Electronic Supplementary Material (ESI) for Chemical Communications

Efficient and Versatile Synthesis of Star Polymers in Water and Their Use as Emulsifiers

Supporting Information

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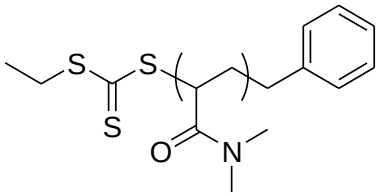
Materials. 2,2′-Azobis(2-methylpropionamidine)dihydrochloride (V-50, 97%), 2-methoxyethyl acrylate (MEA, 98%), poly(ethylene glycol) diacrylate (PEGDA, M_n = 258), poly(ethylene glycol) methyl ether methacrylate (PEGMA, M_n = 475), poly(ethylene glycol) methyl ether acrylate (PEGA, M_n = 480), and fluorescein *o*-acrylate (95%) were purchased from Sigma-Aldrich. *N,N*'-Dimethylacrylamide (98%), *N*-isopropylacrylamide (NIPAM) (99%) and Nile Red (99%) were purchased from J&k. L-ascorbic acid sodium salt (NaAs, 99%) and 1,3,5-trioxane (98%) were purchased from Alfa-Aesar. *N,N'*-Methylenebisacrylamide (MBA) (98+%), *n*-butyl acrylate (BA) (CP), 2,2'-azobis(2-methylpropionitrile) (AIBN, CP), potassium persulfate (KPS, AR), hydroquinone (AR), *N,N'*-dimethylformamide (DMF) (99.5+%), tetrahydrofuran (THF, 99+%) and diethyl ether anhydrous (99.7+%) were purchased from Sinopharm Chemical Reagent Co. Ltd. KPS was recrystallized from cold water. AIBN was recrystallized from methanol twice. All monomers were passed through a column of Al_2O_3 to remove the inhibitor before use.

Characterization.

NMR spectra were collected on a Bruker AV 500 MHz spectrometer and chemical shifts were reported using the solvent residue as the reference. Gel permeation chromatography (GPC) was performed on a Waters Alliance e2695 GPC system, equipped with a styragel guard column, a Waters styragel HR3 (molecular weight range $5.0 \times 10^2 - 3.0 \times 10^4$), a Waters styragel HR4 (molecular weight range $5.0 \times 10^3 - 6.0 \times 10^5$), and a Waters styragel HR5 (molecular weight range $5.0 \times 10^4 - 4.0 \times 10^6$). Detection was performed on a 2414 refractometer using DMF (HPLC grade, containing 1 mg/mL LiBr) as the eluent at a flow rate of 0.8 mL/min. The temperature of the columns was set at 65 °C and the temperature of the refractometer was set at 45 °C. Analysis of molecular weight and polydispersity index of polymers was performed using Empower 2 software against PMMA standard (molecular weight range $2.4 \times 10^2 - 1.0 \times 10^6$). Fluorescence spectroscopy was conducted on a Hitachi F-7000 spectrometer. Star polymer sizing was analyzed using dynamic light scattering (DLS) on a Malvern Zetasizer 3000HSA at 25 °C. Confocal laser scanning microscopy was performed on an Olympus F1000 microscope.



Synthesis of poly(*N,N'*-dimethylacrylamide) (PDMA). Benzyl ethyl trithiocarbonate (1.008 g, 4.41 mmol), *N,N'*-dimethylacrylamide (35.0 g, 0.35 mol), and 1,3,5-trioxane (7.0 g, 77.78 mmol, internal standard) were dissolved in DMF (70 mL). The solution was degassed with nitrogen at 0 °C for 30 min before immersion into a preheated oil bath at 70 °C. After the temperature was stabilized, a degassed AIBN DMF solution (20 μL, 14.5 mg, 0.088 mmol) was injected via a microsyringe. The polymerization was conducted for 4 h and was stopped at 61% monomer conversion as determined by ^{1}H NMR. The polymerization was quenched by immersing the polymerization flask into an ice/water bath and exposing to air. The 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, 19.0 g of a yellow solid was obtained in 53% yield. M_n = 5 000 (^{1}H NMR), M_n = 8 000 (GPC), M_w/M_n = 1.10. ^{1}H NMR (500 MHz, $CDCl_3$): 3.2-2.75 ppm (m, -N(CH_3)$_2$), 2.75-2.4 ppm (m, -(CO)CHCH$_2$-), 1.9-1.1 (m, -CHCH_2-).

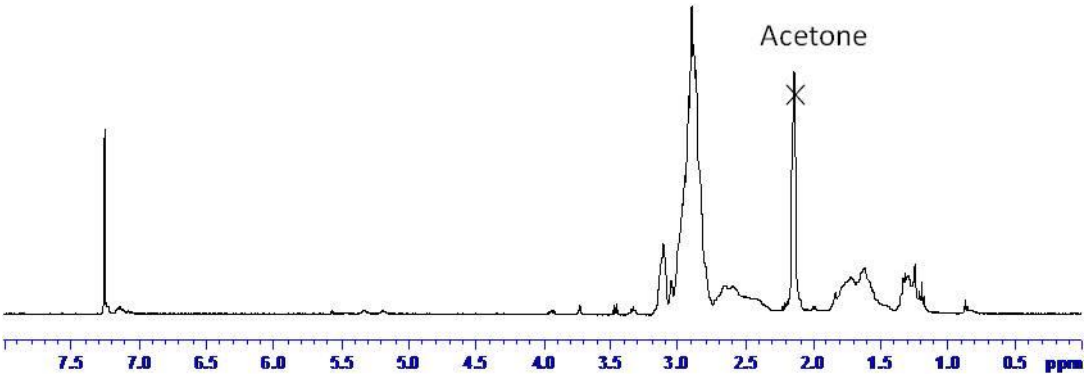
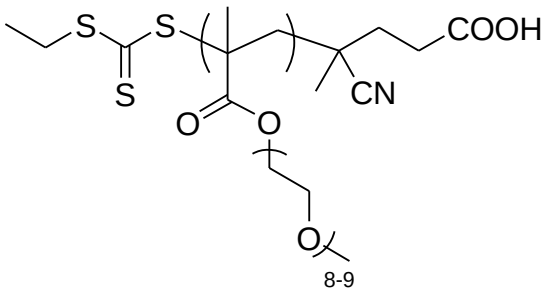


Figure S1. ^{1}H NMR spectrum of purified PDMA in $CDCl_3$.



Synthesis of poly(poly(ethylene glycol) methyl ether methacrylate) (PPEGMA). 4-Cyano-4-(ethylthiocarbonothioylthio)pentanoic acid (0.31 g, 1.17 mmol), PEGMA (16.77 g, 35.40 mmol), AIBN (0.039 g, 0.23 mmol), and DMF (0.258 g, 3.52 mmol, internal standard) were dissolved in dioxane (160 mL). The solution was degassed with nitrogen at 0 °C for 0.5 h before immersion into a preheated oil bath at 80 °C. The polymerization was conducted for 8 h at 73% monomer conversion as determined by ^{1}H NMR. The polymerization was quenched by immersing the polymerization flask into an ice/water bath and exposing to air. The solution was concentrated on a rotary evaporator and the polymer was precipitated into ethyl ether. The polymer was collected by centrifugation and purified four times by precipitation of the polymer THF solution into ethyl ether. 7.53 g of a yellow viscous liquid was obtained in 44% yield after drying the polymer under vacuum overnight. M_n = 11 000 (^{1}H NMR), M_n = 17 000 (GPC), M_w/M_n =1.10 (GPC). ^{1}H NMR (500 MHz, $CDCl_3$): 4.12 ppm (s, -COOCH_2-), 3.8-3.5 ppm (m, -O(CH_2)$_2$O-), 3.37 ppm (s, -OCH_3), 2.2-1.1 ppm (m, backbone -CH_2-), 1.1-0.6 ppm (s, -CH_3).

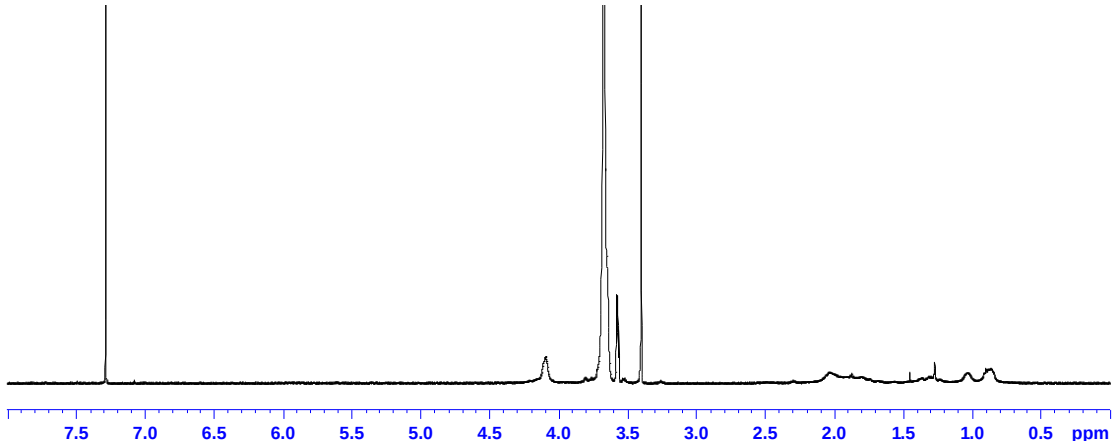
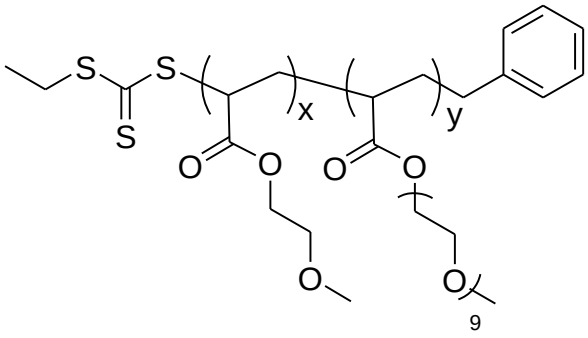


Figure S2. ^{1}H NMR spectrum of purified PPEGMA polymer in $CDCl_3$.



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Synthesis of poly(2-methoxyethyl acrylate-*co*-poly(ethylene glycol) methyl ether acrylate) (P(MEA-*co*-PEGA)). Benzyl ethyl trithiocarbonate (0.133 g, 0.58 mmol), MEA (6.05 g, 46.48 mmol), PEGA (5.58 g, 11.62 mmol), and trioxane (0.53 g, 5.85 mmol) were dissolved in DMF (20 mL). The solution was degassed with nitrogen at room temperature for 0.5 h and then immersed into a preheated oil bath at 70 °C. After the temperature was stabilized, 20 μL of degassed DMF solution containing AIBN (19.1 mg, 0.12 mmol) was injected into the solution via a microsyringe. The polymerization was allowed to continue for 1 h and was quenched at 70% monomer conversion at determined by ^{1}H NMR. The polymer solution was precipitated into ethyl ether and the precipitate was collected, which was dissolved in THF and precipitated into ethyl ether. The purification cycle was repeated three times. After drying under vacuum, 6 g of a yellow material was obtained in 51% yield. M_n = 14 000 (^{1}H NMR), M_n = 21 000 (GPC), M_w/M_n =1.11 (GPC). ^{1}H NMR (500 MHz, $CDCl_3$): 4.2 ppm (s, -COO*CH*$_2$-), 3.7-3.5 ppm (m, -O(*CH*$_2$)$_2$O-), 3.37 ppm (s, -O*CH*$_3$ *of MEA*), 3.34 ppm (s, -O*CH*$_3$ *of PEGA*), 2.4 ppm (m, backbone -*CH*-), 2.0-1.2 ppm (m, backbone -*CH*$_2$-).

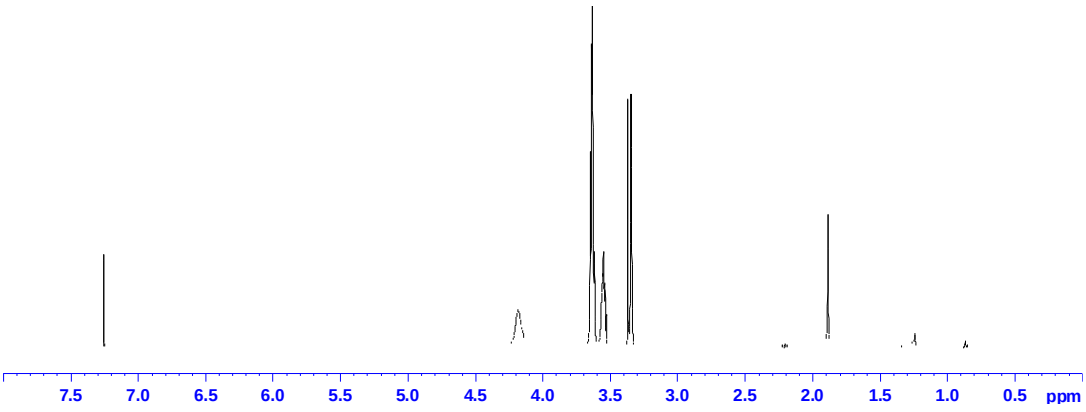

Figure S3. ^{1}H NMR spectrum of purified P(MEA-*co*-PEGA) polymer in $CDCl_3$.

Synthesis of star polymers by emulsion polymerization. The synthesis of core cross-linked star (CCS) polymers by emulsion polymerization was conducted at either 70 °C or 35 °C. For the PDMA and PPEGMA polymers, the synthesis was conducted at 70 °C using V-50 as the initiator. For the P(MEA-*co*-PEGA) polymer, the synthesis was conducted at 35 °C using a redox initiator ascorbic acid sodium salt/potassium persulfate (NaAs/KPS). For star polymer synthesis at 70 °C, the arm polymer (10% w/v relative to water), BA, PEGDA, and water were combined in a septum-sealed vial. The molar ratio of the arm polymer:BA:PEGDA was controlled at 1:10:(4-8, typically 5). The mixture was degassed with nitrogen in an ice/water bath for at least 20 min, which was then immersed into a preheated oil bath at 70 °C. After the temperature was stabilized, the initiator (typically 0.04 equivalent relative to the arm polymer) solution was injected. The polymerization was monitored with GPC by withdrawing samples at predetermined time intervals. The yield of star polymers was calculated from GPC chromatograms as:

Star yield = area of star polymer/(area of star polymer + area of low molecular weight polymer)[1, 2]

An exemplary synthesis of star polymers using PDMA arm polymer is as follows. PDMA (0.2 g, 0.04 mmol) was dissolved in water (2 mL), to which were added BA (0.051 g, 0.4 mmol) and PEGDA (0.051 g, 0.2 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 70 °C. After the temperature was stabilized, a predegassed V-50 solution (20 μL, 0.43 mg, 0.0016 mmol) was injected via a microsyringe. The polymerization was allowed to continue for 1 h under protection of nitrogen. The star polymer of PDMA was synthesized in 92% yield. M_n = 117 000 (GPC), M_w /M_n =1.06 (GPC).

For star polymer synthesis at 35 °C, the arm polymer P(MEA-*co*-PEGA) (0.30 g, 0.021 mmol) was dissolved in water (3 mL), to which were added BA (0.0275 g, 0.214 mmol) and PEGDA (0.0276 g, 0.107 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 (20 μL, 0.42 mg, 0.2 μmol) and KPS (20 μL, 0.58 mg, 0.2 μmol)

were injected via microsyringes. The polymerization was allowed to continue for 1 h under protection of nitrogen, which was then quenched by addition of a small amount of hydroquinone. The star polymer of P(MEA-*co*-PEGA) was synthesized in 85% yield. M_n = 135 000, M_w /M_n =1.07.

Synthesis of star polymers by precipitation/dispersion polymerization. The arm polymer (10% w/v relative to water), NIPAM, MBA, and water were combined in a septum-sealed vial. The molar ratio of the arm polymer:NIPAM:MBA was controlled at 1:10:(4-8, typically 5). The solution was degassed with nitrogen in an ice/water bath for at least 20 min, which was then immersed into a preheated oil bath at 70 °C. After the temperature was stabilized, the initiator solution (typically 0.04 equivalent relative to the arm polymer) was injected. The polymerization was monitored with GPC by withdrawing samples at predetermined time intervals.

An exemplary synthesis of star polymers by precipitation/dispersion polymerization using PDMA is as follows. PDMA (0.4 g, 0.079 mmol) was dissolved in water (4 mL), to which were added NIPAM (0.090 g, 0.79 mmol) and MBA (0.061 g, 0.395 mmol). After the solution was degassed with nitrogen in an ice/water bath for 20 min, it was immersed into a preheated oil bath at 70 °C. After the temperature was stabilized, a predegassed V-50 solution (20 μL, 0.86 mg, 0.003 mmol) was injected via a microsyringe. The polymerization was allowed to continue for 1 h under protection of nitrogen. The star polymer of PDMA was synthesized in 97% yield. M_n = 101 000 (GPC), M_w/M_n =1.14 (GPC). The star polymer was purified by dialysis against water (MWCO 50 000) to remove any low molecular polymers.

Table S1. Parameters of arm polymers and CCS polymers synthesized by emulsion and dispersion polymerization.

	M_n (NMR)[a]	M_n (GPC)[b]	M_w/M_n (GPC)[b]	Star Polymers by Emulsion Polymerization[c]					Star Polymers by Dispersion Polymerization[d]				
				time (h)	yield (%)[e]	M_n (GPC)[b]	M_w/M_n (GPC)[b]	D_h (nm)[f]	time (h)	yield (%)[e]	M_n (GPC)[b]	M_w/M_n (GPC)[b]	D_h (nm)[f]
PDMA	*5*	*8*	*1.10*	*1*	*92*	*117*	*1.06*	*14*	*2*	*94*	*83*	*1.09*	*11*
PPEGMA	*11*	*17*	*1.10*	*2*	*84*	*140*	*1.09*	*22*	*1*	*86*	*90*	*1.12*	*14*
P(MEA-co-PEGA)	*14*	*20*	*1.09*	*1*	*85*	*135*	*1.07*	*11*					

[a]Determined by ^{1}H NMR. [b]Determined by GPC (DMF, PMMA standard). [c]Polymerization conditions: [arm polymer] = 10% w/v, molar ratio of arm polymer:BA:PEGDA:V-50 (KPS/NaAs) = 1:10:5:0.04 (0.1/0.1), V-50 for PDMA and PPEGMA at 70 °C, KPS/NaAs for P(MEA-*co*-PEGA) at 35 °C. [d]Polymerization conditions: [arm polymer] = 10% w/v, molar ratio of arm polymer:NIPAM:MBA:V-50 = 1:10:5:0.04, at 70 °C. [e]Star yield determined by GPC peak area: $A_{\text{star polymer}}/(A_{\text{star polymer}} + A_{\text{low molecular weight polymer}})$. [f]Hydrodynamic diameter determined by DLS.

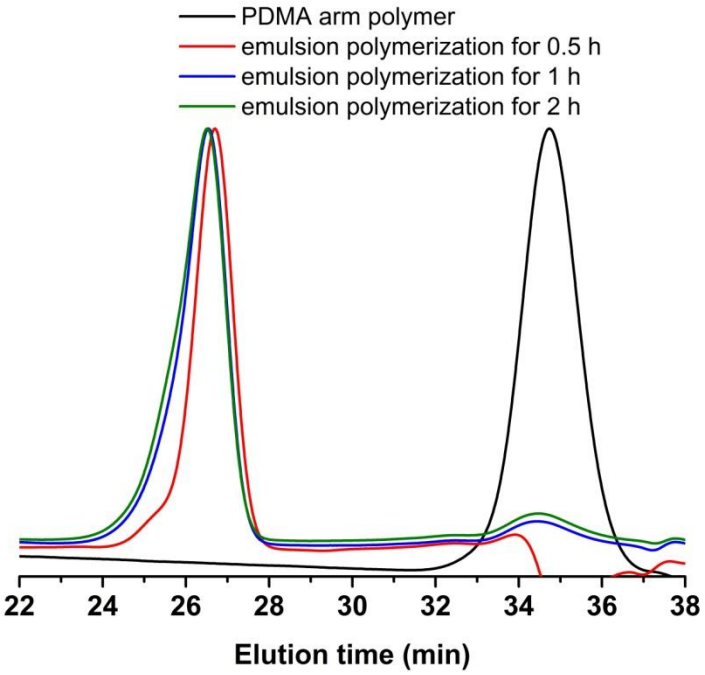

Figure S4. GPC chromatograms of PDMA arm polymer and PDMA CCS polymers synthesized by emulsion polymerization at different time. PDMA:BA:PEGDA:V-50 = 1:10:5:0.04, 70 °C, [PDMA] = 10% w/v.

Table S2. Parameters of PDMA arm polymer and PDMA CCS polymers synthesized by emulsion polymerization at different time. PDMA:BA:PEGDA:V-50 = 1:10:5:0.04, 70 ℃, [PDMA] = 10% w/v.

Time	M_n	M_w/M_n
PDMA arm	*8 000*	*1.10*
0.5 h	*106 000*	*1.04*
1 h	*117 000*	*1.06*
2 h	*1199 000*	*1.06*

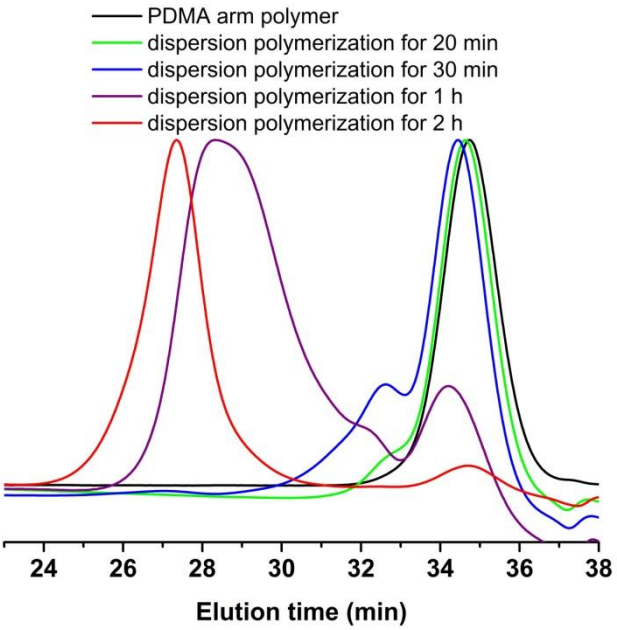

Figure S5. GPC chromatograms of PDMA arm polymer and PDMA CCS polymers synthesized by dispersion polymerization at different time. PDMA:NIPAM:MBA:V-50 = 1:10:5:0.04, 70 °C, [PDMA] = 10% w/v.

Table S3. Parameters of PDMA arm polymer and PDMA CCS polymers synthesized by dispersion polymerization at different time. PDMA:NIPAM:MBA:V-50 = 1:10:5:0.04, 70 °C, [PDMA] = 10% w/v.

Time	M_n	M_w/M_n
PDMA arm	*8 000*	*1.10*
20 min	*9 000*	*1.13*
30 min	*10 000*	*1.27*
1 h	*49 000*	*1.14*
2 h	*83 000*	*1.09*

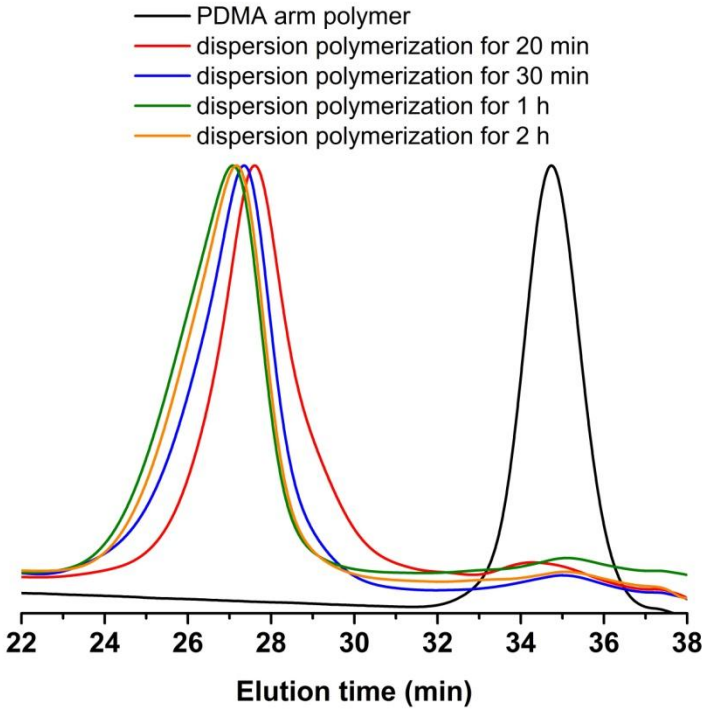

Figure S6. GPC chromatograms of PDMA arm polymer and PDMA CCS polymers synthesized by dispersion polymerization at different time. PDMA:NIPAM:MBA:V-50 = 1:10:7:0.04, 70 °C, [PDMA] = 10% w/v.

Table S4. Parameters of PDMA arm polymer and PDMA CCS polymers synthesized by dispersion polymerization at different time. PDMA:NIPAM:MBA:V-50 = 1:10:7:0.04, 70 °C, [PDMA] = 10% w/v.

Time	M_n	M_w/M_n
PDMA arm	*8 000*	*1.10*
20 min	*73 000*	*1.13*
30 min	*89 000*	*1.16*
1 h	*101 000*	*1.14*
2 h	*96 000*	*1.12*

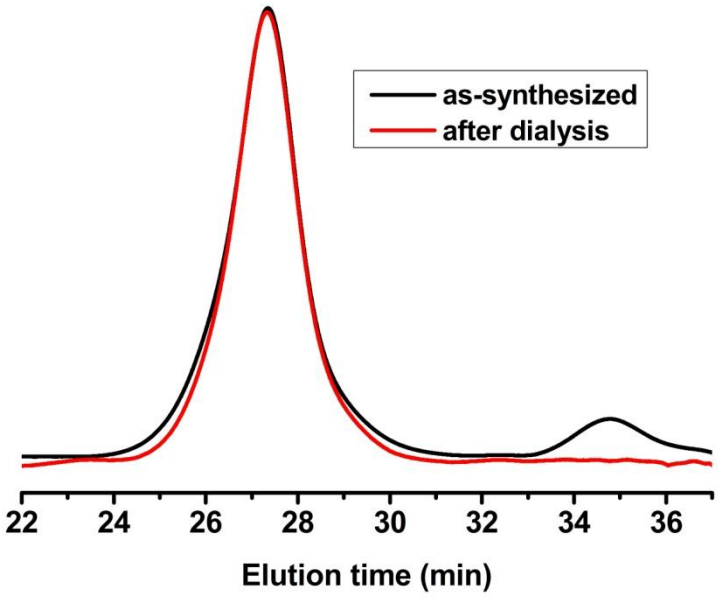

Figure S7. GPC chromatograms of as-synthesized PDMA CCS polymer by dispersion polymerization and the same star polymer after extensive purification by dialysis.

Synthesis of fluorescein-labeled star polymers. Fluorescein-labeled star polymer was synthesized by tandem aminolysis of the CTA in the star polymer and thiol-ene addition of the generated thiol with fluorescein *o*-acrylate.[3, 4] In detail, 0.1 g of the PDMA star polymer synthesized by dispersion polymerization (M_n = 83 000 , M_w/M_n =1.09, D_h = 11 nm, containing approximately 14 μmol of trithiocarbonate) was first dissolved in 1 mL of DMF. To this solution

were added fluorescein *o*-acrylate (27.8 mg, 70 μmol) and triethylamine (9.8 μL, 70 μmol). After the solution was degassed for 30 min, degassed butylamine was injected (50 μL, 2.8 M in DMF, 140 μmol). The reaction was allowed to stir for 1 d at room temperature under protection of nitrogen. Purification was carried out by first precipitation into ether and then by dialysis against water using cellulose membrane (MWCO 50 000) for 10 d. The dialysis process was monitored by fluorescence spectroscopy until no fluorescence was observed from the dialysis solution. The fluorecein-labeled star polymer was isolated by freeze-drying.

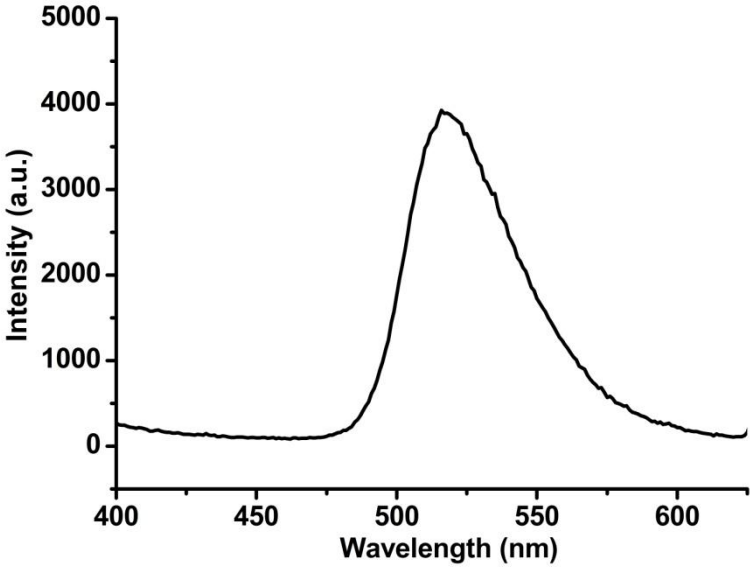

Figure S8. Fluorescence spectrum of fluorescein-labeled CCS polymer in water.

Control experiments for star polymer synthesis in DMF homogeneous solutions. The concentration of PDMA, monomer and cross-linker in DMF homogeneous solution polymerization was the same as in emulsion/dispersion polymerization, and a lypophilic initiator AIBN of higher concentration was used in DMF solution polymerization instead of V-50 in emulsion/dispersion polymerization.

(1) Control experiment with BA and PEGDA. PDMA (0.40 g，0.079 mmol), BA (0.101 g, 0.79 mmol), and PEGDA (0.102 g, 0.395 mmol) were dissolved in DMF (4 mL). The solution was degassed with nitrogen at 0 °C for 30 min before immersion into a preheated oil bath at 70 °C. After the temperature was stabilized, a degassed DMF solution of AIBN (100 μL, 1.3 mg, 0.0079 mmol) was injected via a microsyringe. The polymerization was allowed to continue under protection of nitrogen. Aliquots were withdrawn at predetermined time intervals for GPC measurement. The conversion of BA and PEGDA was calculated to be 92% by ^{1}H NMR at the end of polymerization.

(2) Control experiment with NIPAM and MBA. PDMA (0.40 g，0.079 mmol), NIPAM (89.4 mg, 0.79 mmol), and MBA (60.9 mg, 0.40 mmol) were dissolved in DMF (4 mL). The solution was degassed with nitrogen at 0 ℃ for 30 min before immersion into a preheated oil bath at 70 °C. After the temperature was stabilized, a degassed DMF solution of AIBN (100 μL, 1.3 mg, 0.0079 mmol) was injected via a microsyringe. The polymerization was allowed to continue under protection of nitrogen. Aliquots were withdrawn at predetermined time intervals for GPC measurement. The conversion of BA and PEGDA was calculated to be 94% by ^{1}H NMR.

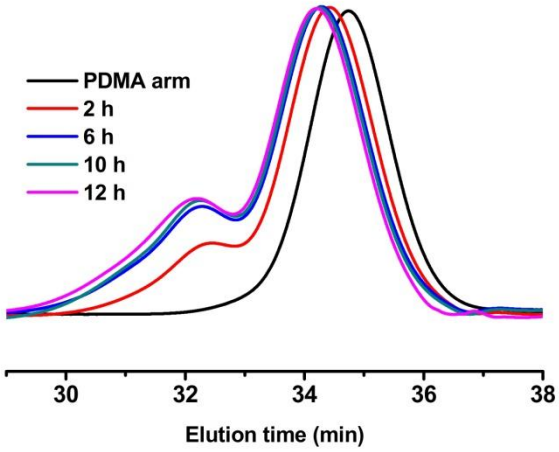

Figure S9. GPC chromatograms of attempted star polymer synthesis in DMF with BA and PEGDA at different polymerization time. PDMA:BA:PEGDA:AIBN = 1:10:5:0.1, 70 °C, [PDMA] = 10% w/v.

Table S5. Results of attempted star synthesis with BA and PEGDA in DMF.

polymerization time	M_n	M_w/M_n
PDMA arm	*8 000*	*1.10*
2 h	*10 000*	*1.19*
6 h	*11 000*	*1.23*
10 h	*11 200*	*1.24*
12 h	*11 700*	*1.23*

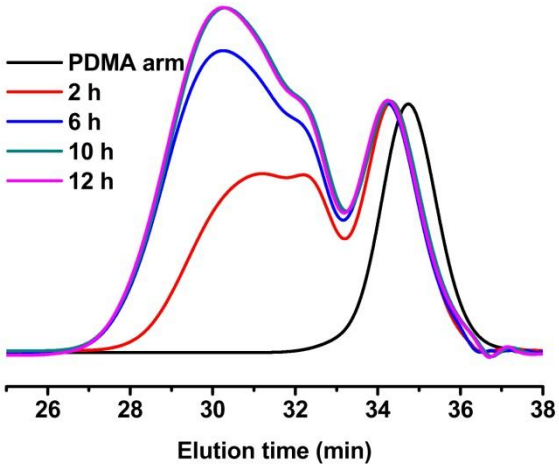

Figure S10. GPC chromatograms of attempted star polymer synthesis in DMF with NIPAM and MBA at different polymerization time. PDMA:NIPAM:MBA:AIBN = 1:10:5:0.1, 70 °C, [PDMA] = 10% w/v.

Table S6. Results of attempted star synthesis with NIPAM and MBA in DMF.

polymerization time	M_n	M_w/M_n
0 h (PDMA)	*8 000*	*1.10*
2 h	*15 000*	*1.44*
6 h	*19 000*	*1.50*
10 h	*19 000*	*1.53*
12 h	*19 000*	*1.53*

Preparation of emulsions stabilized by CCS polymers.

Emulsions were prepared using a Polytron PT 1200E homogenizer (7 mm head) at 25 000 rpm for 1 min at room temperature. The total volume of the emulsions was 4 mL and the volume ratio of toluene to CCS polymer aqueous solution was 4:6. The concentration of PDMA CCS polymers synthesized by dispersion polymerization (D_h = 12 nm) was either 0.02 wt% or 0.2 wt%.

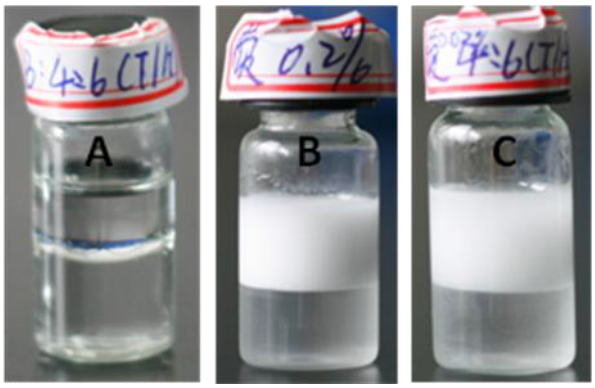

Figure S11. (A) A mixture of toluene and aqueous solution before emulsification; (B) an emulsion of toluene with 0.2 wt% PDMA CCS polymer aqueous solution after storage for 1 month; and (C) an emulsion of toluene with 0.02 wt% PDMA CCS polymer aqueous solution after storage for 1 month. The volume ratio of toluene:water as 4:6. PDMA CCS polymer was synthesized by dispersion polymerization, D_h = 12 nm.

Preparation of polymer particles by emulsion templating.

The emulsions for polymer particle templating consisted of a polystyrene benzene solution (5% w/v), dyed with nile red, and an aqueous solution of PDMA CCS polymer synthesized by dispersion polymerization (D_h = 12 nm, 0.2 wt%). The volume ratio of the oil phase to the aqueous phase was 4:6. Emulsions were prepared with a Polytron PT 1200E homogenizer (5 mm head) at 25 000 rpm for 1.5 min at room temperature. Samples for imaging were obtained by casting the emulsion onto a cover glass for confocal imaging to evaporate the solvents.

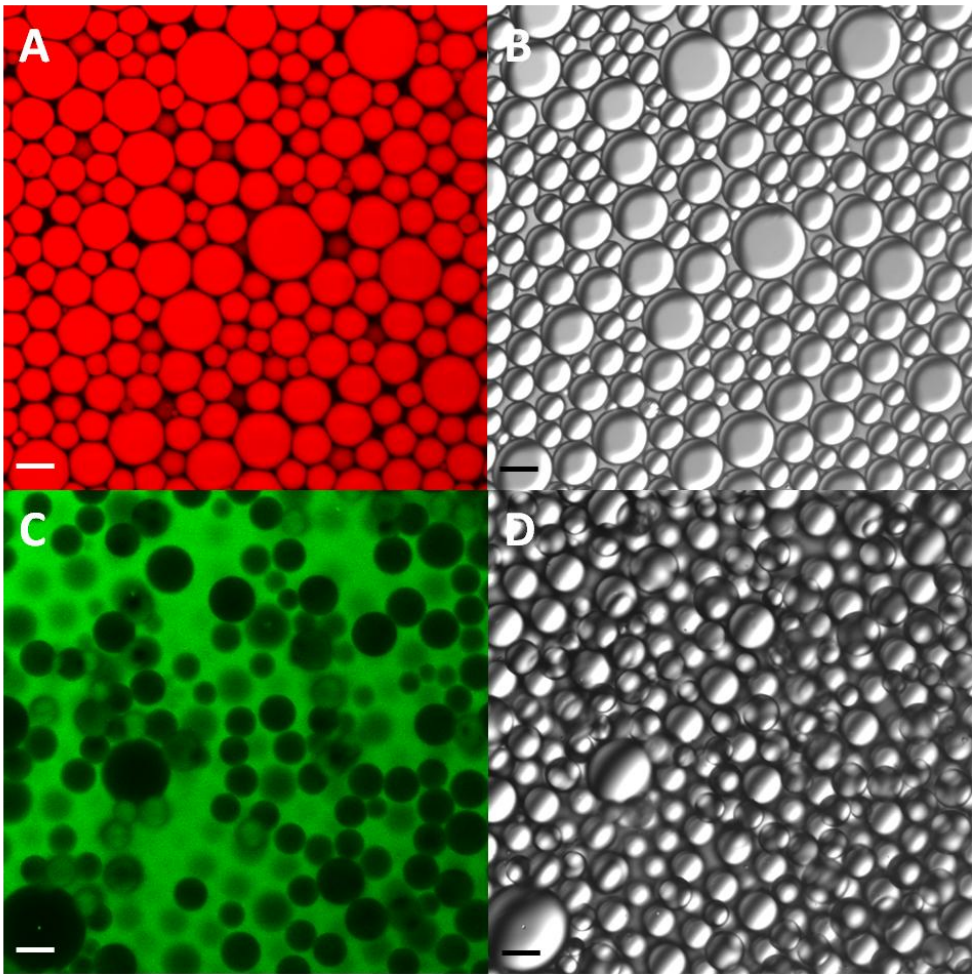

Figure S12. (A) Confocal image of an emulsion of 5% w/v polystyrene benzene solution dyed with nile red in 0.2 wt% PDMA CCS polymer aqueous solution; (B) bright field image of A; (C) confocal image of an emulsion of 5% w/v polystyrene benzene solution in 0.2 wt% PDMA fluorescein-labeled CCS polymer aqueous solution; and (D) bright field image of C. Excitation wavelength for nile red and fluorescein was 515 nm and 488 nm, respectively. Scale bar is 20 micron.

References

1. *J. Ferreira, J. Syrett, M. Whittaker, D. Haddleton, T. P. Davis and C. Boyer, Polym. Chem., 2011,* ***2****, 1671-1677.*
2. *W. Li and K. Matyjaszewski, J. Am. Chem. Soc., 2009,* ***131****, 10378-10379.*
3. *J. A. Syrett, D. M. Haddleton, M. R. Whittaker, T. P. Davis and C. Boyer, Chem. Commun., 2011,* ***47****, 1449-1451.*
4. *Z. S. An, W. Tang, M. H. Wu, Z. Jiao and G. D. Stucky, Chem. Commun., 2008, 6501-6503.*