Supporting Information

Thermoresponsive properties of poly(acrylamide-*co*-acrylonitrile)-based diblock copolymers synthesized (by PISA) in water

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I Preliminary study:

RAFT-controlled radical copolymerization of acrylamide (AAm) and acrylonitrile (AN) in water

Statistical poly(acrylamide-*co*-acrylonitrile) copolymers, P(AAm-*co*-AN), with various initial acrylonitrile content ($f_{AN,0}$) were prepared by RAFT polymerization in water and their thermoresponsive properties were determined.

1. Experimental part

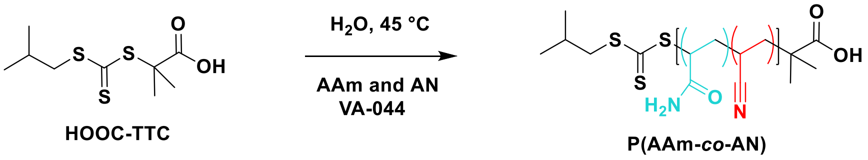
1.1. Synthesis of statistical poly(acrylamide-*co*-acrylonitrile) P(AAm-*co*-AN) *via* RAFT polymerization in water

In a typical experiment (Table S 1, entry 5), 32 mg (0.13 mmol) of RAFT agent (HOOC-TTC), 11 mg (0.034 mmol) of VA-044, 897 mg (12.6 mmol) of AAm and 6 mg (0.057 mmol) of Na_2CO_3 were dissolved in 5.3 g of water in a round bottom flask. The resulting mixture was purged with argon for 30 min in a cold water bath. A solution of degassed AN (830 □L, 12.7 mmol) in degassed water (10 mL) was then injected into the flask. The round-bottom flask was sealed with a Rotaflo teflon stopcock and immersed in a thermostated oil bath at 45 °C, and the polymerization lasted for 6 h. The flask was cooled down at room temperature and the polymerization was quenched by exposure to air. The individual monomer conversions and the overall molar conversion at the end of the polymerization were determined ^1H NMR. The polymer was recovered by precipitation in methanol, filtered and dried under vacuum at 50 °C. The same procedure was used for the free radical polymerization in water except that no RAFT agent was added (Table S1, entry 7).

1.2. FT-IR measurements

FT-IR measurements were performed on a Nicolet iS5 spectrometer with an Attenuated Total Reflectance (ATR) iD5 accessory mounted with a diamond crystal. A calibration curve was used to determine the content of AN in the polymer. Samples for the construction of calibration curve were prepared by mixing powders of the homopolymers, polyacrylamide (PAAm) and polyacrylonitrile (PAN) (synthesized according to a protocol described in the literature[1]), using a freezer/mill. Ten mixtures were prepared in which the molar percentage of AAm was varied from 12 to 86 %. Both samples and calibration standards were measured five times with 16 scans per measurement. The height ratios of the infrared vibrational bands of the carbonyl (CO_h) at 1660 cm^{-1} and nitrile group (CN_h) at 2242 cm^{-1} were determined. The ratio between them was plotted against acrylamide content (Figure S1). The content of AN in a synthesized copolymer (F_{AN}) was deduced from the calibration curve based on the ratio of CO_h/CN_h calculated from corresponding IR spectrum.

2. Results and discussion on the controlled radical copolymerization of acrylamide and acrylonitrile in water



Scheme S1. Synthesis routes for the statistical P(AAm-*co*-AN) copolymers *via* aqueous RAFT polymerization.

Table S1. Experimental conditions and results for the RAFT-mediated copolymerization of AAm and AN in water at 45 °C

Entry	**$f_{AN,0}$**[a]	**Time** (h)	**τ** (wt%)[b]	**Conv**[a] **(%)**			**F_{AN}**		***$DP_{n,th}$***[d]	***$M_{n,th}$***[d] (kg mol^{-1})	***$M_{n,SEC}$***[e] (kg mol^{-1})	***Đ***[e]	**T_{CP}**[f] **(°C)**	
				AN	**AAm**	**Total**	**NMR**[a]	**IR**[c]					**0.2 wt%**	**1 wt%**
1	0.23	7.8	12	94	80	83	0.26	0.24 ± 0.02	166	11.3	15.0	1.18	NO	NO
2	0.29	6.3	10	89	78	81	0.32	0.35 ± 0.01	162	10.9	20.5	1.13	~10[g]	17/21
3	0.37	6.3	10	86	74	78	0.40	0.40 ± 0.01	157	10.3	21.2	1.15	24/28	38/42
4	0.40	6.3	10	79	70	74	0.43	0.44 ± 0.02	147	9.6	12.3	1.23	49/52	65/69
5	0.48	6.0	10	67	56	61	0.52	0.46 ± 0.03	122	7.8	13.4	1.16	76/79	NO
6	0.60	6.2	9	89	59	77	0.69	0.57 ± 0.03	154	9.3	17.0	1.22	N.D*	N.D*
7[h]	0.32	9.0	6	95	93	94	0.32	0.35 ± 0.03	N.D	N.D	58.6	2.80	49/52	48/49

Polymerizations were performed in water at 45 °C in presence of a RAFT agent (HOOC-TTC) using VA-044 as a radical initiator at an initial molar ratio of monomers/HOOC-TTC/VA-044: 200/1/0.3. [a] Determined by ^{1}H NMR analysis. [b] Targeted solids content: τ = [m(monomers) + m(HOOC-TTC)] / m(total). [c] Determined using an IR calibration. [d] Theoretical number-average degree of polymerization, $DP_{n,th}$, and number-average molar mass, $M_{n,th}$, calculated using the experimental conversions. [e] Number-average molar mass M_n and dispersity, Đ, determined by SEC in DMSO (+ LiBr 1g L^{-1}) with a Pullulan calibration. [f] Cloud point temperature determined by turbidimetry in water, on 1st cooling/2nd heating. [g] The T_{CP} was estimated by combined visual observation and turbidimetry. [h] Free radical polymerization (without RAFT agent). NO: no transition between 10 and 80 °C. N.D: not determined. * Not dispersible.

Statistical poly(acrylamide-*co*-acrylonitrile) copolymers, P(AAm-*co*-AN), were synthesized using RAFT polymerization in water at 45 °C with different feed ratios (Table S1). The mol% of acrylonitrile in the copolymer (F_{AN}) was tuned from 26 to 69% by adjusting the amount of acrylonitrile in the feed ($f_{AN,0}$), while keeping constant the targeted degree of polymerization (DP) of the copolymer at 200. To prevent any loss of AN due to volatilization, degassed AN was added with a syringe to the degassed reaction medium prior to the polymerization. The series of polymerizations was performed at a fixed monomer concentration (about 10 wt%)

using a trithiocarbonate RAFT agent (HOOC-TTC, Scheme S1) and 2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (VA-044) as a thermal initiator, see Table S1, experiments 1 to 6.

As shown in Table S1, RAFT polymerizations reached generally an overall molar conversion ≥ 74% in less than 7 h (calculated from the consumption of the AAm and AN by ^{1}H NMR). In all experiments, the consumption of AN was faster than that of AAm, as expected with respect to the reactivity ratios determined in water,[2] resulting in a composition drift and a higher fraction of AN in the final copolymer (F_{AN}) compared to the feed ratio ($f_{AN,0}$). It should be noted that for the polymerizations performed with the lowest fraction of AN ($f_{AN,0} < 0.4$), at the end of the polymerization (still at 45 °C) transparent solutions were obtained, whereas turbid dispersions were obtained for higher fraction of AN ($f_{AN,0} > 0.5$) indicating that the polymerization mechanism could differ (in solution or dispersion) according to $f_{AN,0}$.

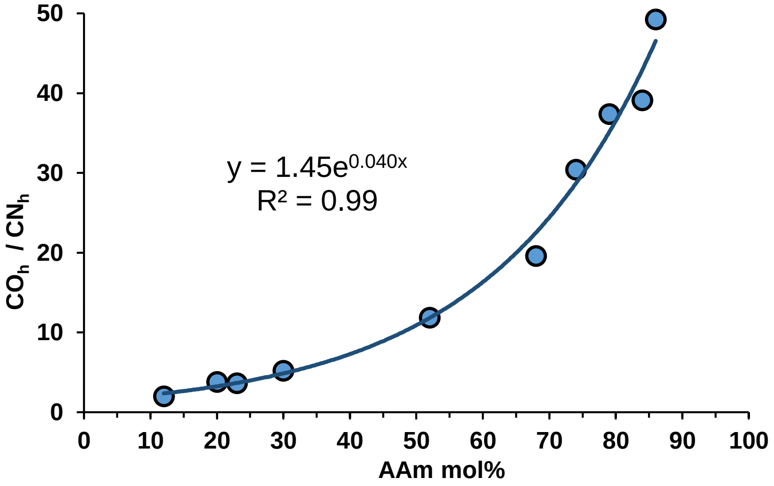


Figure S1. Calibration curve used for the determination of the copolymer compositions of P(AAm-*co*-AN) obtained by attenuated total reflection Fourier-transform infrared spectroscopy.

After purification by precipitation in methanol, the copolymers were characterized by FT-IR spectroscopy and size exclusion chromatography (SEC). To determine the AN content in the final copolymer (F_{AN}), we performed FT-IR analyses on all copolymers using a calibration curve (see Figure S1) made from powder mixtures of polyacrylamide and polyacrylonitrile homopolymers.

Using such method, the estimated AN content was close to that determined from the AAm and AN consumption values (determined by ^{1}H NMR), except for copolymer containing the highest AN content (entry 6 in Table S1). Therefore, the determination of F_{AN} from the monomer conversions appeared to be a reliable method and for sake of simplicity, we selected this method for the systematic determination of the copolymer composition in the rest of the article. As shown in Figure S2, by SEC analysis in DMSO, monomodal signals with narrow molar mass distribution ($Đ$ < 1.25) were generally obtained indicating that a good control over the polymerizations was achieved. It should be noted that a secondary distribution at the high molar mass side was observed for entry 1, which is the sample with the lowest AN content and for which the highest overall monomer conversion was reached. The M_{peak} of this minor population is about twice that of the main population indicating some bimolecular coupling, which are favored for prolonged polymerization times in RAFT polymerizations.

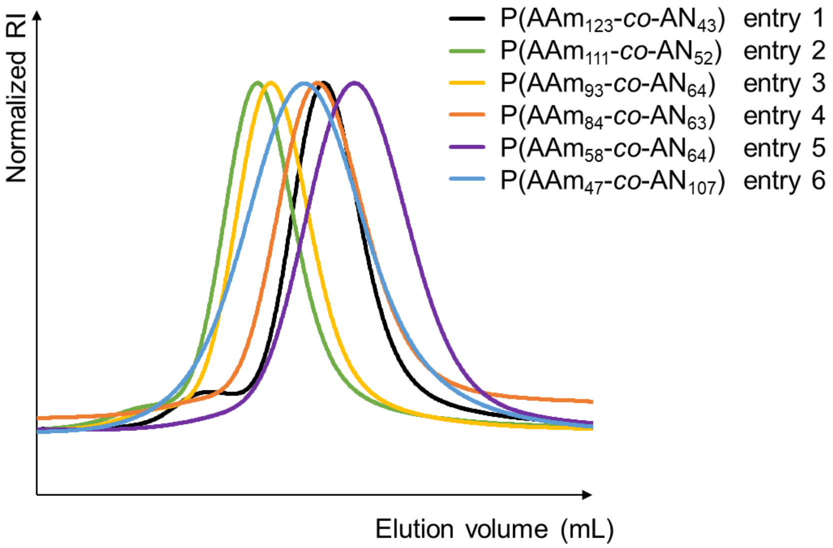


Figure S2. SEC chromatograms in DMSO (+ LiBr) of the P(AAm-*co*-AN) with different compositions (see Table S1).

The thermoresponsiveness of the P(AAm-*co*-AN) copolymers dispersed in water at 0.2 wt% and 1 wt% was then investigated by turbidimetry upon cooling and heating the polymer solutions (Figures S3 and S4).

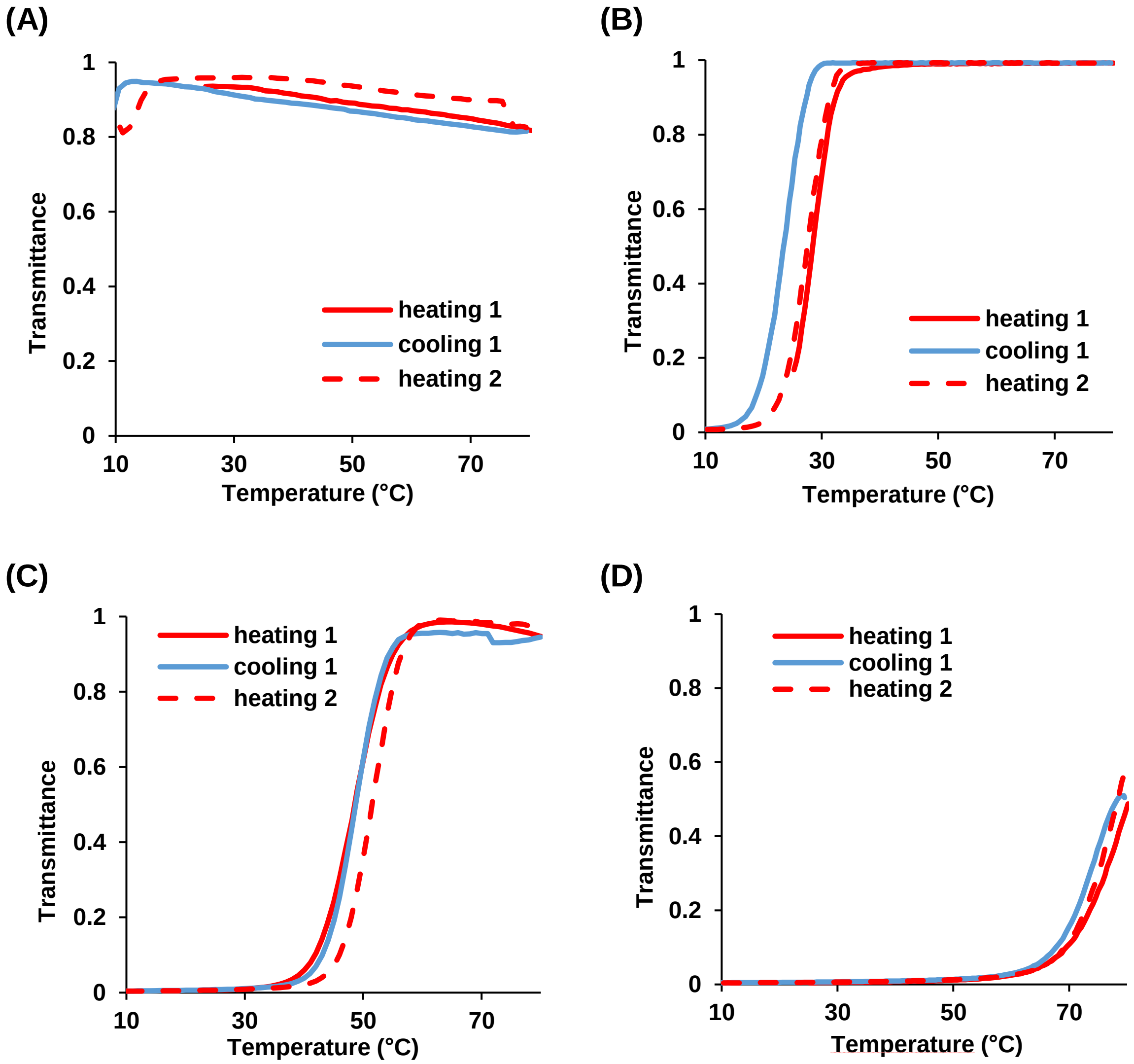


Figure S3. Turbidity curves (first heating, first cooling and second heating) of P(AAm-*co*-AN) dispersions at 0.2 wt% with different copolymer compositions : (A) F_{AN} = 0.32 (Table S1, entry 2), (B) F_{AN} = 0.40 (Table S1, entry 3), (C) F_{AN} = 0.43 (Table S1, entry 4) and (D) F_{AN} = 0.52 (Table S1, entry 5).

A phase transition was only observed, when the copolymer contained more than 30 mol% of AN (at least in the studied temperature range, between 10 and 80 °C), in accordance with the literature.[3] In this case, the thermal response of the solutions was sharp and reversible with a slight hysteresis (< 5 °C) between the cooling curve and the heating curve. As summarized in Table S1 and presented in Figure S4, the cloud point temperature (T_{CP}) increases with increasing the AN content in the copolymer, as expected.[3,4]

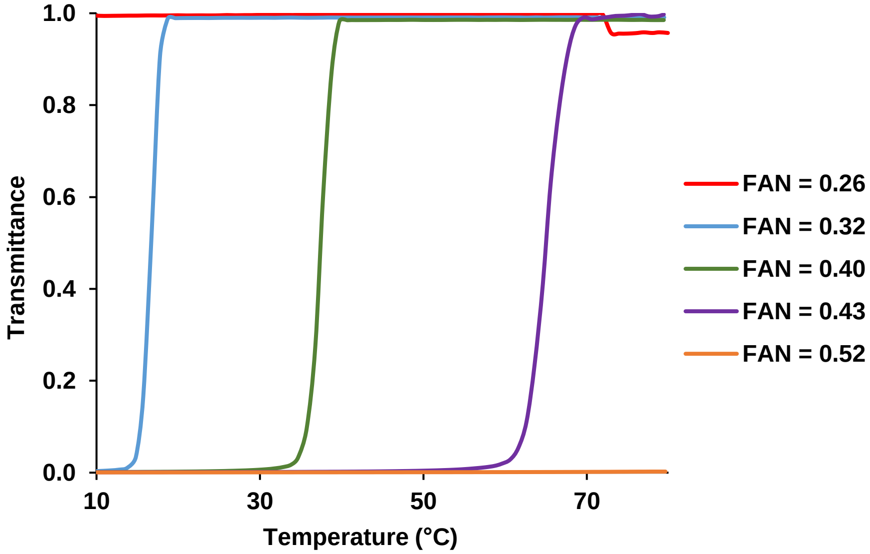


Figure S4. Turbidity curves (first cooling) of P(AAm-*co*-AN) copolymers with various AN fractions (F_{AN}) at 1 wt% in water.

It had formerly been reported that the T_{CP} of P(AAm-*co*-AN) copolymers synthesized in DMSO was different when synthesized by FRP or RAFT polymerization.[5] We found that the transition temperature was also process-dependent when synthesized in water. Comparing the T_{CP} of two copolymers with similar F_{AN} (32 mol% of AN), synthesized in water by either RAFT or free radical polymerization (FRP), the T_{CP} of the FRP-derived copolymer was much higher (at least by 30 °C) than that of the RAFT-derived copolymer (see entries 2 and 7 in Table S1 and Figures S3A and S5A respectively). This difference might be explained either by the heterogeneity in the composition of the polymer chains obtained by FRP or by the higher number-average molar mass, M_n, of the copolymer.

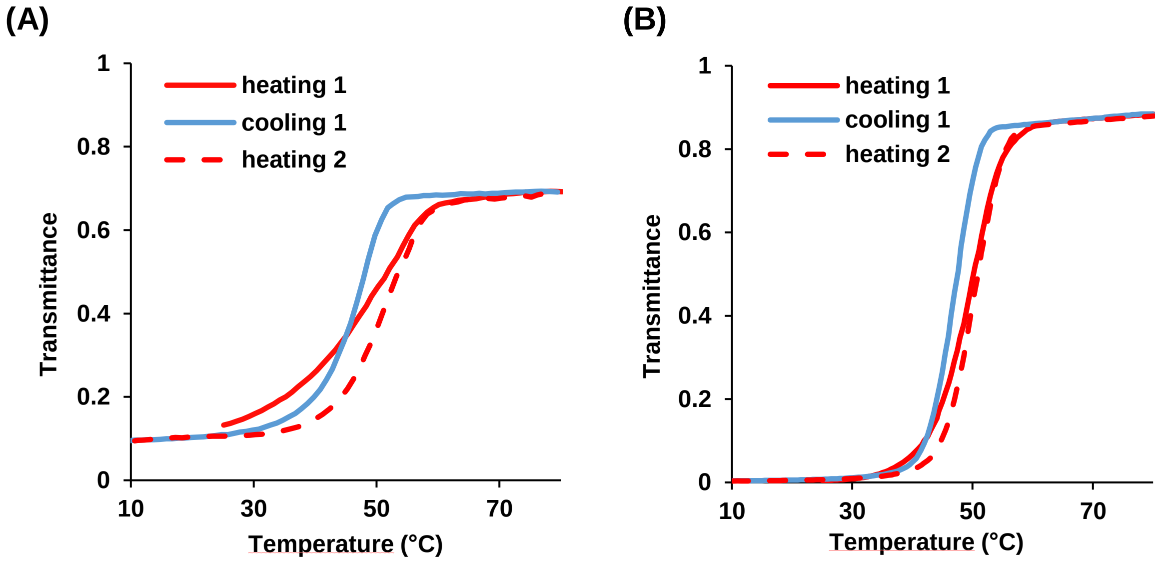


Figure S5. Turbidity curves (first heating, first cooling and second heating) of a P(AAm-*co*-AN) dispersion at (A) 0.2 wt% and (B) 1 wt% for copolymer obtained by FRP containing 32 mol% of AN (Table S1, Entry 7).

II Supplementary material:

Synthesis and characterization of PDMAc-*b*-P(AAm-*co*-AN) diblock copolymers

Table S2. Polymerization conditions and characteristics of the poly(*N*,*N*-dimethylacrylamide) macroRAFT agents prepared by polymerization of DMAc in DMF at 70 °C

Entry	$DP_{n,0}$	Time (min)	Conv.[a] (%)	$M_{n,th}$[b] (kg mol^{-1})	$DP_{n,NMR}$[c]	$M_{n,NMR}$[c] (kg mol^{-1})	$M_{n,SEC}$[d] (kg mol^{-1})	$Đ$[d]
M1	28	88	76	2.4	23	2.6	0.9	1.16
M2	43	75	55	2.6	27	2.9	1.1	1.17

The polymerizations were performed with a initial molar ratio HOOC-TTC/AIBN = 20. [a] Monomer conversion determined by ^{1}H NMR. [b] Theoretical number-average molar mass $M_{n,th}$ calculated using the experimental conversion. [c] Number-average degree of polymerization, $DP_{n,NMR}$ and number-average molar mass $M_{n,NMR}$, determined by ^{1}H NMR from the purified polymer by precipitation. [d] Number-average molar mass $M_{n,SEC}$ and dispersity, $Đ$, determined by SEC in DMSO (+ LiBr 1g L^{-1}) with a Pullulan calibration.

Table S3. Characterization of the AN content within copolymers using ^{1}H NMR and ^{13}C NMR

Entry	$f_{AN.0}$[a]	$F_{AN,\ 1H\ NMR}$	$F_{AN,\ 13C\ NMR}$
3	0.37	0.41	0.40
11	0.38	0.42	0.36

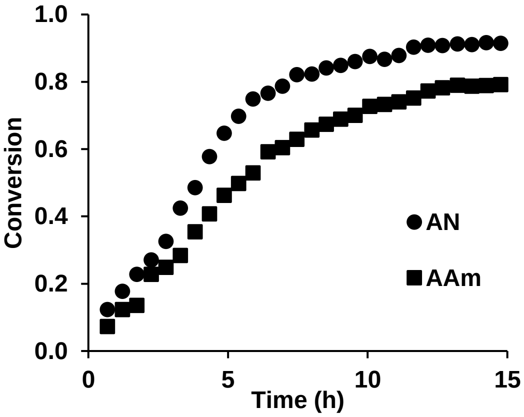


Figure S6. Monomer conversions monitored by ^{1}H NMR in D_2O. Polymerization performed with $f_{AN,0} = 0.44$ using an initial molar ratio of monomers/macroRAFT/initiator of 800/1/0.3 and VA-044 as initiator at 45 °C.

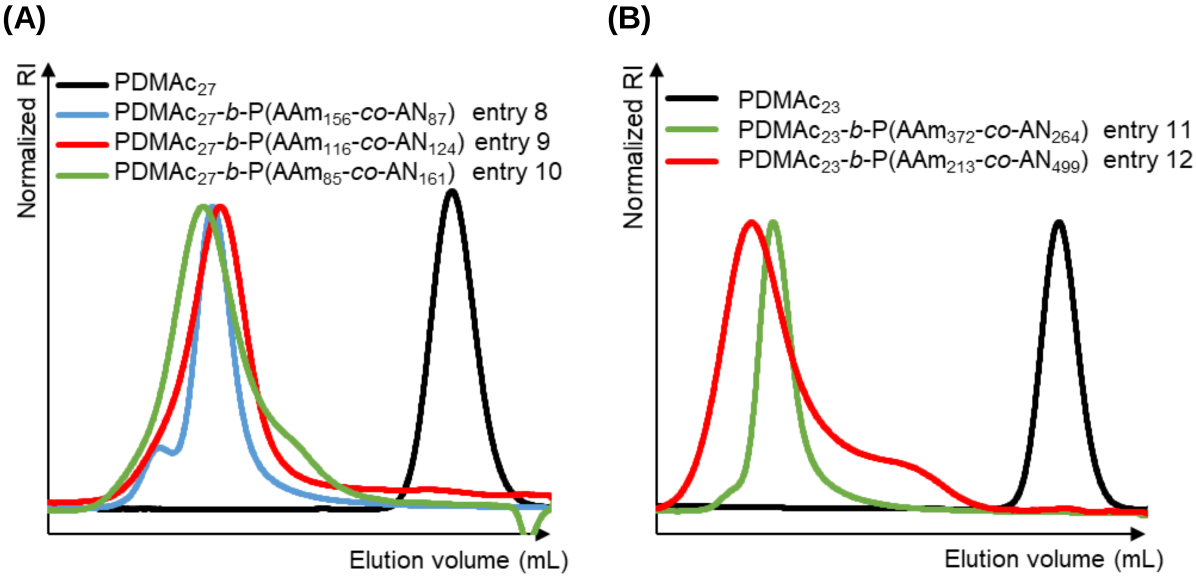


Figure S7. Normalized size exclusion chromatograms of PDMAc macroRAFT agents and the resulting PDMAc-*b*-P(AAm-*co*-AN) block copolymers prepared by copolymerization of AAm and AN in water at 45 °C targeting (A) a DP = 250 and (B) a DP = 800, and various AN contents (Table 1).

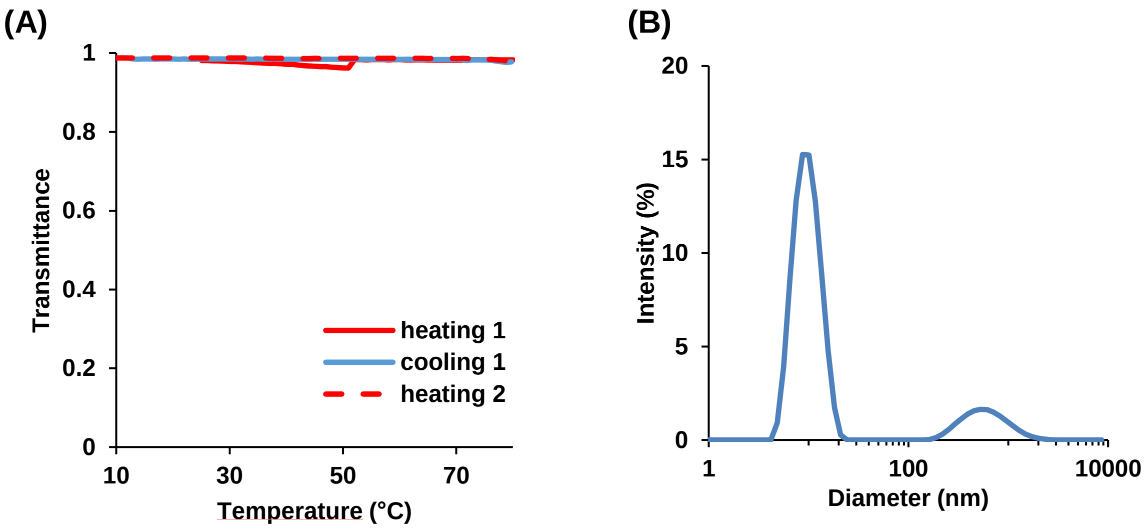


Figure S8. (A) Turbidimetry measurements (first heating, first cooling and second heating) of PDMAc-*b*-P(AAm-*co*-AN) dispersion prepared at 1 wt% (Entry 8, Table 1) and (B) size distribution determined by DLS at 25 °C.

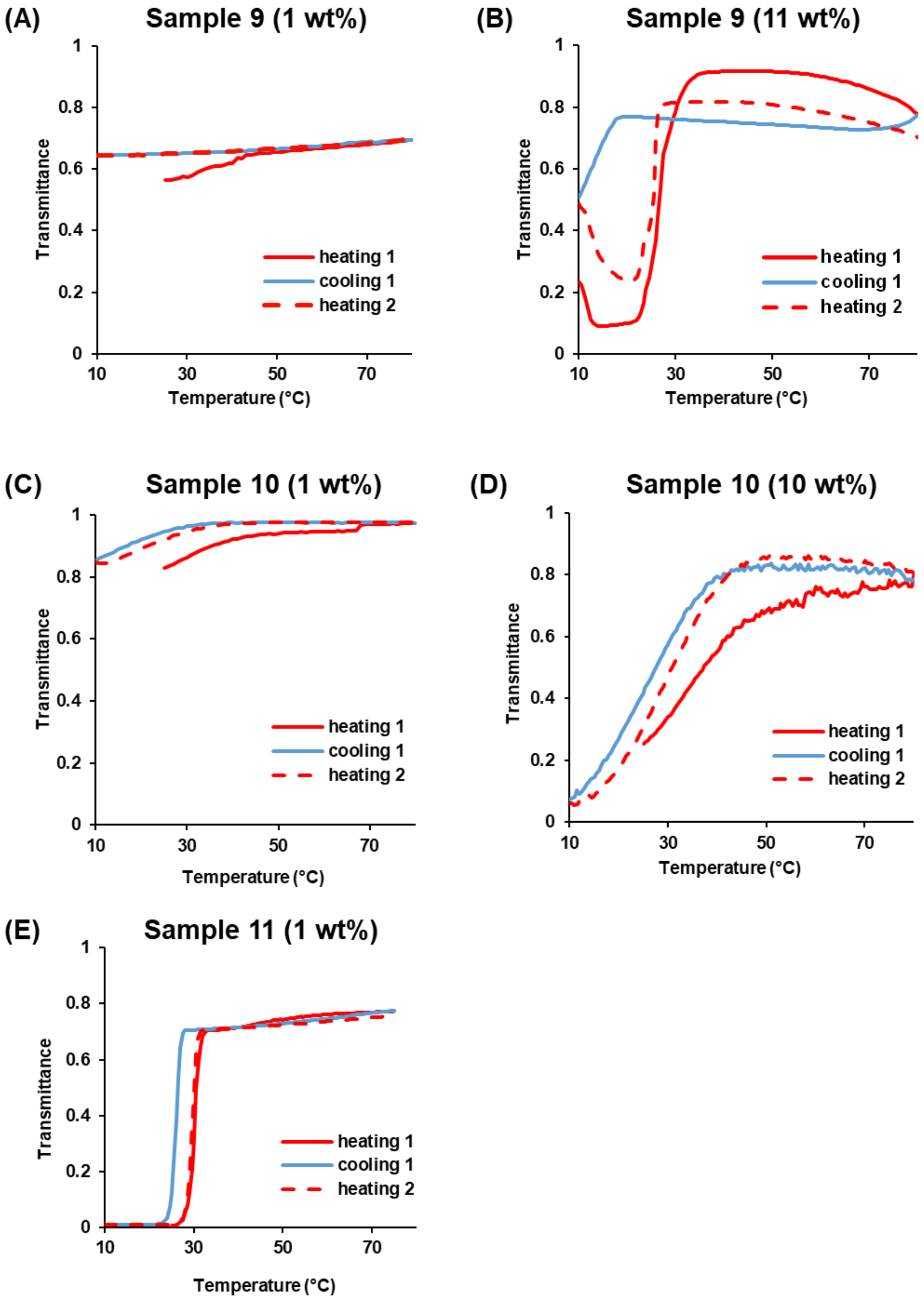


Figure S9. Turbidimetry measurements (first heating, first cooling and second heating) of PDMAc-*b*-P(AAm-*co*-AN) dispersions (Samples 9, 10 and 11 in Table 1).

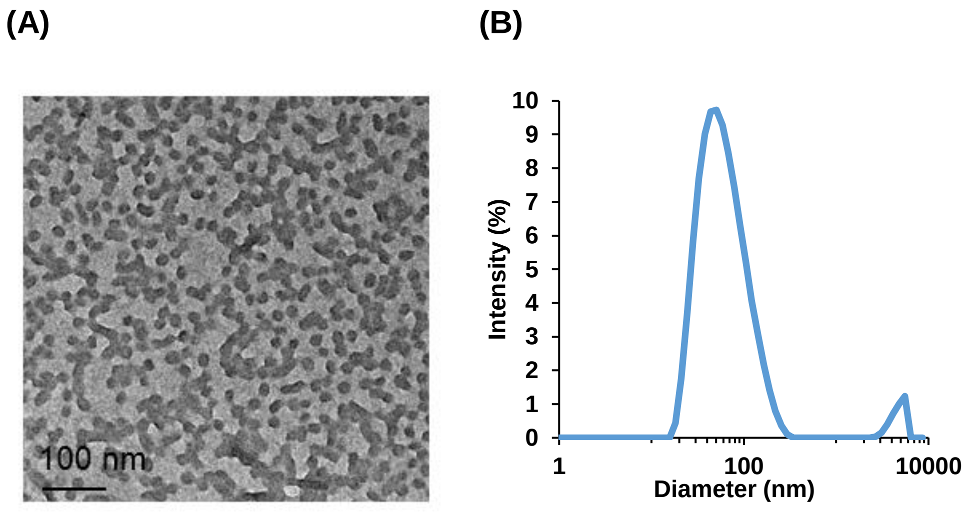


Figure S10. (A) Representative TEM image prepared at 0.03 wt% stained with phosphotungstic acid at 25 °C and (B) final size distribution determined by DLS prepared at 0.03 wt% at 25 °C of the aqueous solution PDMAc-*b*-P(AAm-*co*-AN) (Entry 10, Table 1).

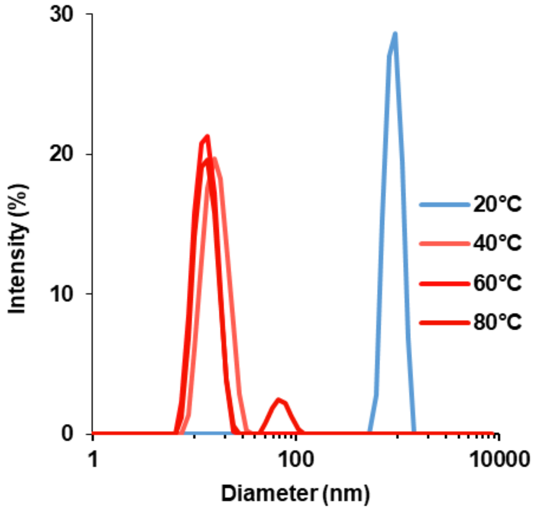


Figure S11. Overlay of DLS profiles of sample 11 (Table 1) at 1 wt% in water upon heating from 20 to 80 °C.

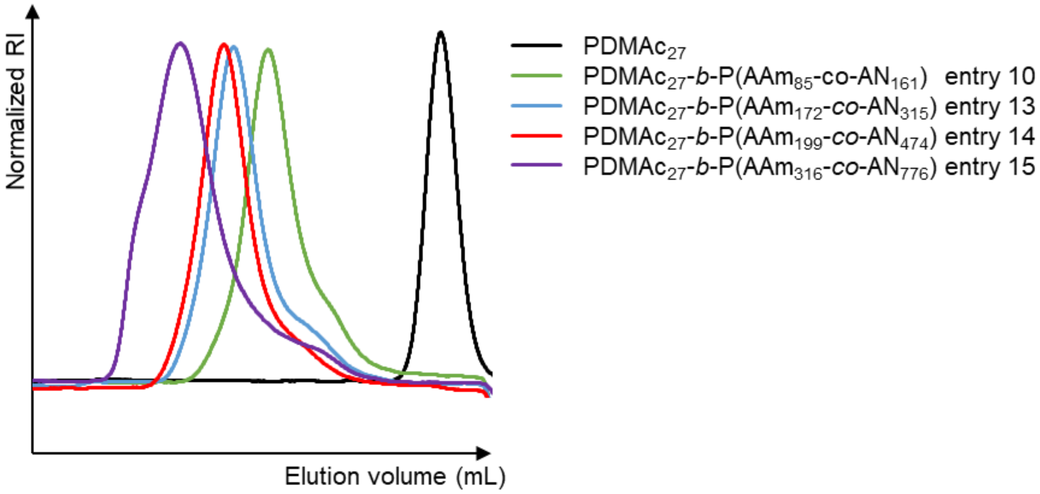


Figure S12. Normalized size exclusion chromatograms of PDMAc macroRAFT agent and the resulting PDMAc-*b*-P(AAm-*co*-AN) block copolymers prepared by copolymerization of AAm and AN in water at 45 °C with a constant initial f_{AN} of 0.65 targeting various DP.

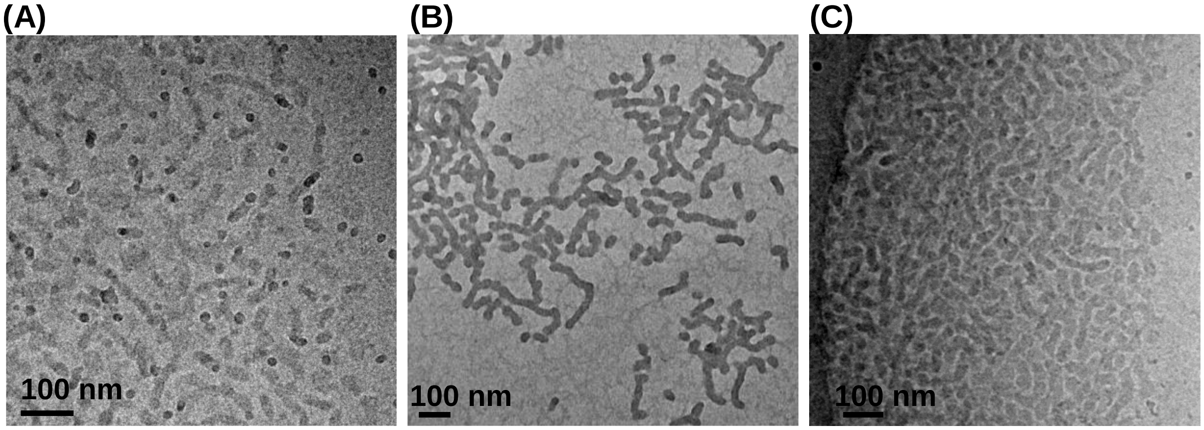


Figure S13. (A) Representative cryo-TEM image of sample 13, PDMAc-*b*-P(AAm-*co*-AN) with a DP_n (P(AAm-*co*-AN) = 510 prepared at 1 wt% (the dark spots are surface contaminations stemming from water crystals on the sample surface); (B) TEM and (C) cryo-TEM images of sample 14 with DP_n (P(AAm-*co*-AN) = 760 prepared at 0.03 wt% (TEM) and at 0.3 wt% (cryo-TEM), respectively.

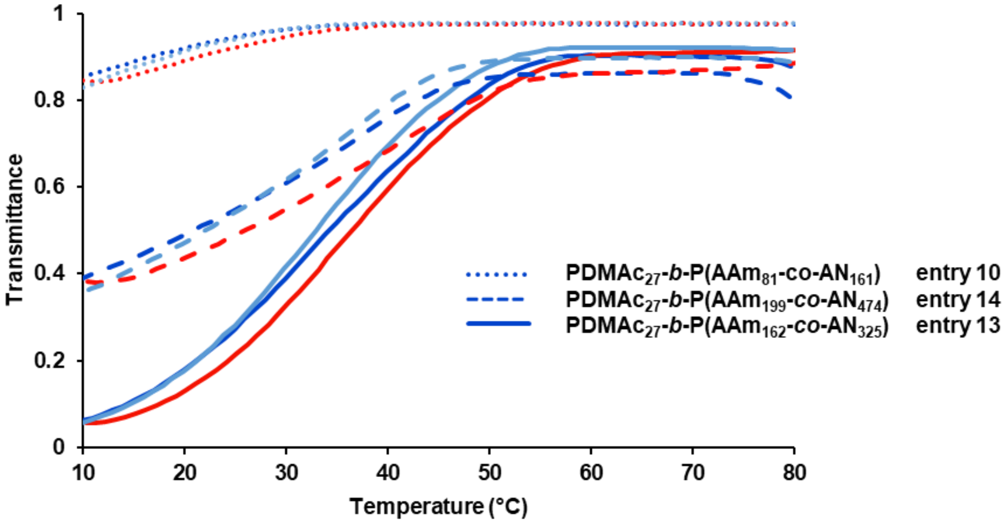


Figure S14. Turbidity curves of PDMAc-*b*-P(AAm-*co*-AN) dispersions at 1 wt% (entries 10, 13 and 14 in Table 3). First and second cooling in dark and light blue, second heating in red.

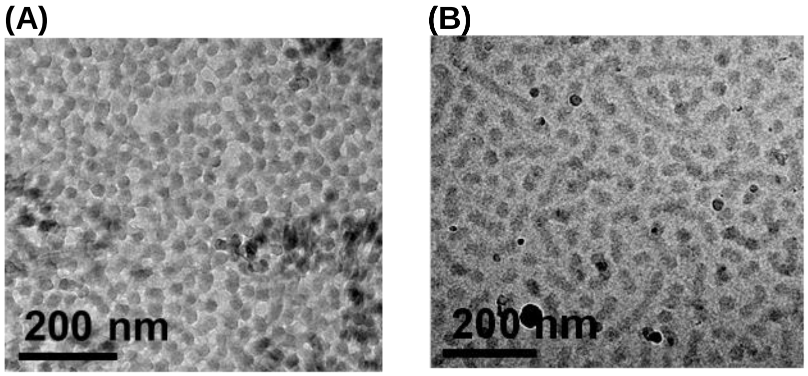


Figure S15. Representative cryo-TEM images of sample 16: (A) heated at ~10 wt% to 70 °C, then diluted at 1 wt% at 70 °C and analyzed after deposition at 70 °C; (B) heated at ~10 wt% to 70 °C, then cooled to room temperature and diluted at 1 wt%.

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