Core cross-linked star (CCS) polymers with temperature and salt dual responsiveness: synthesis, formation of high internal phase emulsions (HIPEs) and triggered demulsification

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Supporting Information



Scheme S1 RAFT synthesis of thermally responsive copolymers as Macro-CTAs.

Synthesis of thermally responsive copolymers as Macro-CTAs

Thermally responsive copolymers, P(MEA-co-PEGA)s, were synthesized by RAFT copolymerization of MEA and PEGA in DMF at 70 °C (Scheme S1). The target number-average degree of polymerization (DP) was set to 100 and the molar ratio of MEA/PEGA was varied to prepare copolymers with adjustable cloud points (CPs). Three molar ratios of MEA : PEGA (80 : 20, 86 : 14, and 90 : 10) were used to synthesize the copolymers. The concentration of chain transfer agent (CTA) was 29 mM, and for all the syntheses, the molar ratio of CTA : monomers : AIBN was controlled at 1 : 100 : 0.2. The code of the copolymers synthesized is expressed as P(MEA_x-co-PEGA_y), where x and y denote the actual DP of MEA and PEGA, respectively. An exemplary synthesis for the copolymer of $P(MEA_{74}-co-PEGA_8)$ starting with molar ratio of MEA : PEGA = 90 : 10 is given as follows. CTA benzyl ethyl trithiocarbonate (135.7 mg, 0.69 mmol), MEA (6.96 g, 53.47 mmol), PEGA (2.85 g, 5.94 mmol) and 1,3,5-trioxane (535.2 mg, 5.94 mmol, internal standard) were dissolved in 20.4 mL of DMF. The solution was degassed with nitrogen at 0 °C for 40 min before immersion into a preheated oil bath at 70 °C. After the temperature was stabilized, a degassed solution of AIBN (19.5 mg, 0.12 mmol) in DMF was injected via a microsyringe. The polymerization was conducted for 2 h and was stopped at 83% monomer conversion as determined by ¹H NMR. The polymerization solution was diluted and the polymer was precipitated into ethyl ether. The polymer was collected by centrifugation and purified one more time by precipitation of the polymer THF solution into ethyl ether. After drying under vacuum, 7.57 g of a yellow, viscous liquid was obtained in 77% yield. $M_{\rm n, th} =$

13.9 kg mol⁻¹, $M_n = 10.6$ kg mol⁻¹ (RI-GPC, PMMA standard), D = 1.11 (RI-GPC, PMMA standard). ¹H NMR (500 MHz, CDCl₃): 4.22 ppm (s, -COO*CH*₂-), 3.73-3.54 ppm (m, -O(*CH*₂)₂O-), 3.43-3.33 ppm (s, -O*CH*₃), 2.54-2.33 ppm (backbone -*CH*-), 2.01-1.62 ppm (backbone -*CH*₂-).



Fig. S1 ¹H NMR spectra in CDCl₃ of P(MEA_x-*co*-PEGA_y) copolymers.

Code of arm polymers	Target DP MEA/PEGA	Conv. $(\%)^a$	Yield $(\%)^b$	$M_{\rm n, th}$ (kg mol ⁻¹) ^c	$M_{\rm n}$ (kg mol ⁻¹) ^d	${oldsymbol{\mathcal{D}}}^d$
P(MEA ₈₀ -co-PEGA ₂₀)	80/20	99	89	19.8	12.9	1.09
P(MEA ₅₆ -co-PEGA ₉)	86/14	66	45	12.0	9.6	1.10
P(MEA ₇₄ -co-PEGA ₈)	90/10	83	77	13.9	10.6	1.08

^{*a*}Monomer conversion determined by ¹H NMR. ^{*b*}Isolated polymer yield. ^{*c*}Theoretical molecular weight. ^{*d*}Determined by RI-GPC (DMF, PMMA standard). Polymerization conditions: concentration of CTA = 29 mM, molar ratio of CTA : (MEA+PEGA) : AIBN = 1:100:0.2, 70 °C, DMF.



Synthesis of CCS polymers by RAFT heterogeneous polymerizations

Scheme S2 Synthesis of CCS polymers by RAFT emulsion polymerization in water.

Procedure for the synthesis of S(16 nm, 51 °C) (Scheme S2):

The arm polymer P(MEA₈₀-*co*-PEGA₂₀) (3.10 g, 0.16 mmol) was dissolved in water (31.0 mL), to which were added BA (0.20 g, 1.57 mmol) and PEGDA (0.20 g, 0.78 mmol). After the mixture was degassed with nitrogen in an ice/water bath for 20 min, it was immersed into a preheated oil bath at 35 °C. After the temperature was stabilized, predegassed solutions of NaAs (80 μ L, 3.1 mg, 15.6 μ mol) and KPS (80 μ L, 4.2 mg, 15.6 μ mol) were injected via microsyringes, respectively. The polymerization was allowed to continue for 6 h under protection of nitrogen, which was then quenched by addition of a small amount of hydroquinone. The CCS polymer S(16 nm, 51 °C) was synthesized in 80% yield. $M_n = 127$ kg mol⁻¹ (RI-GPC, PMMA standard), $D_h = 1.16$ (RI-GPC, PMMA standard), $D_h = 16$ nm.



Scheme S3 Synthesis of CCS polymers by RAFT dispersion polymerization in water/ethanol (1:1).

Procedure for the synthesis of S(19 nm, 31 °C) (Scheme S3)

This procedure represents a typical synthesis via dispersion polymerization. P(MEA₇₄-*co*-PEGA₈) (3.02 g, 0.02 mmol) was dissolved in 1:1 water/ethanol (30.2 mL), to which was added HDDA (0.49 g, 2.17 mmol). After the mixture was degassed with nitrogen in an ice/water bath for 40 min, it was immersed into a preheated oil bath at 70 °C. After the temperature was stabilized, a predegassed V-50 solution (60 μ L, 5.9 mg, 0.02 mmol) was injected via a microsyringe. The polymerization was allowed to continue for 3 h under protection of nitrogen. The CCS polymer of S(19 nm, 31 °C) was synthesized in 83% yield. $M_n = 94 \text{ kg mol}^{-1}$ (RI-GPC, PMMA standard), D = 1.17 (RI-GPC, PMMA standard), $D_h = 19$ nm.



Fig. S2 DLS results of CCS polymers in water (0.5 wt%) at 25 °C.



Fig. S3 Photographs of emulsions stabilized by S(16 nm, 51 °C) as a function of dodecane volume fraction (indicated number on vial) at two aqueous concentrations of S(16 nm, 51 °C). (A) 1.0 wt% and (B) 2.0 wt%.



Fig. S4 Photographs of emulsions stabilized by S(35 nm, 40 °C) as a function of dodecane volume fraction (indicated number on vial) at four aqueous concentrations of S(35 nm, 40 °C). (A) 0.3 wt%, (B) 0.4 wt%, (C) 0.5 wt% and (D) 1.0 wt%.



Fig. S5 Photographs of emulsions stabilized by S(43 nm, 38 °C) as a function of dodecane volume fraction (indicated number on vial) at three aqueous concentrations of S(43 nm, 38 °C). (A) 0.3 wt%, (B) 0.5 wt% and (D) 1.0 wt%.



Fig. S6 Photographs of emulsions stabilized by $S(19 \text{ nm}, 31 \text{ }^{\circ}\text{C})$ as a function of dodecane volume fraction (indicated number on vial) at three aqueous concentrations of $S(19 \text{ nm}, 31 \text{ }^{\circ}\text{C})$. (A) 0.4 wt%, (B) 0.5 wt% and (D) 1.0 wt%.



Fig. S7 Photographs of emulsions stabilized by S(43 nm, 31 $^{\circ}$ C) as a function of dodecane volume fraction (indicated number on vial) at three aqueous concentrations of S(43 nm, 31 $^{\circ}$ C). (A) 0.3 wt%, (B) 0.5 wt% and (D) 1.0 wt%.



Fig. S8 Photographs of emulsification of different volumetric fractions of dodecane (indicated number on vial) using linear arm polymer of P(MEA₅₆-*co*-PEGA₁₄) ($M_n = 20.1$ kDa, $M_w/M_n = 1.09$, CP = 40 °C) at 1.0 wt%. (A) After emulsification for 30 min, (B) after emulsification for 5 h.



Fig. S9 Photographs of (A) HIPE (80 vol% dodecane) stabilized by S(16 nm, 51 °C) (0.5 wt%) at ambient temperature and of phase separation after thermally induced demulsification: (B) after heating at 50 °C for 15 min, (C) after heating at 60 °C for 12 min, (D) after heating at 70 °C for 90 min, and (D) after heating at 80 °C for 2 min.



Fig. S10 Photographs of (A) HIPEs (80 vol% dodecane) stabilized by S(35 nm, 40 °C) (0.5 wt%) and of thermally induced demulsification: (B) 40 °C for 15 min, (C) 50 °C for 8 min, and (D) 60 °C for 5 min.



Fig. S11 Photographs of (A) HIPE (80 vol% dodecane) stabilized by S(43 nm, 38 °C) (0.5 wt%) at ambient temperature and of phase separation after thermally induced demulsification: (B) after heating at 50 °C for 10 min, and (C) after heating at 60 °C for 5 min.



Fig. S12 Photographs of (A) HIPE (80 vol% dodecane) stabilized by S(43 nm, 31 °C) (0.5 wt%) at ambient temperature and of phase separation after thermally induced demulsification: (B) after heating at 30 °C for 11 min, (C) after heating at 40 °C for 9.5 min, (D) after heating at 50 °C for 8 min, and (E) after heating at 60 °C for 6 min.



Fig. S13 Photographs of emulsification-demulsification cycles of a HIPE (80 vol% dodecane) stabilized by S(19 nm, 31 °C) (1.0 wt%). Demulsification temperature 50 °C, time 3 min.