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Supporting Information

Loop-stabilized BAB block copolymer morphologies by PISA in water

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Synthesis of (C_4-TTC-PDMAc)$_2$-EG MacroRAFT agent and (C_4-TTC-PDAAm-*b*-PDMAc)$_2$-EG Block Copolymers

The macroRAFT agent (C_4-TTC-PDMAc)$_2$-EG (**Table S1**, entry **C**) has been synthesized following the same protocol as for the macroRAFT agents A and B (see experimental section in the main article) using (C_4-TTC)$_2$-EG as a RAFT agent synthesized as previously reported.[1] The RAFT dispersion polymerizations of DAAm in presence of the macroRAFT agent were performed following the protocol described in the experimental section and using the conditions detailed in **Table S2**.

Table S1. Polymerization Conditions and Characteristics of the Poly(*N*,*N*-dimethylacrylamide) MacroRAFT Agents Prepared by Solution Polymerization of DMAc in DMF at 70 °C[a]

Entry	RAFT agent	time (min)	conv.[b] (%)	$DP_{n,th}$[c]	$M_{n,th}$[c] (kg mol^{-1})	$M_{n,RMN}$[d] (kg mol^{-1})	$M_{n,LS}$[e] (kg mol^{-1})	$M_{n,PMMA}$[f] (kg mol^{-1})	$Đ$[f]
A	(C_{12}-TTC)$_2$-BA	133	75	86	9.3	9.5	9.6	6.0	1.21
B	(C_4-TTC)$_2$-BA	129	73	84	8.9	9.0	10.0	5.4	1.21
C	(C_4-TTC)$_2$-EG	135	74	85	8.9	8.4	10.0	6.7	1.13

[a] $[DMAc]_0$ = 2 M, $[RAFT\ agent]_0/[AIBN]_0$ = 10. [b] Monomer conversion determined by ^{1}H NMR. [c] Theoretical number-average molar mass, $M_{n,th}$, and number-average degree of polymerization, $DP_{n,th}$, calculated using the experimental conversion. [d] Number-average molar mass $M_{n,RMN}$, determined by ^{1}H NMR. [e] Number-average molar mass $M_{n,LS}$ determined by SEC in DMF (+ LiBr 1g L^{-1}) with light scattering (LS) detector (d*n*/d*C* = 0.081 mL g^{-1}). [f] Number-average molar mass $M_{n,PMMA}$ and dispersity $Đ$ determined by SEC in DMF (+ LiBr 1g L^{-1}) with a PMMA calibration.

Table S2. Experimental Conditions and Results for the Dispersion Polymerizations of DAAm in the Presence of the MacroRAFT Agent (C_4-TTC-PDMAc)$_2$-EG in Water at 70 °C[a]

Entry	$[DAAm]_0$ (wt%)	$[ACPA]_0$ (mmol L^{-1})	$[RAFT]_0$ (mmol L^{-1})	$[RAFT]_0/[ACPA]_0$	pH	time (min)	conv.[b] (%)	$DP_{n,th}$[c] (PDAAm)	$M_{n,th}$[c] (kg mol^{-1})
C-1	19	1.45	7.4	5.1	5.7	125	95	203	44.9
C-2	7	0.90	2.2	2.4	5.1	279	94	203	44.4

[a] $M_{n,LS}$ (macroRAFT agent C) = 10.0 kg mol^{-1}. [b] Monomer conversion determined by ^{1}H NMR. [c] Theoretical number-average degree of polymerization, $DP_{n,th}$ (PDAAm), and number-average molar mass, $M_{n,th}$ calculated using the experimental conversion.

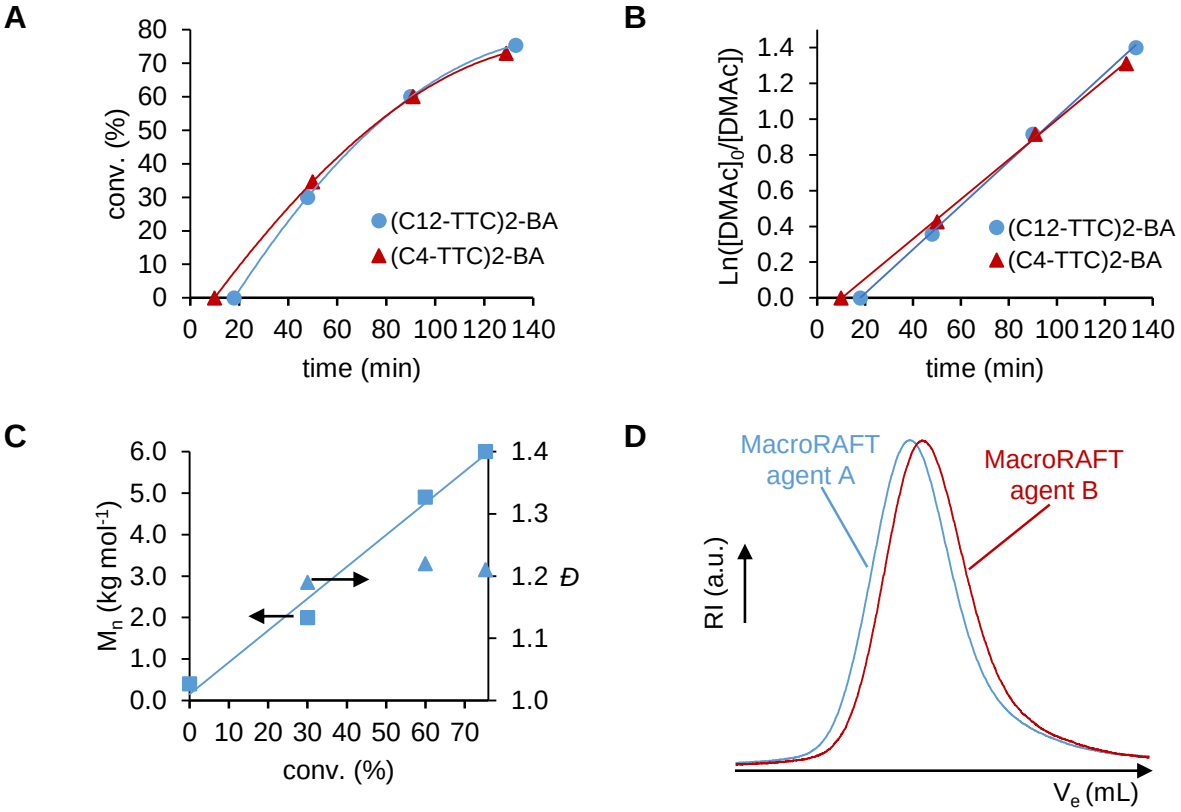
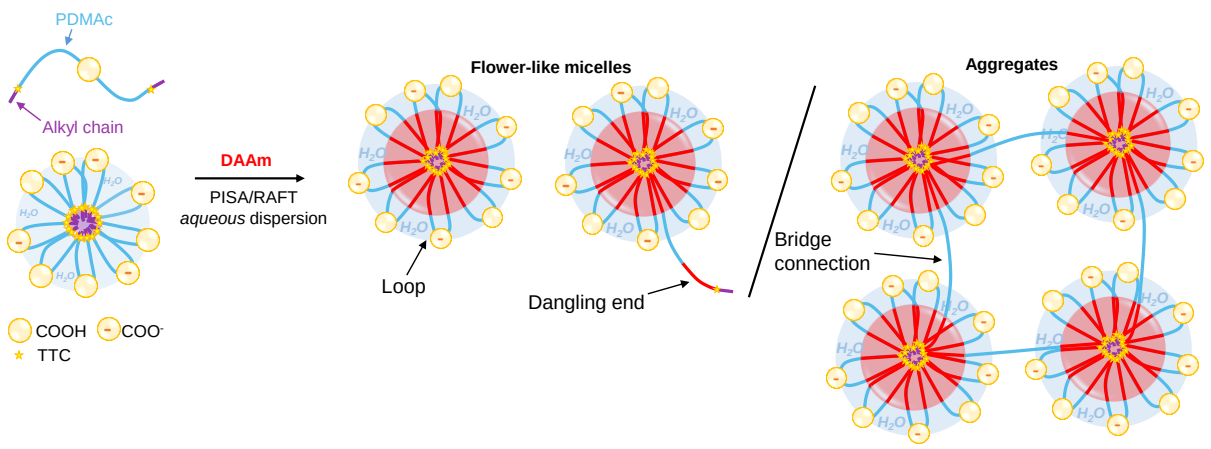


Figure S1. (A) Evolution of DMAc conversion versus time in presence of the RAFT agents $(C_{12}\text{-TTC})_2$-BA and $(C_4\text{-TTC})_2$-BA. (B) Semilogarithmic kinetic curve for RAFT polymerizations of DMAc in presence of the RAFT agents $(C_{12}\text{-TTC})_2$-BA and $(C_4\text{-TTC})_2$-BA. (C) Evolution of the M_n (square and trend line) (derived from a PMMA calibration) and *Đ* (triangle) with monomer conversion for the polymerization of DMAc with the RAFT agent $(C_{12}\text{-TTC})_2$-BA. (D) SEC chromatograms in DMF of the macroRAFT agents A and B (Table S1) (D).



Scheme S1. Self-assembly of PDAAm-*b*-PDMAc-*b*-PDAAm block copolymer *via* PISA in water showing the formation of flower-like micelles and bridged micelles/aggregates.

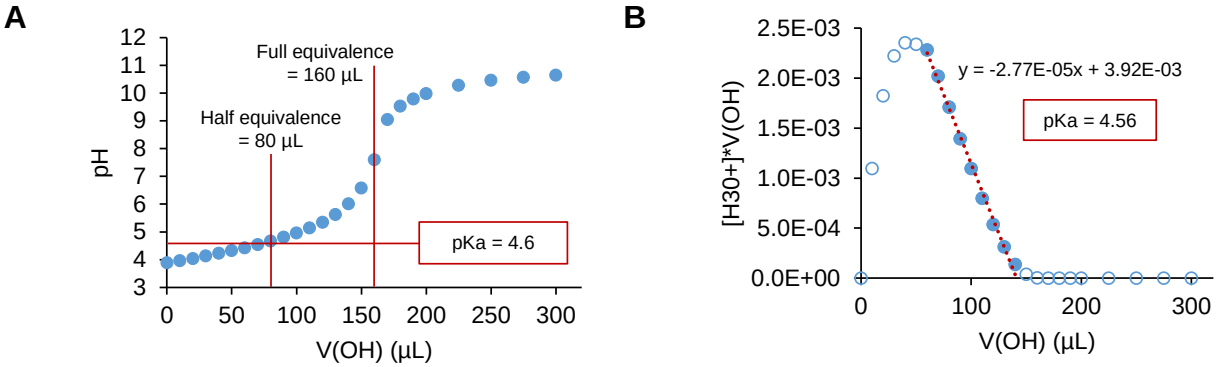


Figure S2. (A) Acid titration curve to determine the pKa of a $(C_{12}\text{-TTC-PDMAc})_2$-BA macroRAFT agent ($M_{n,RMN}$ = 5.0 kg mol^{-1}) with a NaOH solution (0.01 M). (B) pKa determination using the Gran method (see ***Equation 1*** in the main article).

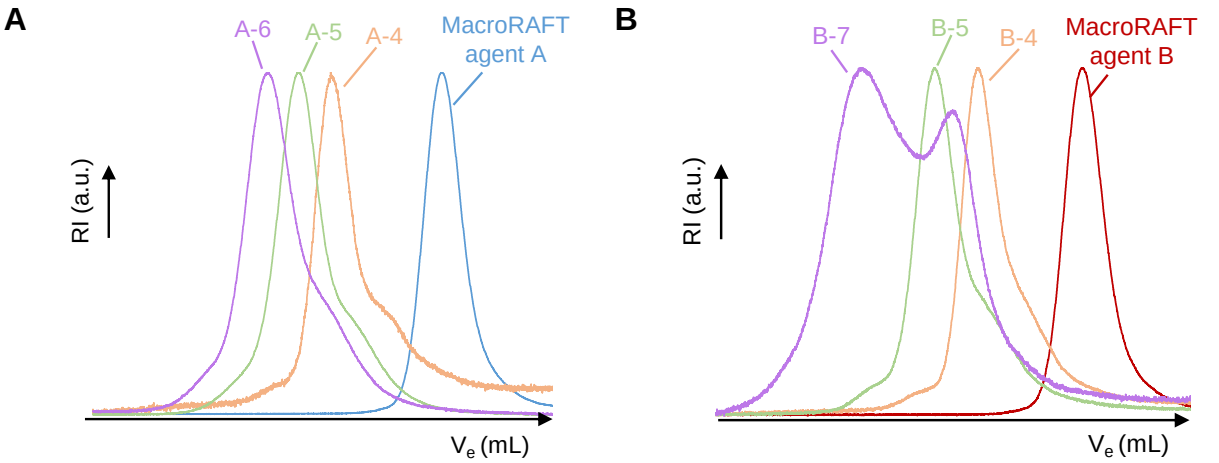


Figure S3. SEC chromatograms for block copolymers **A-4**, **A-5** and **A-6** (A) (Table 1) and **B-4**, **B-5** and **B-7** (B) prepared by dispersion polymerization of DAAm in water at 70 °C, at pH = 4.2 with the macroRAFT agents A and B respectively.

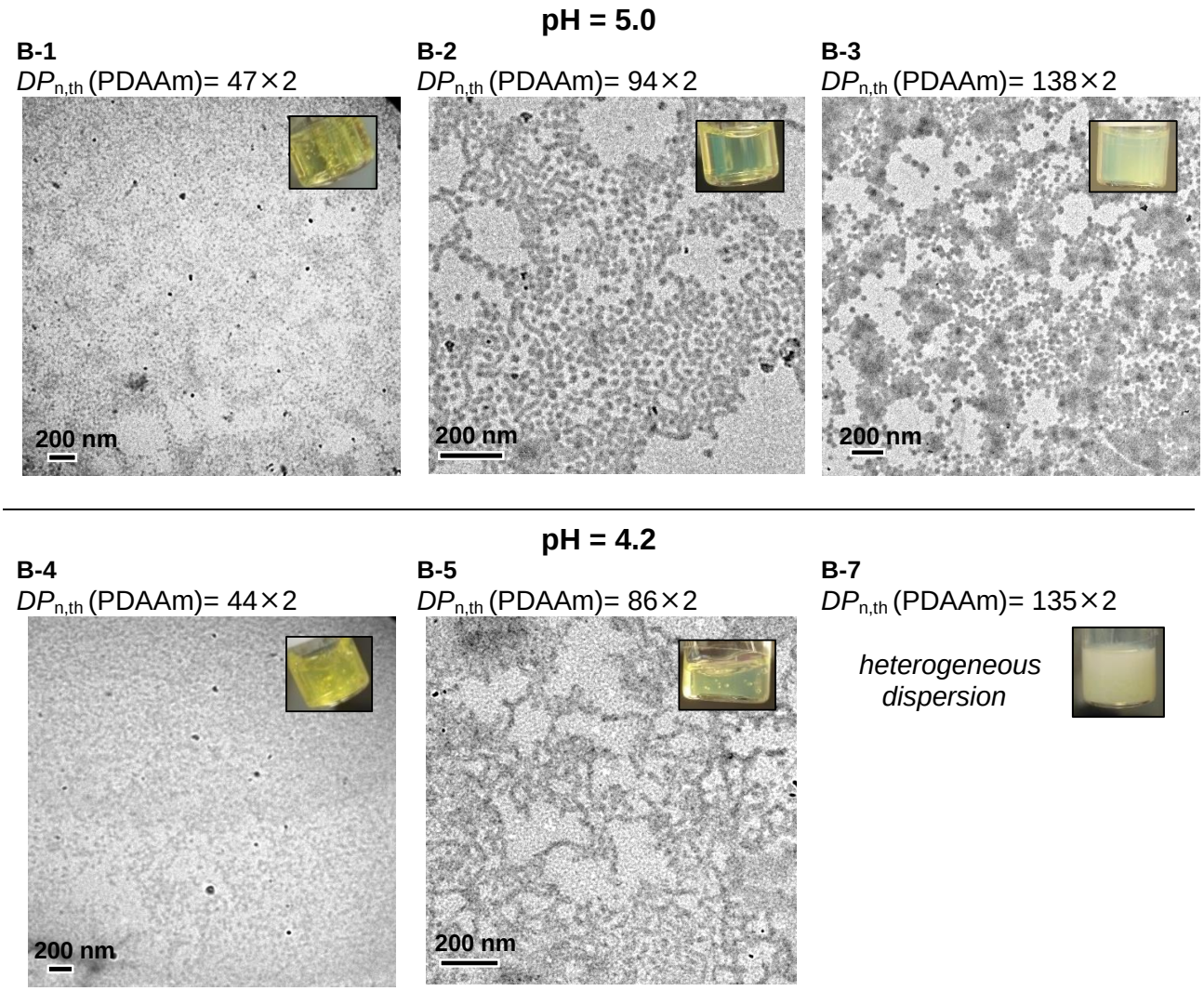


Figure S4. TEM images and macroscopic aspects for samples **B-1** to **B-5** and macroscopic aspect for the heterogeneous sample **B-7** prepared by the dispersion polymerization of DAAm with the macroRAFT agent **B** $(C_4\text{-TTC-PDMAc})_2$-BA at pH = 5.0 and pH = 4.2.

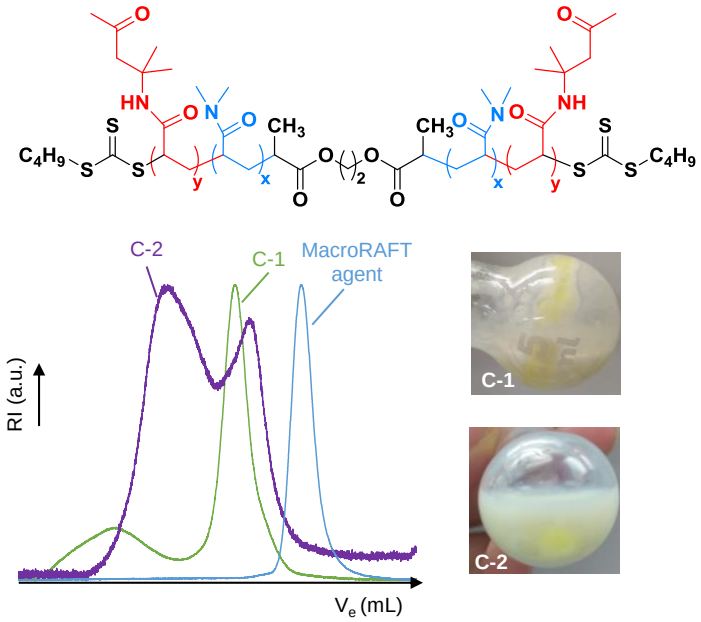


Figure S5. SEC chromatograms and macroscopic aspects for block copolymers **C-1** and **C-2** (Table S2) prepared by dispersion polymerization of DAAm in water at 70 °C with the macroRAFT agent $(C_4\text{-TTC-PDMAc})_2$-EG.

References

1 L. Voorhaar, B. De Meyer, F. Du Prez and R. Hoogenboom, *Macromol. Rapid Commun.*, 2016, **37**, 1682–1688.