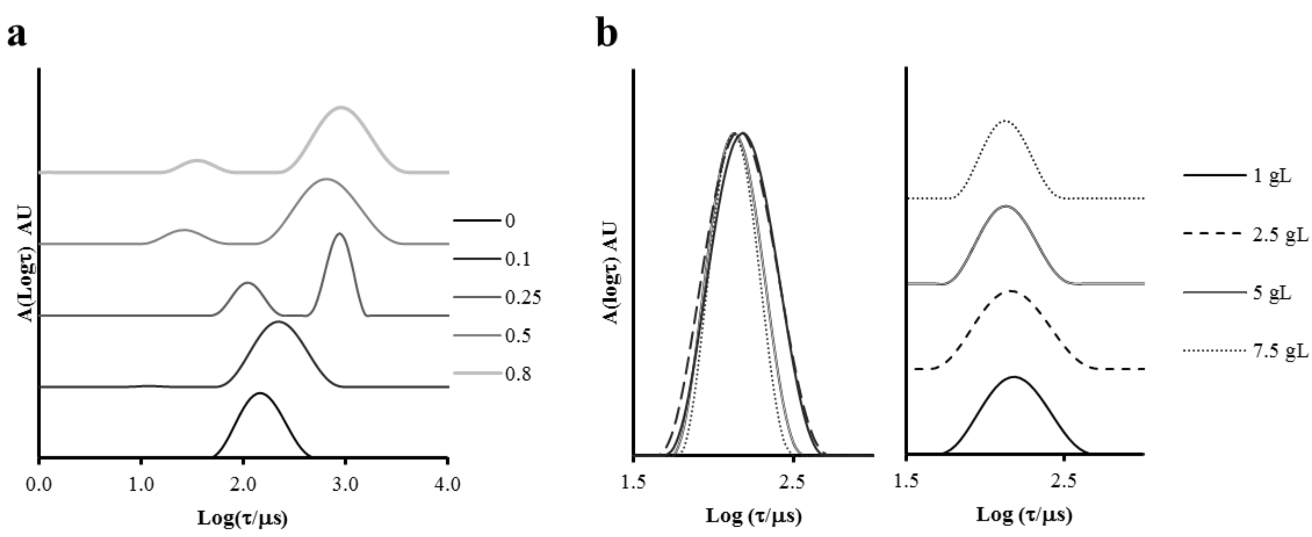

Figure S7. a) Intensity weighted distribution of relaxation times for **3** at 2.5 gL^{-1} in a 0.1 M NaCl solution with varying the ionization, α = 0 – 0.8, measured at θ = 130°. b) Effect of concentration on the intensity weighted distribution of relaxation times for **3**, measured at θ = 130°, α = 0. Note, the distributions have been shifted vertically by a factor of 1.1 to improve clarity.

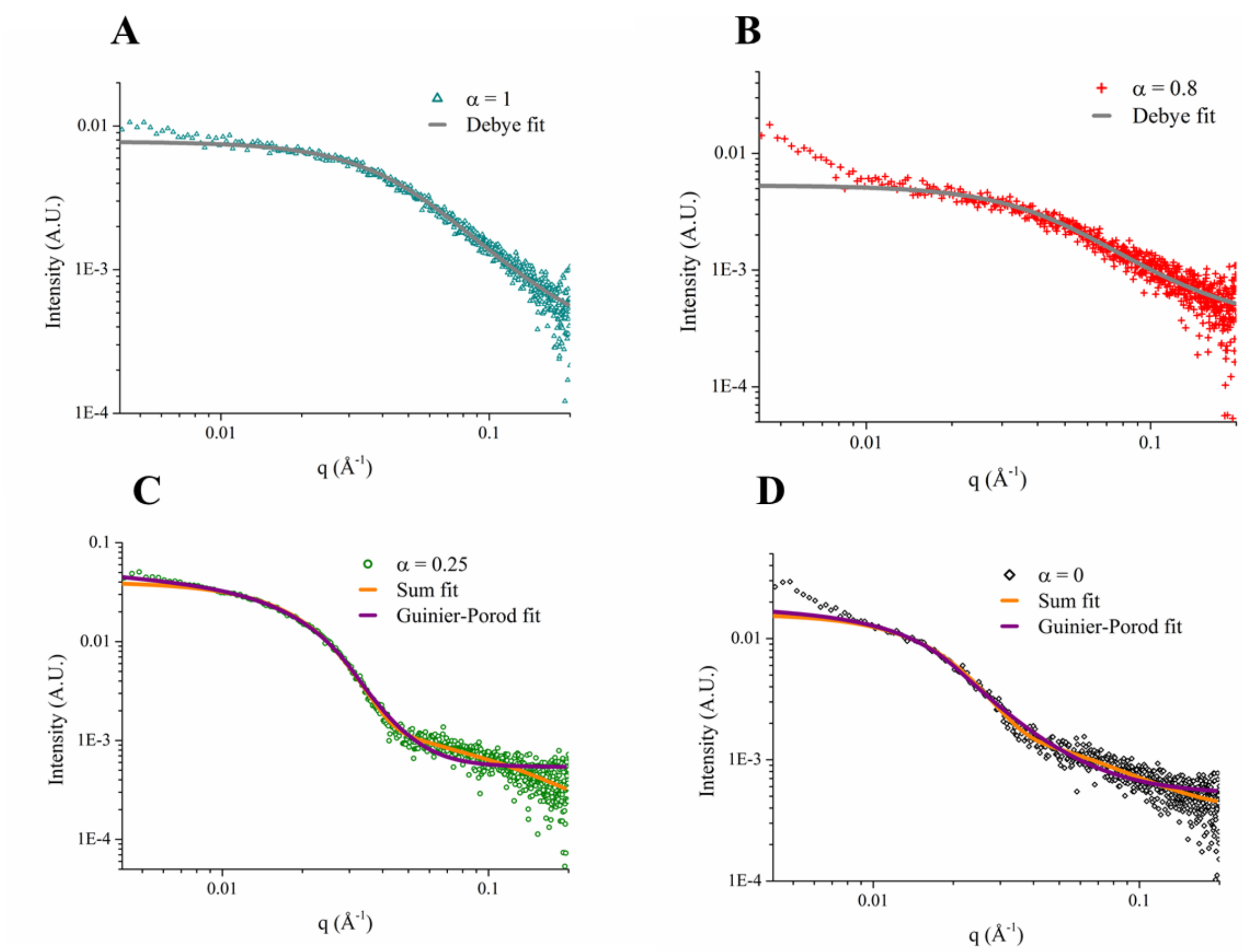

Figure S8. Small-angle X-ray scattering (SAXS) profiles of **3** with varying α. A) α = 1, B) α = 0.8, C) α = 0.25, D) α = 0, all at 2.5 g/L and in 0.1 M NaCl solution.

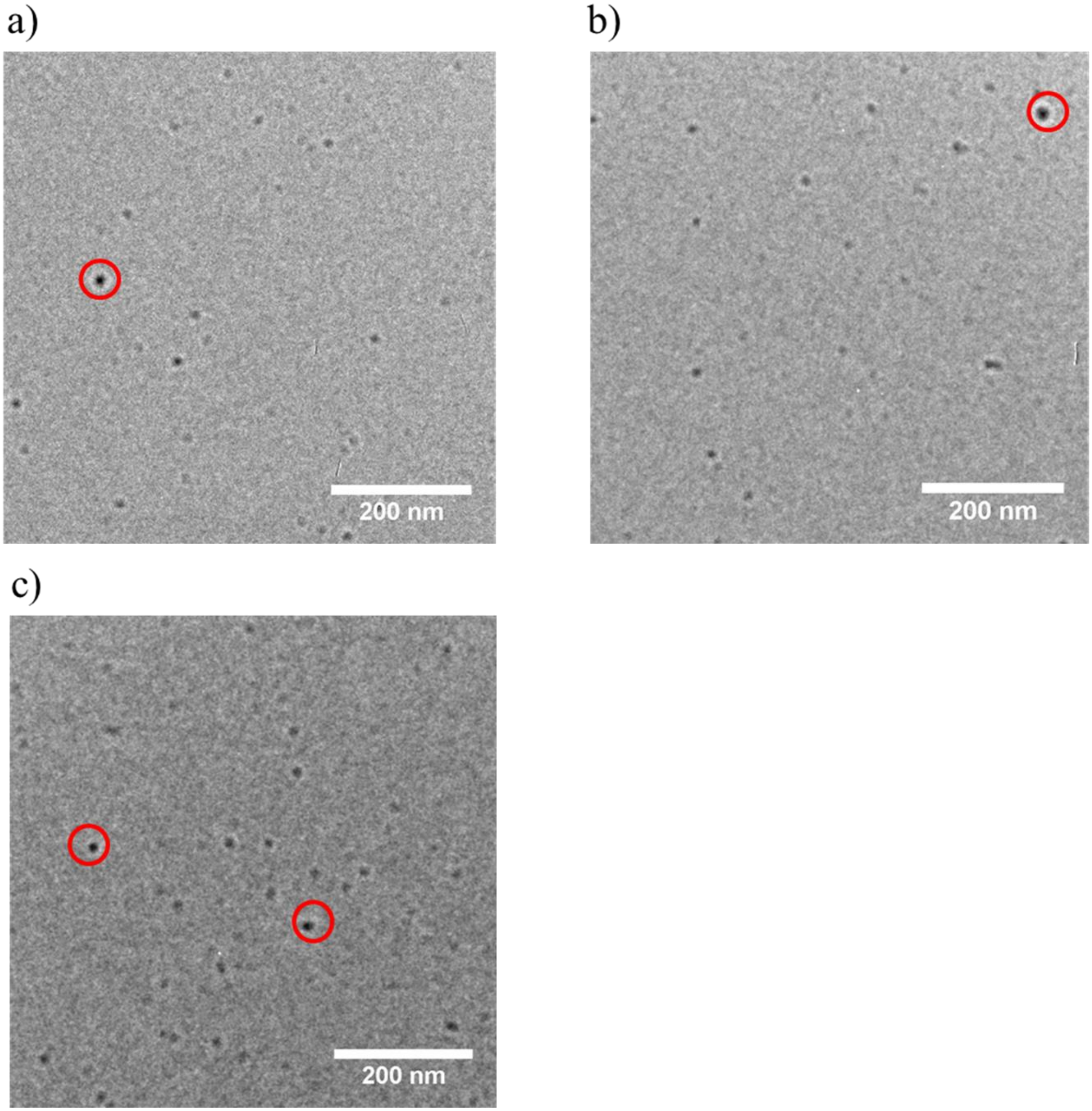

Figure S9. Cryo-TEM images at α = 0, 2g/L and in 0.1 M NaCl solution. a) **2**, b) **3**, c) **4**. Red circles indicate ice crystals. Scale bar 200nm.

Notes and references

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(1) Van Herk, A. M.; Dröge, T. *Macromol. Theory Simul.* **1997**, *6*, 1263.