Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Thermoresponsive dynamic BAB block copolymer networks synthesized by aqueous PISA in one-pot

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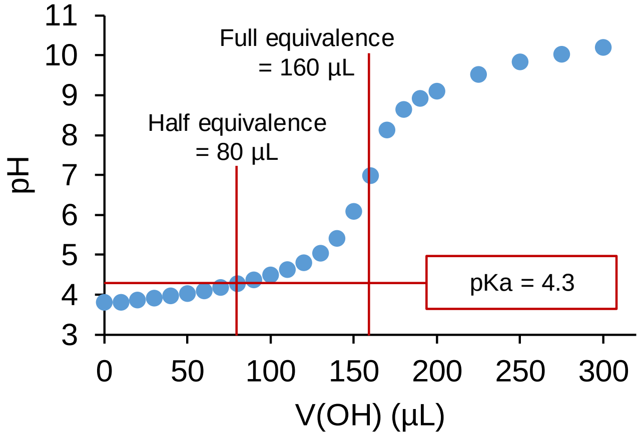


Figure S1. Acid titration curve to determine the pK_a of a $(C_4\text{-TTC-PDMAc})_2\text{-BA}$ macroRAFT agent ($M_{n,NMR}$ = 8.8 kg mol^{-1}). Titration at C = 1 mmol L^{-1} with a NaOH solution (C = 10 mmol L^{-1}).

Table S1. Polymerization conditions and characteristics of the poly(*N*,*N*-dimethylacrylamide) macroRAFT agents prepared by polymerization of DMAc at 70 °C and natural pH.[a]

Entry	**$[DMAc]_0/[RAFT]_0$**	**time (min)**	**conv.[b] (%)**	**τ[c] (%)**	**$DP_{n,th}$[d]**	**$M_{n,th}$[d] (kg mol^{-1})**	**$M_{n,NMR}$[e] (kg mol^{-1})**	**$M_{n,PMMA}$[f] (kg mol^{-1})**	**Đ[f]**
I	88	79	90	19	79	8.4	8.2	5.6	1.14
I *bis**	115	129	73	-	84	8.9	9.2	5.4	1.21
II	197	136	93	19	182	18.7	18.5	11.0	1.46
II *bis*	197	105	90	19	177	18.1	18.4	11.1	1.23
III	436	115	90	18	394	39.6	*N.D.*[g]	34.2	1.15
I *tris***	110	75	88	20	97	10.2	9.8	6.5	1.15

[a] The polymerizations were started in bulk conditions ($[DMAc]_0$ = 9.7 mol L^{-1}) and at about 50% monomer conversion water was added to dilute the reaction medium by a factor of five. $[\text{RAFT agent}]_0/[ACPA]_0 = 10$. [b] Monomer conversion determined by ^{1}H NMR. [c] Final solids content, $\tau_{polym} = m_{polymer}/m_{tot} = [m(DMAc)_0 \times \text{conv.} + m(RAFT)_0]/m_{tot.}$ [d] Theoretical number-average molar mass, $M_{n,th}$, and number-average degree of polymerization, $DP_{n,th}$, calculated using the experimental conversion. [e] Number-average molar mass $M_{n,NMR}$, determined by ^{1}H NMR. [f] Number-average molar mass $M_{n,PMMA}$ and dispersity, *Đ*, determined by SEC in DMF (+ LiBr 1g L^{-1}) with a PMMA calibration. [g] The number-average molar mass $M_{n,NMR}$, could not be determined by ^{1}H NMR. * Sample I *bis* was prepared in DMF according to the protocol described in our previous work.[1] ** *I tris* has a slightly higher DP_n than I and I *bis*. It was only used for preliminary tests, see **Table S2** and **Figure S3**.

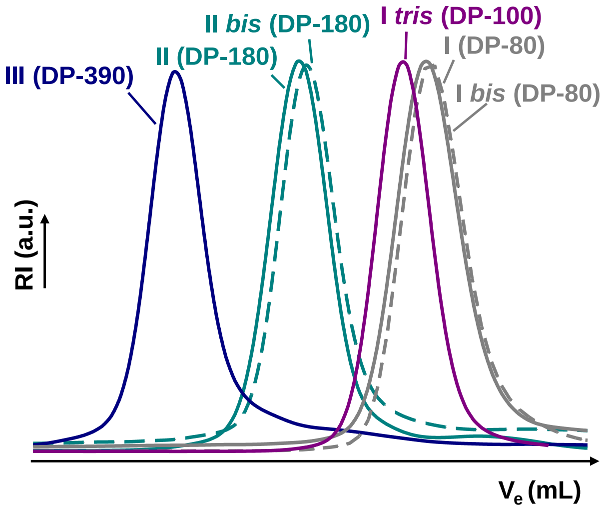


Figure S2. SEC chromatograms in DMF of the PDMAc macroRAFT agents (see **Table S1**).

Table S2. Experimental conditions and results for aqueous dispersion copolymerizations of DAAm and DMAc in the presence of PDMAc macroRAFT agent I *tris* synthesized in water in the first polymerization step (Table S1).[a]

Entry	**α^b (%)**	**mol% DMAc^c**	**time (min)**	**DMAc conv. (%)^d**	**DAAm conv. (%)^d**	**$DP_{n,th}^e$ (2nd block)**	**$M_{n,th}^e$ (kg mol^{-1})**	**$M_{n,PMMA}^f$ (kg mol^{-1})**	**$Đ^f$**	**Stability**
A	**47**	6.4	120	93	95	188	40.8	41.3	1.59 *(bi-modal)*	Preci-pitate
B	**85**	6.4	120	93	97	192	41.4	43.2	1.23	Stable

[a] Polymerizations conditions: T = 70 °C, $[\text{monomers}]_0$ = 11 wt%, $[\text{monomers}]_0/[\text{macroRAFT}]_0$ = 198, $M_{n,NMR}$ (PDMAc I *tris*) = 9.8 kg mol^{-1}, $[\text{PDMAc}]_0$ = 37 g L^{-1} = 3.8 mmol L^{-1}, [ACPA added in 2nd polymerization step]$_0$ = 0.77 mmol L^{-1}. [b] Ionization degree of the central benzoic acid moiety of the PDMAc macroRAFT agent. [c] Molar percentage of DMAc in the second polymer block. mol% DMAc = [n(DMAc$_{\text{residual}}$) + n(DMAc$_{\text{added}}$)] / [n(DAAm) + n(DMAc$_{\text{residual}}$) + n(DMAc$_{\text{added}}$)] × 100. [d] Monomer conversion determined by ^{1}H NMR. [e] Theoretical number-average degree of polymerization, $DP_{n,th}$, and number-average molar mass, $M_{n,th}$, calculated using the experimental conversion and using $M_{n,NMR}$ for the PDMAc block. [f] Number-average molar mass $M_{n,PMMA}$ and dispersity, $Đ$, determined by SEC in DMF (+ LiBr 1g L^{-1}) with a PMMA calibration, see **Figure S3**.

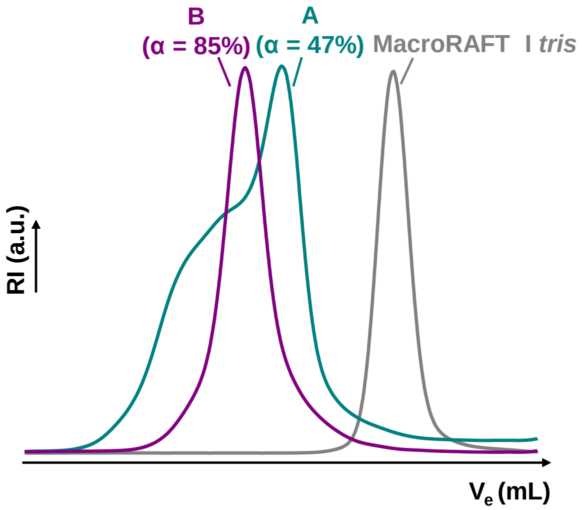


Figure S3. Normalized size exclusion chromatograms of PDMAc macroRAFT agent (entry I *tris* in **Table S1**) and the resulting [C_4-P(DAAm-*co*-DMAc)-*b*-PDMAc]$_2$-BA copolymers A and B (**Table S2**) obtained by RAFT polymerization dispersion in water respectively at α = 47 and 85%.

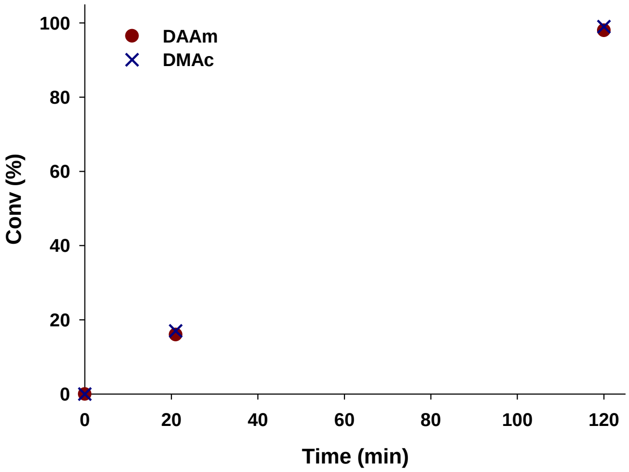


Figure S4. Monitoring of the individual conversion of DAAm and DMAc by ^{1}H NMR during the chain-extension of PDMAc macroRAFT agent with DAAm and DMAc (33 mol% of DMAc), for experimental conditions see entry 80-100-33 in **Table 1**.

Table S3. Aqueous dispersion copolymerizations of DAAm and DMAc at α = 85% in the presence of PDMAc macroRAFT.[a]

Entry	PDMAc Macro RAFT (ref Table S1)	$M_{n,NMR}$ [b] Macro RAFT (kg mol^{-1})	[macroRAFT]$_0$ (mmol L^{-1})	[M$_{tot}$]$_0$/ [macroRAFT]$_0$	mol% DMAc[c]	time (min)	DMAc conv. (%)[d]	DAAm conv. (%)[d]	total $DP_{n,}$[e] (B blocks)	$M_{n,th}$ [e] (kg mol^{-1})	$M_{n,PMMA}$ [f] (kg mol^{-1})	Đ [f]
Series I – $DP_{n, A block}$ ~ 80												
80-100-0*	I *bis*	9.2	7.8	89	0	187	-	97	86	23.8	17.5	1.23
80-100-20	I	8.2	8.7	109	20	120	100	100	108	24.8	20.3	1.19
80-100-33	I	8.2	8.9	110	33	120	99	98	111	24.1	20.9	1.18
80-100-50	I	8.2	9.0	112	50	124	98	99	111	23.1	19.2	1.21
80-400-42	I	8.2	2.8	391	42	134	98	100	391	63.2	54.3	1.23
Series II – $DP_{n, A block}$ ~ 180												
180-100-20	II	18.5	9.4	96	20	120	85	88	96	33.4	29.3	1.22
180-100-33	II *bis*	18.4	10.1	98	33	120	88	90	98	32.8	25.0	1.21
180-100-50	II *bis*	18.4	11.2	106	50	120	94	96	105	32.5	25.0	1.20
180-400-20	II *bis*	18.4	2.4	390	20	137	100	100	390	78.9	70.5	1.28
180-400-42	II	18.5	2.6	391	42	120	98	99	391	73.0	62.3	1.21
Series III – $DP_{n, A block}$ ~ 400												
400-100-50	III	39.6 [g]	4.1	112	50	137	100	100	111	54.9	46.6	1.17
400-400-42	III	39.6 [g]	1.8	388	42	137	100	100	388	94.2	74.8	1.26

[a] Polymerization conditions: T = 70 °C, [monomers]$_0$ = 12 wt%, α (BA) = 85% (corresponding to pH = 5), [ACPA added in the 2nd polymerization step]$_0$ = 0.76 mmol L^{-1}. [b] Number-average molar mass $M_{n,NMR}$ of PDMAc macroRAFT, determined by ^{1}H NMR. [c] Molar percentage of DMAc in the two B blocks. mol%DMAc = [n(DMAc$_{residual}$) + n(DMAc$_{added}$)] / [n(DAAm) + n(DMAc$_{residual}$) + n(DMAc$_{added}$)] × 100. [d] Monomer conversion determined by ^{1}H NMR. [e] Total theoretical number-average degree of polymerization, $DP_{n, B blocks}$, and number-average molar mass, $M_{n,th}$, calculated using the experimental conversion and using $M_{n,NMR}$ for the PDMAc block. [f] Number-average molar mass $M_{n,PMMA}$ and dispersity, Đ, determined by SEC in DMF (+ LiBr 1g L^{-1}) with a PMMA calibration. [g] Theoretical number-average molar mass $M_{n,th}$ calculated using the experimental conversion. * Not an all-water polymerization process (1st step in DMF).[12] BAB triblock copolymers are noted "X-Y-Z", where "X" stands for the $DP_{n, A block}$ of PDMAc macroRAFT used, "Y" indicates the overall $DP_{n, B blocks}$ and "Z", the mol% of DMAc in the hydrophobic block.

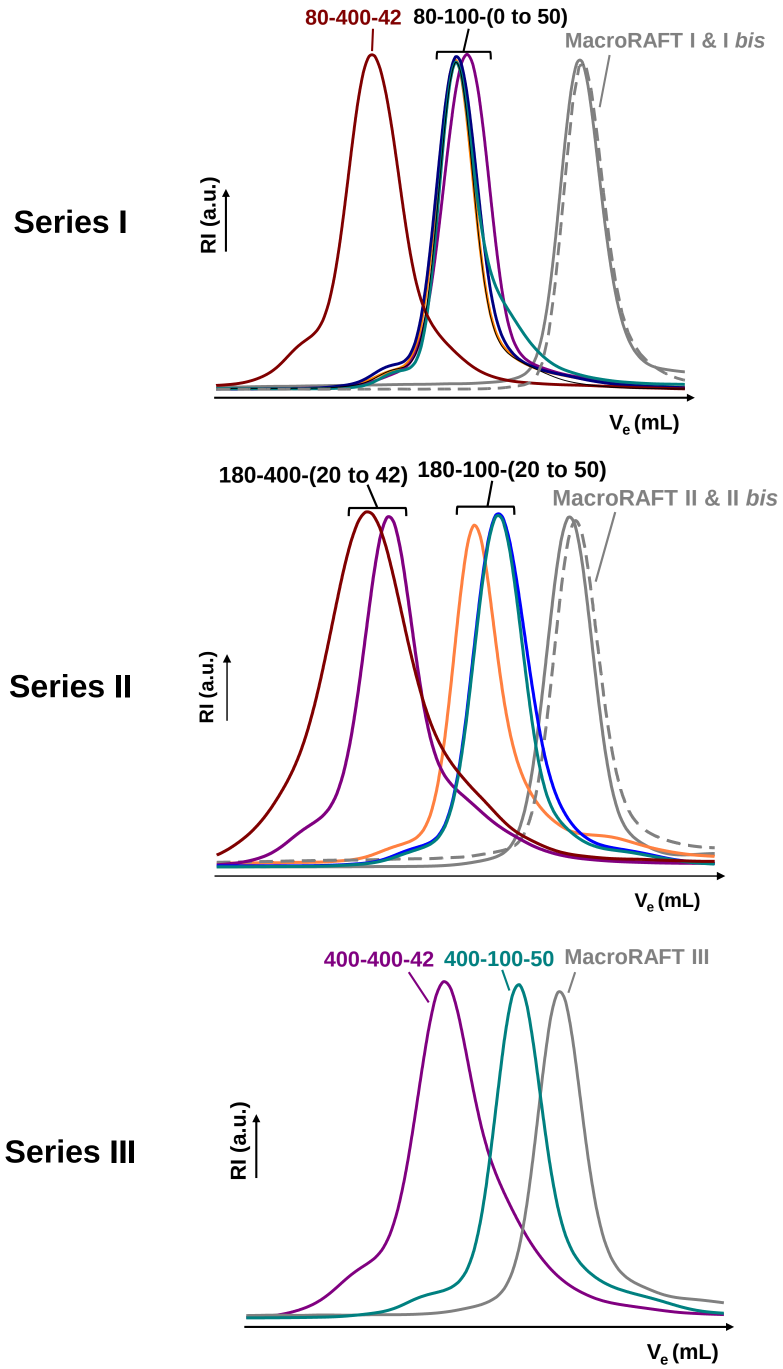
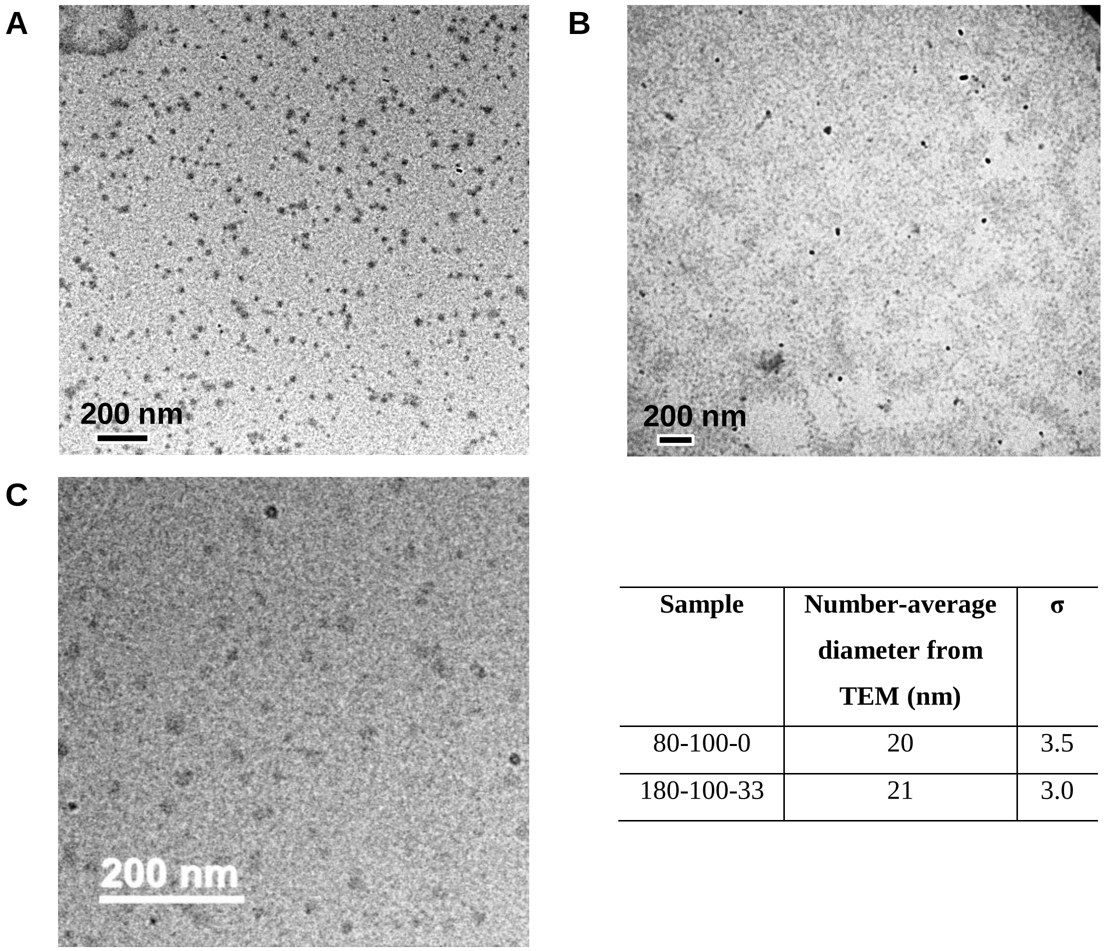


Figure S5. Normalized size exclusion chromatograms of PDMAc macroRAFT agents and the resulting [C_4-P(DAAm-*co*-DMAc)-*b*-PDMAc]$_2$-BA copolymers obtained by RAFT dispersion polymerization in water of series **I** (with macroRAFT of $DP_{\mathrm{n,\ A\ block}}$ ~ 80), series **II** (with macroRAFT of $DP_{\mathrm{n,\ A\ block}}$ ~ 180) and series **III** (with macroRAFT of $DP_{\mathrm{n,\ A\ block}}$ ~ 400). See experimental conditions in **Table 1** and details in **Table S3**.

Table S4. Viscosity η in the Newtonian regime of triblock copolymers at 5 wt% in water and 30 °C.

Sample	*DP*$_n$, PDMAc	mol% DMAc[a]	η (Pa.s)
180-100-20	177	20	0.309
180-100-33	177	33	0.054
80-100-33	79	33	≤ 0.015 [b]

[a] Molar percentage of DMAc in the two B blocks; [b] The oil added on the geometry to limit water evaporation from the sample (see experimental section) causes an error on the measurement of very-low viscosity aqueous solutions. Indeed, the viscosity of water covered with this oil is also 0.015 Pa.s instead of 0.0008 Pa.s.[38] It follows that the viscosity of 80-100-33 at 5 wt% lies between 0.0008 and 0.015 Pa.s but cannot be measured more precisely. This information is sufficient to conclude though.



Sample	Number-average diameter from TEM (nm)	σ
80-100-0	20	3.5
180-100-33	21	3.0

Figure S6. TEM images and number-average diameter (*d*$_n$) of **(A)** sample 80-100-33 stained with phosphotungstic acid (0.05 wt%), and **(B)** sample 80-100-0. The samples were prepared at 25°C and 0.1wt%. Cryo-TEM image (**C**) for sample 180-100-33 (prepared at 25 °C and 1 wt%).

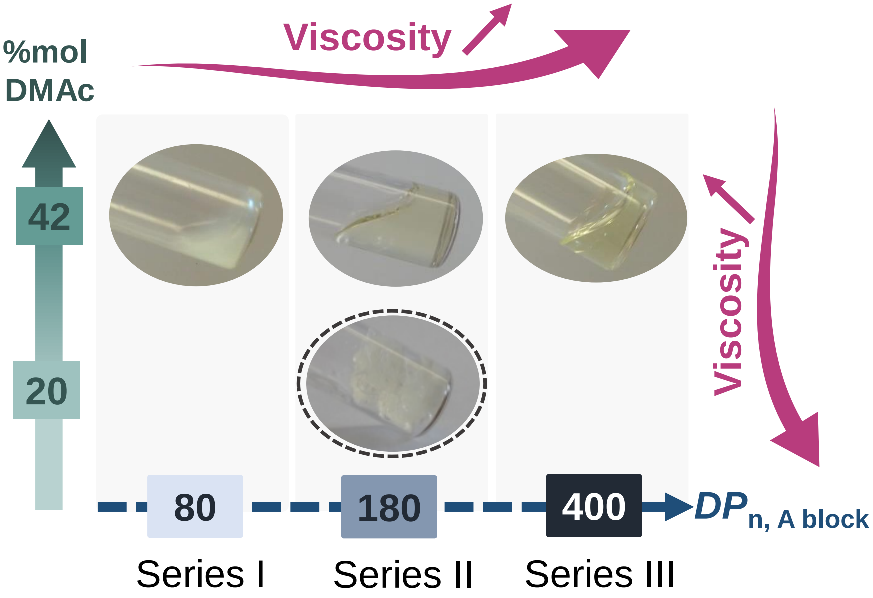


Figure S7. Macroscopic aspect of triblock copolymers with total $DP_{\text{n, B blocks}}$ ~ 400 at 18 wt% in water at 25 °C observed 5s after vial tilting. The dotted circle indicates a gel-like dispersion.

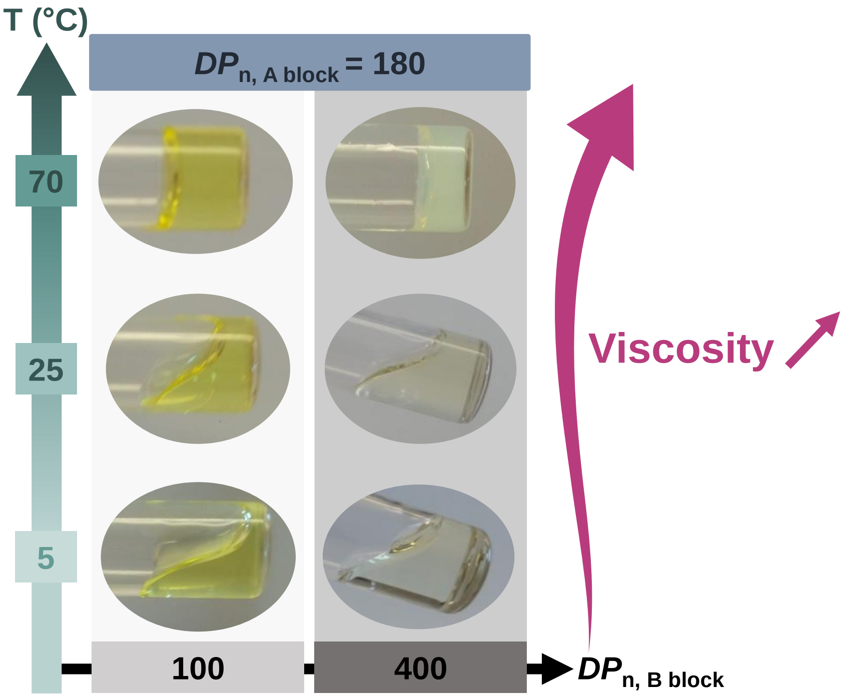


Figure S8. Macroscopic aspect at different temperatures for block copolymer dispersions 180-100-33 and 180-400-42 at C ~ 18 wt% (see **Table 1**) observed 5s after vial tilting. Sample 180-100-33: $DP_{\text{n, A block}}$ ~ 180, $DP_{\text{n, B blocks}}$ ~ 100 with 33 mol% DMAc and sample 180-400-42: $DP_{\text{n, A block}}$ ~ 180, $DP_{\text{n, B blocks}}$ ~ 400 with 42 mol% DMAc.

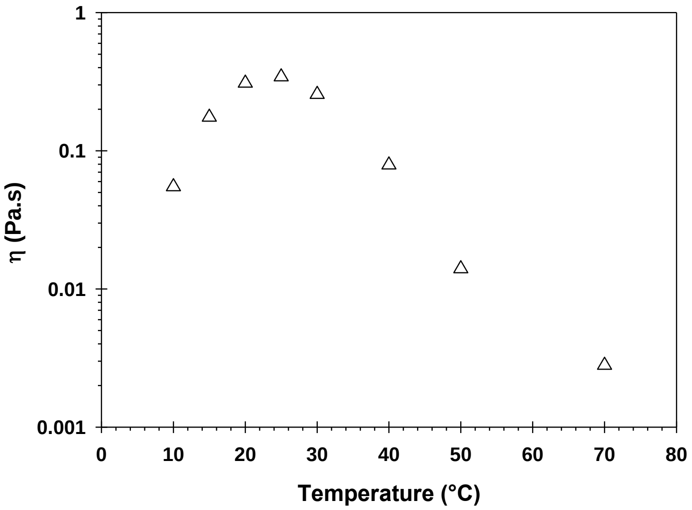


Figure S9. Temperature-dependency of the viscosity (η) in the Newtonian regime at C = 5 wt% for sample 180-100-20 (△). The solid lines are guides to the eye.

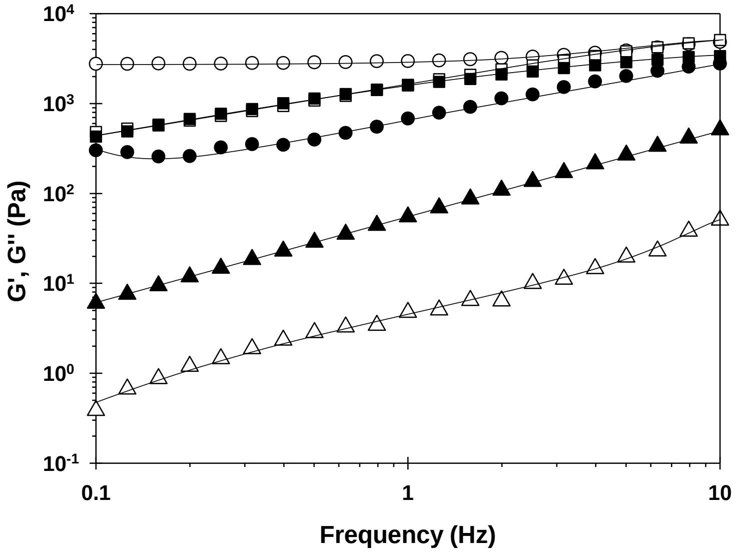


Figure S10. Frequency dependence of the storage and loss moduli for a 14 wt% dispersion of copolymer 180-100-33 at an applied strain of 1% and at different temperatures: 27 °C (G'△ and G''▲), 50 °C (G'○ and G''●) and 70 °C (G'□ and G''■). The solid lines are guides to the eye.

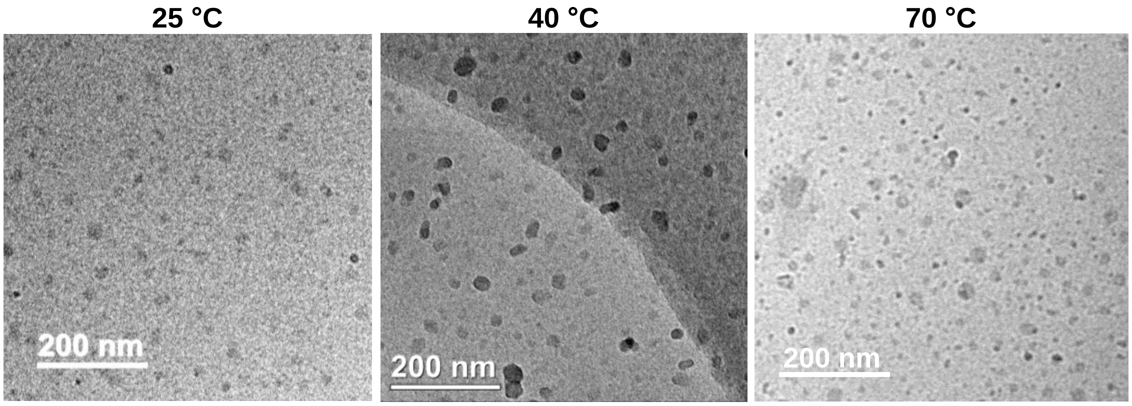
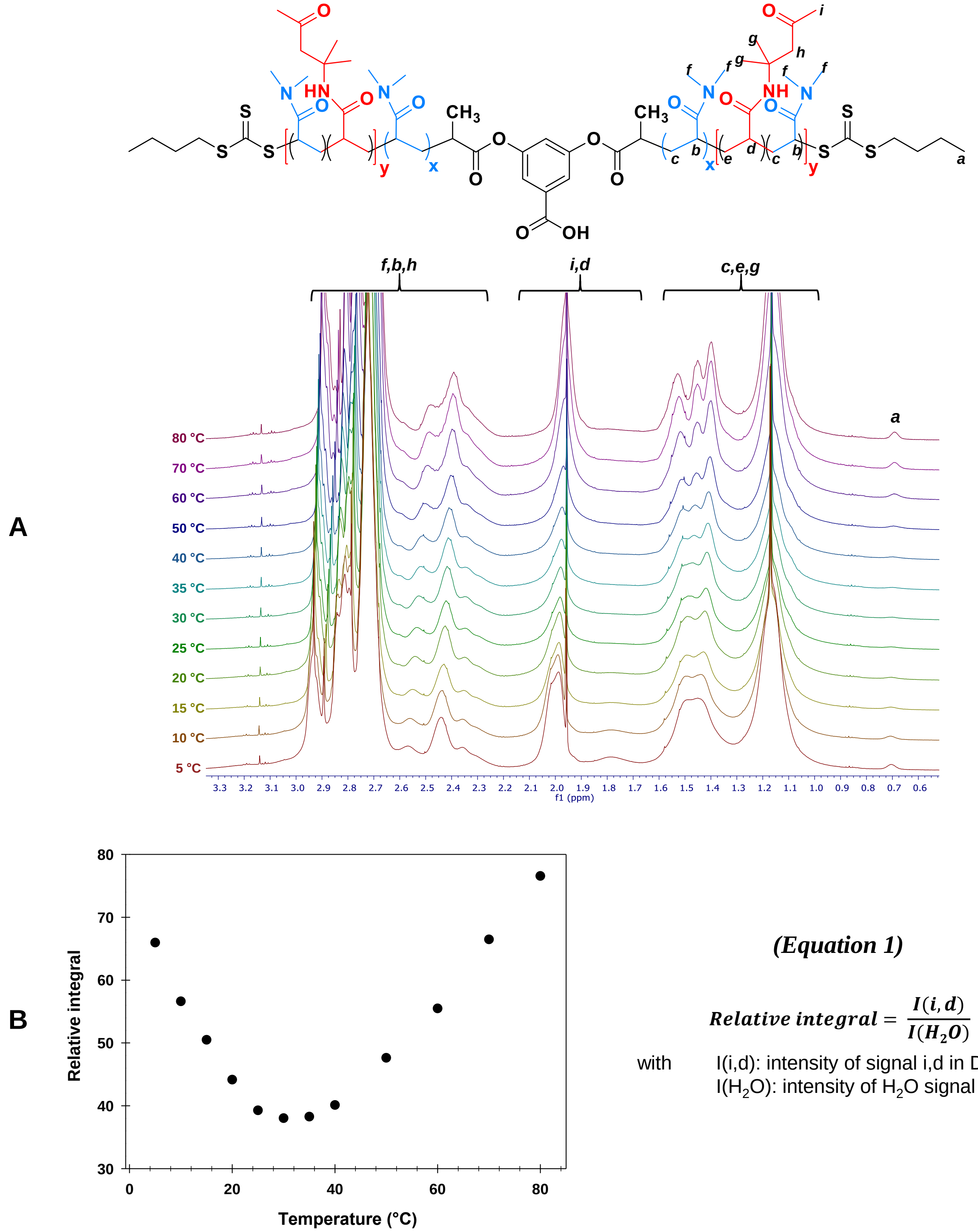


Figure S11. Cryo-TEM images prepared at 25, 40 and 70 °C of sample 180-100-33 (1 wt%).

Table S5. Number-average diameter, d_n, determined by cryo-TEM for sample 180-100-33 at 1 wt%.

Sample	**Temp. (°C)** [a]	d_n **(nm)** [b]	**σ** [c]
180-100-33	25°C	22	5.2
	40°C	21	3.5
	70°C	27	7.3

[a] Temperature at which the sample was deposited on the TEM grid; [b] number-average diameter determined on more than 25 particles; [c] standard deviation



(Equation 1)

$$\textbf{Relative integral} = \frac{I(i,d)}{I(H_2O)}$$

with I(i,d): intensity of signal i,d in D_2O
I(H_2O): intensity of H_2O signal in D_2O

Figure S12. (**A**) Variable temperature ^{1}H NMR study of a thermoresponsive BAB triblock copolymer (sample 180-100-33 in **Table 1**) in D_2O at 2.5 wt% upon heating from 5 °C to 80 °C. The signal intensity of protons ***i,d*** reaches a minimum at ~ 35 °C which could be attributed to the minimum of mobility of the core-forming blocks B. (**B**) The relative integral of signal ***i,d*** is calculated according ***(Equation 1)***.

References

[1] P. Biais, P. Beaunier, F. Stoffelbach and J. Rieger, *Polymer Chemistry*, 2018, **9**, 4483–4491.