Supporting information to

Surfactant-free RAFT emulsion polymerization using a novel biocompatible thermoresponsive polymer

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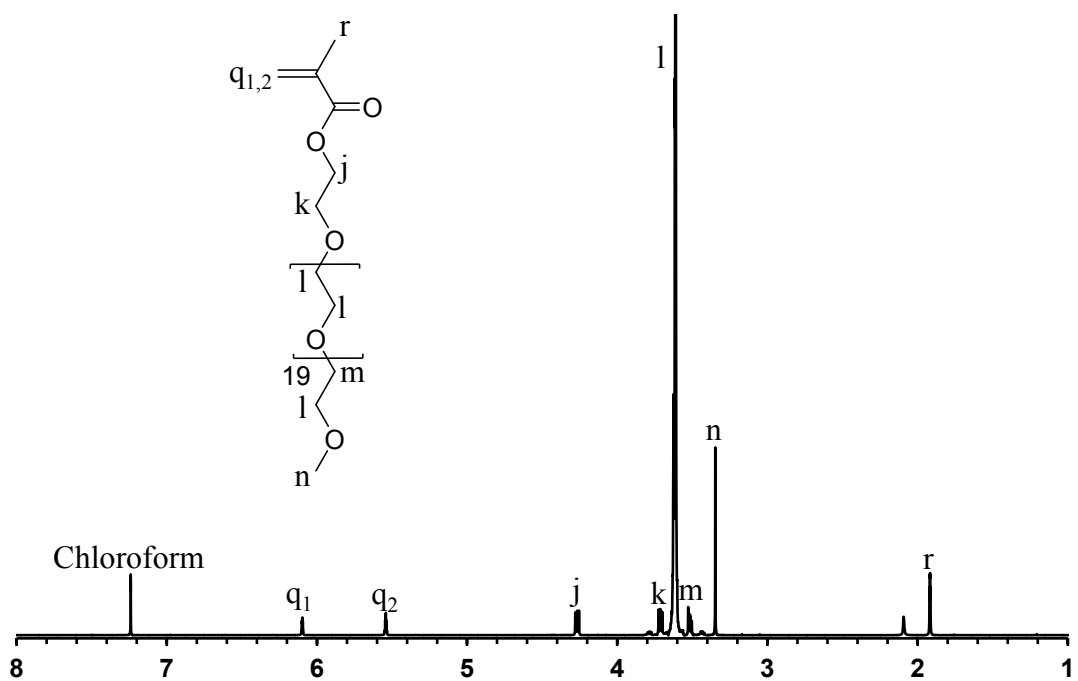
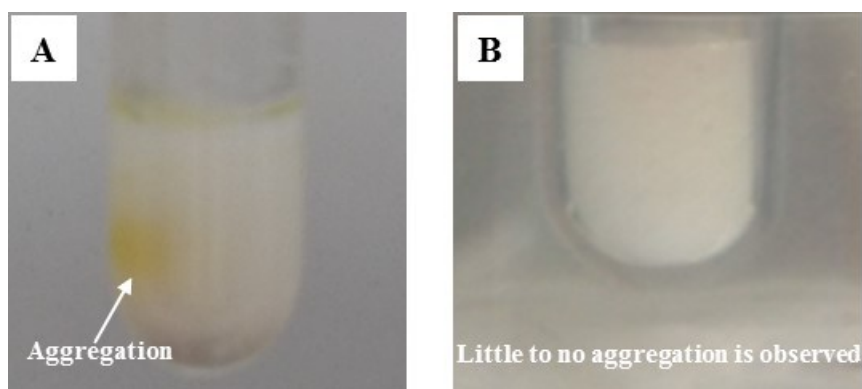Fig. S1 ^{1}H NMR for the PEGMA macro-monomer in chloroform-d.

Fig. S2 Images of latexes of (A) thermoresponsive polymer A3 and (B) thermoresponsive polymer A4 after surfactant-free RAFT emulsion polymerization of styrene for 3 h.

Table S1. ^{1}H NMR and kinetic data for the surfactant-free RAFT emulsion polymerization of styrene in water at 70 °C using AIBN as initiator and A4 as a macro-CTA and macro-stabilizer. The molar ratio of [styrene]:[macro-CTA]:[I] was 450:5:1.

| Time (min) | ^{1}H NMR | | SEC[c] | |
	Conversion[a] (%)	$M_{n,theory}$ [b] (g mol^{-1})	Mn (g mol^{-1})	Đ
0	0	10,800	10,800	1.18
45	6	11,362	12,300	1.22
90	24	13,046	12,900	1.23
150	47	15,199	14,800	1.26
210	60	16,416	16,500	1.27
270	88	19,037	18,800	1.30

[a] Conversions of styrene were calculated by the integral area of a peak at 5.7 ppm ($I_{5.7}$) and a peak in the range 6.3-7.5 ($I_{6.3-7.3}$) using the following equation: Conversion of styrene = 100 x (1 - 5 x $I_{5.7}$ / ($I_{6.3-7.3}$ - $I_{5.7}$)). [b] $M_{n,theory}$ were calculated using the following equation: $M_{n,theory}$ = Conversion / 100 x 90 x 104 + 10,800. [c] SEC data measured in DMAc + 0.03 wt% of LiBr solution and using PSTY standards for calibration.

Table S2. SEC data for the surfactant-free RAFT emulsion polymerization of styrene or methyl methacrylate in water at 70 °C using AIBN as initiator and A4 or A6 as a macro-CTA and macro-stabilizer.

| Copolymer | Monomer | Macro-CTA | [Monomer]:[Macro-CTA]:[I] | Time (h) | SEC[a] | |
					$M_{n,SEC}$ (g mol^{-1})	Đ
B1	Styrene	A4	900:10:1	3.5	16,400	1.22
B2	Styrene	A6	1200:10:1	3.5	19,800	1.30
B3	MMA	A4	1500:10:1	2.0	14,900	1.23

[a] SEC data measured in DMAc + 0.03 wt% of LiBr solution and using PSTY standards for calibration.
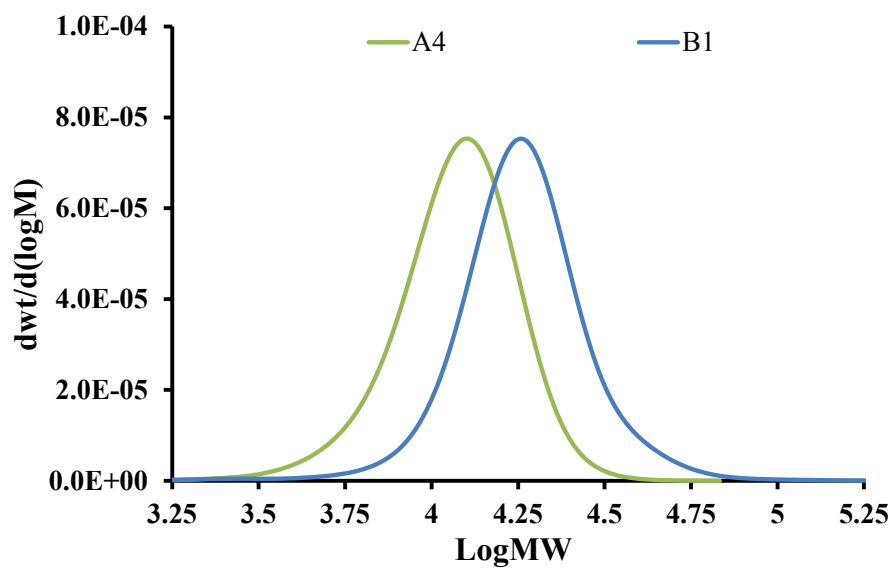
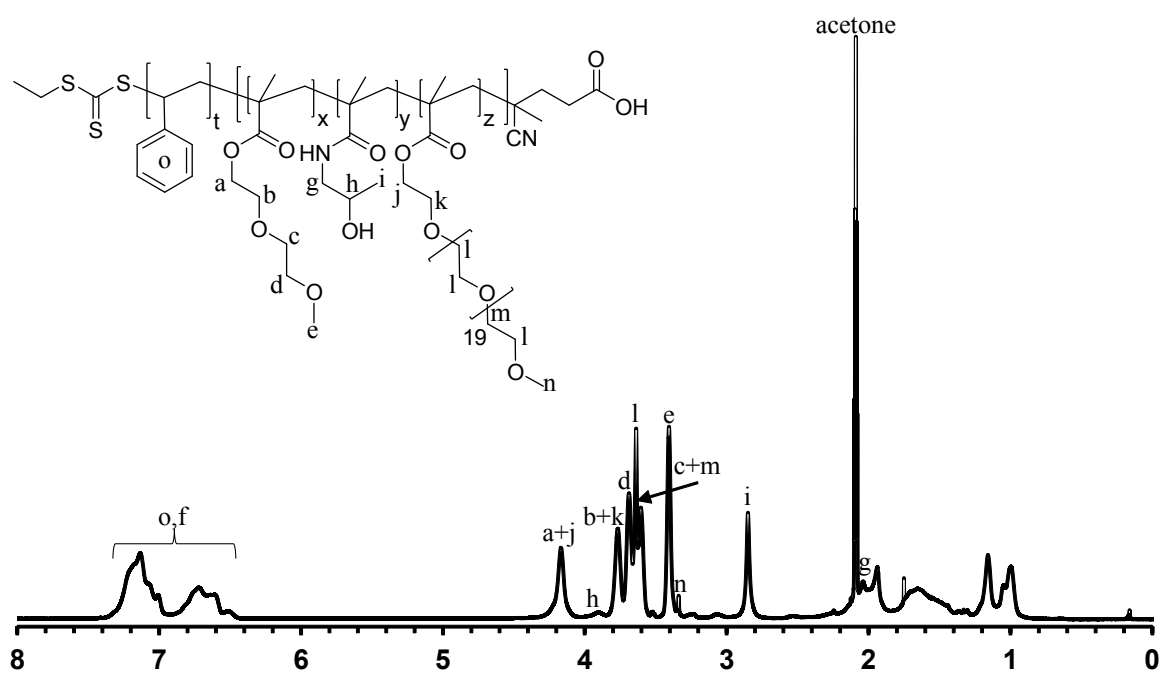Fig. S3 MWDs for the macro-CTA A4 and copolymer B1.

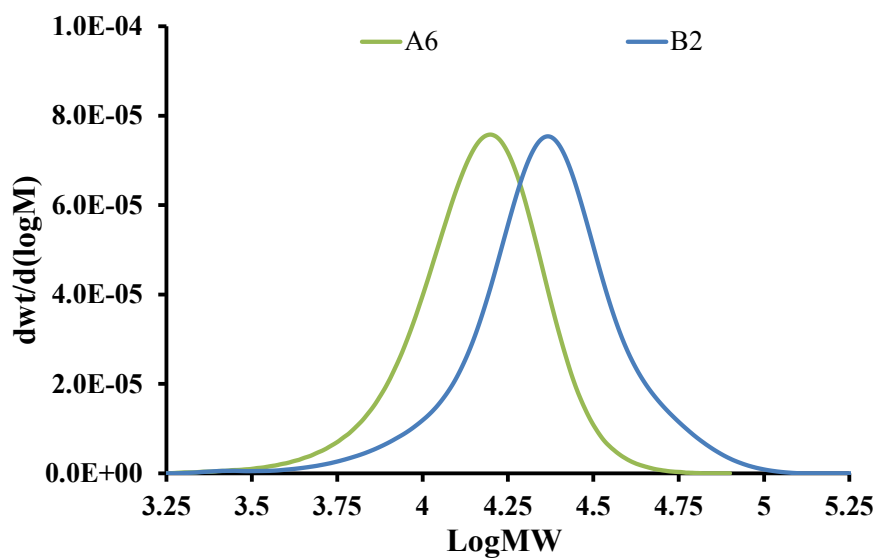Fig. S4 ^{1}H NMR for block copolymer B1 in acetone-d_6.

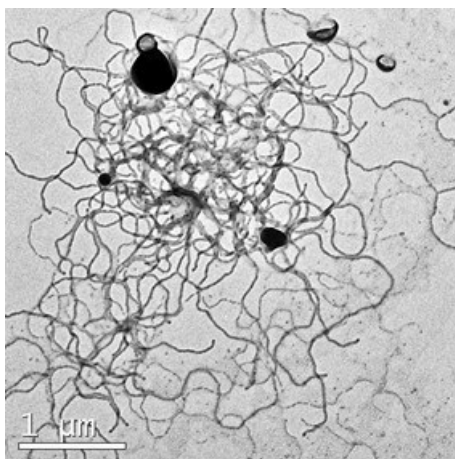Fig. S5 MWDs for the Macro-CTA A6and copolymer B2.

Fig. S6 Representative TEM images of the latexes of diblock copolymer B2 in water obtained by concentrated and high-scale surfactant-free RAFT emulsion polymerization followed by morphological transformation overnight.
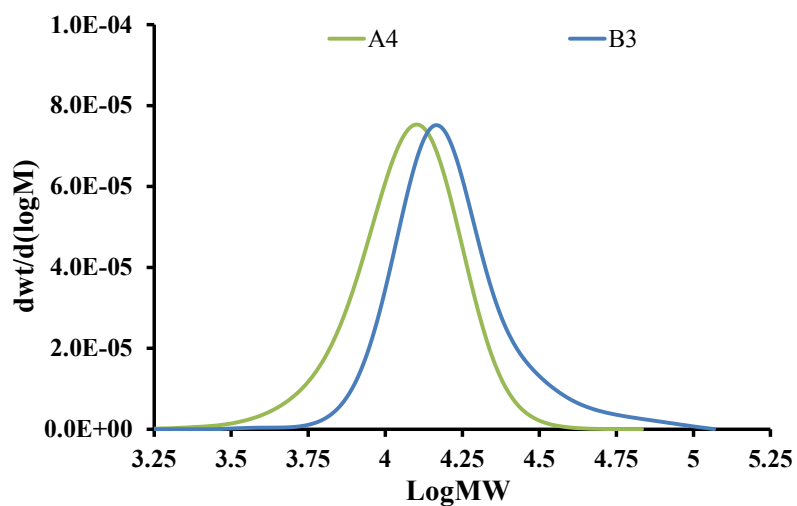
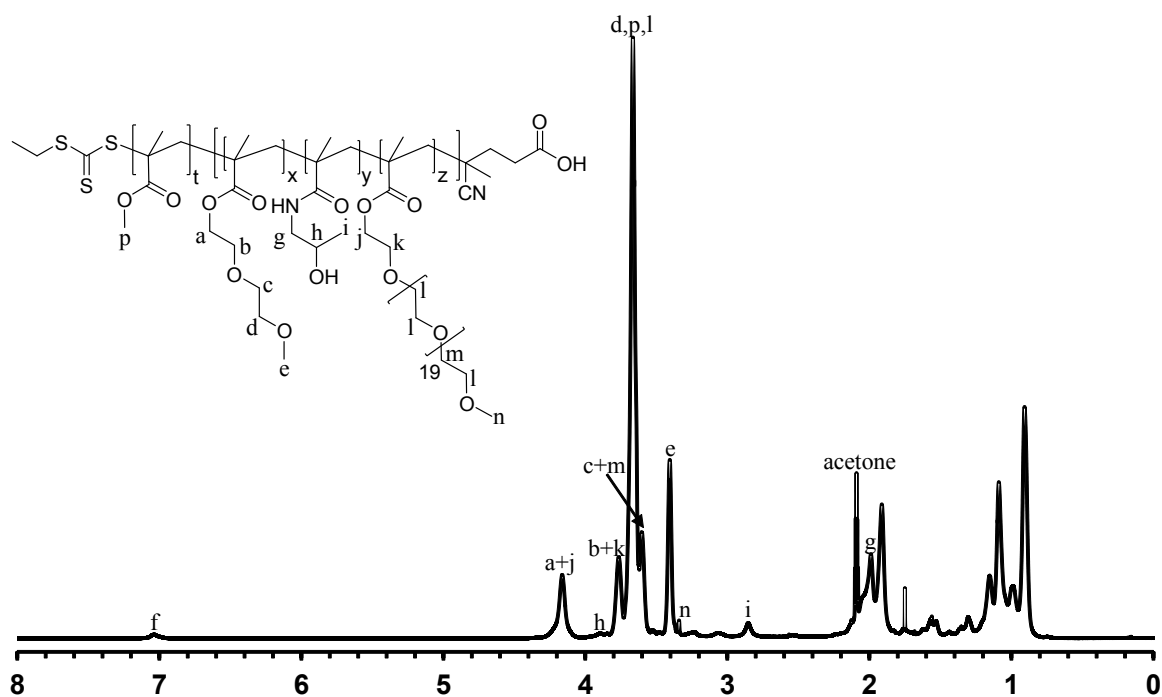Fig. S7 MWDs for the Macro-CTA A4 and copolymer B3.

Fig. S8 ^{1}H NMR for block copolymer B3 in acetone-d$_6$.