

## SUPPORTING INFORMATION:

# The effect of surface-active statistical copolymers in low-energy miniemulsion and RAFT polymerization

Manon Rolland,<sup>a</sup> Eric Dufresne,<sup>a, b</sup> Nghia P. Truong,<sup>a, c\*</sup> Athina Anastasaki<sup>a,\*</sup>

<sup>a</sup>Laboratory of Polymeric Materials, Department of Materials, ETH Zürich, Vladimir-Prelog-Weg 5, 8093 Zürich, Switzerland.

<sup>b</sup>Laboratory of Soft and Living Materials, Department of Materials, ETH Zürich, Vladimir-Prelog-Weg 5, 8093 Zürich, Switzerland.

<sup>c</sup>Monash Institute of Pharmaceutical Sciences, Monash University, 399 Royal Parade, Parkville, VIC 3152, Australia.

## Materials

4-Cyano-4-[(ethylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (ECT, 95%) was procured from ABCR. Styrene (STY, 99%), 2,2'-azobis(2-methylpropionitrile) (AIBN), di(ethylene glycol) methyl ether methacrylate (DEGMA, 95%), 2-hydroxypropyl methacrylamide (HPMA, 99%), diethyl ether (> 99.8%), triethylene glycol methyl ether methacrylate (TEGMA, 93%), poly(ethylene glycol) methyl ether methacrylate (PEGMA,  $M_n=300$ ), methacrylamide (MAAm, 98%), sodium dodecyl sulfate (SDS), 4,4'-azobis(4-cyanovaleric acid) (ACPA) were obtained from Sigma Aldrich. 2-Hydroxyethyl methacrylate (HEMA, 97%) was bought from ACROS. Dimethyl sulfoxide (DMSO, 95%) was bought from Chemie Brunschwig. Petroleum ether, (40 - 60°C analysis, < 2% Hexane) was obtained from ProLabo. Acetone was acquired from Thommen-Furler. Acetone-d<sub>6</sub> (99.8%), chloroform-d (CDCl<sub>3</sub>, 99.8%), dimethyl sulfoxide-d<sub>6</sub> (DMSO-d<sub>6</sub>, 99.8%), deuterium oxide-<sup>18</sup>O (99%) were purchased from ResaChem. The AIBN was recrystallized in methanol before use. A membrane with molecular weight cut-off of 3.5 kDa was utilized for dialysis. Deionized water was utilized for all miniemulsion experiments. All monomers were purified through basic alumina before being used. Other chemicals were used as received.

## Instrumentations

**Manual shaking** was utilized to form all miniemulsion.

**<sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H-NMR)** spectra were measured in DMSO-d<sub>6</sub>, Deuterium oxide-<sup>18</sup>O or a mixture of Acetone-d<sub>6</sub> : Chloroform-d (5:1, v/v) on a Bruker Avance-300 or 400 spectrometer. Chemical shifts are given in ppm and are referenced to residual solvent proton signals.

**Size-exclusion chromatography (SEC)** was measured on Shimadzu equipment with a CBM-20A system controller, a SIL-20A automatic injector, an LC-20AD pump (flow rate at 1 mL min<sup>-1</sup>), a 10.0 μm bead-size guard column (50 × 7.5 mm) followed by three KF-805L columns (300 × 8 mm, bead size: 10 μm, pore size maximum: 5000 Å), an SPD-20A ultraviolet detector, and a RID-20A differential refractive

index detector. Column temperature was maintained at 40 °C using a CTO-20A oven. *N,N*-dimethylacetamide was used as eluent (HPLC grade, Acros, with 0.03% w/v LiBr). Molecular weights were determined according to calibration with commercial narrow molecular weight distribution poly(methyl methacrylate) standards with molecular weights ranging from 5000 to  $1.5 \times 10^6$  g mol<sup>-1</sup> (Agilent Technology). Before injection, all samples were passed through 0.45 μm filters and water was removed by drying sample under air (only for miniemulsion experiments).

**Transmission electron microscopy (TEM)** images were taken using Jeol JEM 1400 (High Voltage: 80 kV, 120 kV, Emitter: LaB6 crystal) transmission electron microscope. TEM samples were prepared as follows: 2 μL of latex were diluted in 400 μL of deionized water and a droplet was put onto a carbon film grid (300 Mesh, Cu, Electron Microscopy Science), after which samples were allowed to dry under ambient atmosphere and temperature.

**Dynamic light scattering (DLS)** measurements were carried out using Malvern Zetasizer Advance Series-Pro (Red Label, 10 mW, 633 nm). The sample refractive index (RI) was set at 1.59 for styrene. The dispersant viscosity and RI were set to 0.89 Ns m<sup>-2</sup>. To determine particle size, all measurements were carried out without dilution.

**Inverse Pendant** measurements were undertaken with an optical setup comprising a light source (3.5" × 6" White, LED Backlight (Edmundoptics)), a lens (0.5 × -1.0 × VariMagTL™ Telecentric Lens (Edmundoptics)) and a camera (CMOS Camera from Thorlabs, DCC3240M – High-Sensitivity USB 3.0, 1280 × 1024, Global Shutter, Monochrome Sensor).

## Procedures

### 1.1- Standard synthesis of P(HPMA-*co*-DEGMA)-SC(=S)SC<sub>2</sub>H<sub>5</sub> (A0, A1, A2, A3 and A4 - 0, 10, 20, 30 and 43 % HPMA) utilized as macro-chain transfer agent (macro-CTA) - Model example: A2 (20 % HPMA)

DEGMA (2 g, 0.0106 mol, 40 equiv.), ECT (70 mg, 0.00027 mol, 1 equiv.), HPMA (0.76 g, 0.0053 mol, 20 equiv.), and ACPA (7 mg, 0.00002 mol, 0.1 equiv.) were dissolved in DMSO (10 mL) and placed in a 25 mL round bottom flask. After closing the flask with a septum, the solution was degassed with nitrogen for one hour and placed in a preheated oil bath (70 °C) at 300 rpm. After 8.5 hours, the reaction was cooled down in an ice bath, exposed to air and sampled to determine the DEGMA and HPMA conversion by <sup>1</sup>H-NMR. The solution was then dialyzed against acetone (500 mL) for 1 hour to remove DMSO from the solution. Then, the solution was precipitated in a mixture of petroleum ether: diethyl ether (1:1, v/v), isolated by centrifugation, and re-dissolved in acetone. This step was repeated three times to remove unreacted monomers. The product was dried in a vacuum oven for 48 h and analyzed by SEC and <sup>1</sup>H-NMR. Conversion of DEGMA was calculated by the integral area of a peak at 6.0 ppm ( $I_{6.0}$ ) and a peak in the range 3.8–4.3 ( $I_{3.8-4.3}$ ) using the following equation: Conversion of DEGMA =  $100 \times [1 - (2 \times I_{6.0} / I_{3.8-4.3})]$ . Conversion of HPMA was calculated by the integral area of a peak at 5.3 ppm ( $I_{5.3}$ ) and a peak in the range 4.6–4.7 ( $I_{4.5-4.8}$ ) using the following equation: Conversion of HPMA =  $100 \times [1 - (I_{5.3} / I_{4.5-4.8})]$ .

For A0 (0 % HPMA), A1(10 % HPMA), A3(30 % HPMA), and A4(43 % HPMA), the same standard procedure was followed by only modifying the molar ratio between ECT, DEGMA and HPMA and by monitoring the reaction time and conversion by <sup>1</sup>H-NMR . For A0 the molar ratio was maintained at [ECT]: [DEGMA] : [HPMA]= 1: 40: 0 (5h), for A1 at [ECT]: [DEGMA] : [HPMA]= 1: 40: 9 (8h30), for A3 at [ECT]: [DEGMA] : [HPMA]= 1: 40: 40 (7h10) and for A4 at [ECT]: [DEGMA] : [HPMA]= 1: 40: 60 (7h). It is noted that for polymer A0, the polymer was purified by precipitating in only petroleum benzene instead of the mixture with diethyl ether.

## **1.2- Standard procedure for the formation of styrene miniemulsion by simple hand shaking (A0-A6, B0-B4, C0, D0, E0 and F0-F2) and study of the miniemulsion stability - Mass ratio**

A macro-CTA (25 mg) was placed in a 2 mL glass vial and was dissolved with an aqueous solution of SDS (0.25 mg of SDS in 2 mL of deionized water). Then, styrene (35  $\mu$ L) was added on the top of the SDS and macro-CTA solution. The vial was capped and then shaken by hand for 10 seconds. The resulting latexes were photographed just after shaking and subsequently analyzed by DLS to determine particle size and polydispersity. Latexes formed with A0, A1 and A2 were then placed on the bench and photographed after 2 and 8 days to monitor phase separation.

## **1.3- Standard procedure for interfacial tension measurement (IFT) using inverse pendant measurements (A0-A6, B0-B4, C0, D0, E0 and F0-F2)**

Aqueous solution of macro-CTA (25 mg / 2 ml) were prepared and placed in a quartz cuvette. Then, a stabilized styrene droplet was formed inside the solution and illuminated by an external light source. For each measurement of the interfacial tension, a series of ten different droplets were imaged through telecentric lens and analyzed through MATLAB codes<sup>1</sup> where the droplets contour is detected and fitted to its theoretical shape. It is noted that for the inverse pendant drop method, pictures were taken upside down and flipped before analyzing with the MATLAB code. Also for macro-CTAs A0, B0 and E0 the mixture was cooled down in the fridge prior the measurement to avoid emulsification as their  $T_{cp}$  is very close from room temperature.

## **1.4- Evaluation of macro-CTAs (A0-A4) solubility in the styrene and water phase**

The macro-CTAs (25 mg) were dissolved in 1 mL of styrene and 1 mL of water separately. Then, a digital picture was taken to show the macro-CTAs immediate solubility. For the remaining vials showing lower

solubility in either phases, the vials were vortexed until solubilized. It is noted that for the mixture of water + A0, it required to cooled down in the fridge to be fully solubilized and that for the mixture of A4 + styrene, the macro-CTA did not solubilized.

### **1.5- Standard procedure for the formation of styrene miniemulsion by simple hand shaking (A0-A4) - Molar Ratio**

Procedure 1.2 was followed by only modifying the mass of macro-CTA from 19 mg (A0), 22.4 mg (A1), 25 mg (A2), 30.2 mg (A3) to 36.7 mg (A4) to maintain a molar ratio constant of [macro-CTA] : [STY] : [SDS] = 1 : 108 : 0.3.

### **1.6- Synthesis of P(HPMA-co-DEGMA)-SC(=S)SC<sub>2</sub>H<sub>5</sub> (B0, B1, B2, B3 and B4 - 0, 10, 18, 30 and 40 % HPMA) utilized as macro-chain transfer agent (macro-CTA)- $M_n$ , copolymer constant**

For the polymerization of B0-B4, procedure 1.1 was followed by only modifying the molar ratio between ECT, DEGMA and HPMA and by monitoring the reaction time and conversion by <sup>1</sup>H-NMR. For B0, the molar ratio was maintained to [ECT]: [DEGMA] : [HPMA]= 1: 50: 0 (5.45 h), for B1 to [ECT]: [DEGMA] : [HPMA]= 1: 40: 9 (8h30), for B2 to [ECT]: [DEGMA] : [HPMA]= 1: 40: 20 (7.5 h), for B3 to [ECT]: [DEGMA] : [HPMA]= 1: 30: 30 (9 h), for B4 to [ECT]: [DEGMA] : [HPMA]= 1: 30: 45 (7 h). It is noted that for polymer B0, the random copolymer was purified by precipitating in only petroleum benzene instead of the 1: 1 mixture with diethyl ether.

### **1.7- RAFT miniemulsion *in situ* <sup>1</sup>H-NMR kinetic study of styrene for macro-CTAs A2 - Mass ratio**

The macro-CTA (6.25 mg) was added in an NMR tube and was dissolved with an aqueous solution of SDS (0.06 mg of SDS in 0.5 mL of deuterium oxide). The NMR tube was then sealed and degassed for 15 minutes. In parallel, a degas stock solution was prepared containing 2 mg of AIBN dissolved in 1166  $\mu$ L of styrene. From this degas stock solution, 8.75  $\mu$ L (0.015 mg of AIBN) was transferred into the

NMR tube under a nitrogen blanket. The tube was, then, shaken for 10 seconds by hand at room temperature. Next, the tube was placed in a preheated 400 MHz solid-state NMR spectrometer (Bruker Avance III 400 MHz triple-resonance spectrometer) for 2 hours and the polymerization was monitored *in situ* by  $^1\text{H-NMR}$ . Conversion was calculated by the integral area of a peak at 5.8 ppm ( $I_{5.8}$ ) and a peak in the range of 6.5 to 7.7 ppm ( $I_{6.5-7.7}$ ) using the following equation: Conversion of Styrene =  $100 \times (1 - [(5 \times I_{5.8}) / (I_{6.5-7.7} - I_{5.8})])$ .

### **1.8- RAFT miniemulsion polymerization of styrene for macro-CTAs A0-A6, B0-B4 and for F0 - Mass ratio**

The macro-CTA (25 mg) was added in a 2 mL glass vial and was dissolved with an aqueous solution of SDS (0.25 mg of SDS in 2 mL of deionized water). In parallel, a stock solution was prepared containing 2 mg of AIBN dissolved in 1166  $\mu\text{L}$  of styrene. From this stock solution, 35  $\mu\text{L}$  (0.06 mg of AIBN) was transferred on the top of the SDS and macro-CTA solution. The vial was closed with a cap and shaken for 10 seconds by hand at room temperature. Then, the vial was placed in a preheated oven (70  $^{\circ}\text{C}$ ). Polymerization was stopped, after 6 hours (unless specified otherwise), by exposing the latex to air. Aliquots of the latex were analyzed by  $^1\text{H-NMR}$  and SEC to determine conversion, molecular weight and dispersity. Conversion was calculated by the integral area of a peak at 5.8 ppm ( $I_{5.8}$ ) and a peak in the range of 6.5 to 7.7 ppm ( $I_{6.5-7.7}$ ) using the following equation: Conversion of Styrene =  $100 \times (1 - [(5 \times I_{5.8}) / (I_{6.5-7.7} - I_{5.8})])$ . In parallel, the hot latex (70  $^{\circ}\text{C}$ ) was analyzed by DLS to determine the particle size and polydispersity.

### **1.9- RAFT miniemulsion polymerization of styrene for macro-CTAs A0 to A4 - Molar ratio**

Procedure 1.7 was followed by keeping the molar ratio between [macro-CTA] : [STY] : [AIBN] : [SDS] to 1 : 108 : 0.1 : 0.3 and thus, varying the mass of macro-CTA as followed : 19 mg for A0, 22.4 mg for A1, 25 mg for A2, 30.2 mg for A3 and 36.7 mg for A4.

**1.10- Synthesis of P(HPMA-*co*-DEGMA)-SC(=S)SC<sub>2</sub>H<sub>5</sub>, A5 and A6, utilized as macro-chain transfer agent (macro-CTA) -  $M_n$ , copolymer vary while the % of HPMA is kept constant to ~ 20 %.**

Procedure 1.1 was followed by only modifying the molar ratio between ECT, DEGMA and HPMA and monitoring the conversion and reaction time and conversion by <sup>1</sup>H-NMR. For A5, the molar ratio was maintained to [ECT]: [DEGMA] : [HPMA]= 1: 20: 10 (8h), and for A6 to [ECT]: [DEGMA] : [HPMA]= 1: 80: 40 (8h).

**1.11- Synthesis of P(TEGMA-*co*-DEGMA)-SC(=S)SC<sub>2</sub>H<sub>5</sub> utilized as macro-CTA – C0 (19 % TEGMA)**

DEGMA (2 g, 0.010 mol, 50 equiv.), ECT (56 mg, 0.0002 mol, 1 equiv.), TEGMA (0.59 g, 0.0026 mol, 12 equiv.), and ACPA (5.61mg, 0.00002 mol, 0.1 equiv.) were dissolved in dioxane (10 mL) and placed in a 25 mL round bottom flask. After closing the flask with a septum, the solution was degassed with nitrogen for one hour and placed in a preheated oil bath (70 °C) at 300 rpm. After 8.5 hours, the reaction was cooled down in an ice bath, exposed to air and sampled to determine the DEGMA and TEGMA conversion by <sup>1</sup>H-NMR. The solution was then dialyzed against acetone (500 mL) for 1 hour to remove dioxane from the solution. Then, the solution was precipitated in petroleum ether, isolated by centrifugation, and re-dissolved in acetone. This step was repeated three times to remove unreacted monomers. The product was dried in a vacuum oven for 48 h and analyzed by SEC and <sup>1</sup>H-NMR. Conversion of DEGMA and TEGMA were calculated by the integral area of a peak at 6.0 ppm ( $I_{6.0}$ ) and a peak in the range 3.8–4.3 ( $I_{3.9-4.3}$ ) using the following equation: Conversion =  $100 \times [1 - (2 \times I_{6.0} / I_{3.9-4.3})]$ .

**1.12- Synthesis of P(PEGMA-*co*-DEGMA)-SC(=S)SC<sub>2</sub>H<sub>5</sub> utilized as macro-CTA – D0 (19 % PEGMA)**



DEGMA (2 g, 0.010 mol, 50 equiv.), ECT (56 mg, 0.0002 mol, 1 equiv.), PEGMA (0.76 g, 0.0026 mol, 12 equiv.), and ACPA (5.61mg, 0.00002 mol, 0.1 equiv.) were dissolved in dioxane (10 mL) and placed in a 25 mL round bottom flask. After closing the flask with a septum, the solution was degassed with nitrogen for one hour and placed in a preheated oil bath (70 °C) at 300 rpm. After 8 hours, the reaction was cooled down in an ice bath, exposed to air and sampled to determine the DEGMA and PEGMA conversion by <sup>1</sup>H-NMR. The solution was then dialyzed against acetone (500 mL) for 1 hour to remove dioxane from the solution. Then, the solution was precipitated in petroleum ether, isolated by centrifugation, and re-dissolved in acetone. This step was repeated three times to remove unreacted monomers. The product was dried in a vacuum oven for 48 h and analyzed by SEC and <sup>1</sup>H-NMR. Conversion of DEGMA and PEGMA were calculated by the integral area of a peak at 6.0 ppm ( $I_{6.0}$ ) and a peak in the range 3.8–4.3 ( $I_{3.9-4.3}$ ) using the following equation: Conversion =  $100 \times [1 - (2 \times I_{6.0} / I_{3.9-4.3})]$ .

### **1.13- Synthesis of P(HEMA-*co*-DEGMA)-SC(=S)SC<sub>2</sub>H<sub>5</sub> utilized as macro-CTA – E0 (19 % HEMA)**

DEGMA (2 g, 0.010 mol, 50 equiv.), ECT (56 mg, 0.0002 mol, 1 equiv.), HEMA (0.44 g, 0.0034 mol, 16 equiv.), and ACPA (5.61mg, 0.00002 mol, 0.1 equiv.) were dissolved in DMSO (10 mL) and placed in a 25 mL round bottom flask. After closing the flask with a septum, the solution was degassed with nitrogen for one hour and placed in a preheated oil bath (70 °C) at 300 rpm. After 6 hours, the reaction was cooled down in an ice bath, exposed to air. The solution was then dialyzed against acetone (500 mL) for 1 hour to remove DMSO from the solution. Then, the solution was precipitated in petroleum ether: diethyl ether (1:1, v/ v), isolated by centrifugation, and re-dissolved in acetone. This step was repeated three times to remove unreacted monomers. The product was dried in a vacuum oven for 48 h and analyzed by SEC and <sup>1</sup>H-NMR. The ratio of DEGMA and HEMA was calculated by the integral area of a peak at 4.7 ppm ( $I_{4.7}$ ) and a peak in the range 3.8–4.3 ( $I_{3.8-4.3}$ ) using the following equation: Ratio HEMA/DEGMA =  $100 \times [I_{4.7} / (I_{3.8-4.3} - 4I_{4.7}) + I_{4.7}]$ .

#### 1.14- Synthesis of P(MAAm-co-DEGMA)-SC(=S)SC<sub>2</sub>H<sub>5</sub> utilized as macro-CTA – F0 (23 % MAAm), F1(14 % MAAm), and F2 (35 % MAAm)

DEGMA (2 g, 0.010 mol, 60 equiv.), ECT (46 mg, 0.0002 mol, 1 equiv.), MAAm (0.71 g, 0.0083 mol, 47 equiv.), and ACPA (4.67 mg, 0.00002 mol, 0.1 equiv.) were dissolved in DMSO (10 mL) and placed in a 25 mL round bottom flask. After closing the flask with a septum, the solution was degassed with nitrogen for one hour and placed in a preheated oil bath (70 °C) at 300 rpm. After 7 hours, the reaction was cooled down in an ice bath, exposed to air. The solution was then dialyzed against acetone (500 mL) for 1 hour to remove DMSO from the solution. Then, the solution was precipitated in petroleum ether: diethyl ether (1:1, v/ v), isolated by centrifugation, and re-dissolved in acetone. This step was repeated three times to remove unreacted monomers. The product was dried in a vacuum oven for 48 h and analyzed by SEC and <sup>1</sup>H-NMR. Conversion of DEGMA and MAAm were calculated by the integral area of a peak at 6.0 ppm ( $I_{6.0}$ ) and a peak in the range 3.8–4.3 ( $I_{3.8-4.3}$ ) using the following equation: Conversion of DEGMA =  $100 \times [1 - (2 \times I_{6.0} / I_{3.8-4.3})]$ . Conversion of MAAm was calculated by the integral area of a peak at 5.3 ppm ( $I_{5.3}$ ) and a peak in the range 4.6–4.7 ( $I_{4.6-4.7}$ ) using the following equation: Conversion of MAAm =  $100 \times [1 - (2I_{5.3} / I_{4.6-4.7})]$ .

For F1 (14 % MAAm) and F2 (35 % MAAm), the same procedure was followed by only modifying the molar ratio between ECT, DEGMA and MAAm and monitoring the polymerization by <sup>1</sup>H-NMR. For F1 the molar ratio was maintained at [ECT]: [DEGMA] : [MAAm]= 1: 40: 10 (6 h30) and, for F2 at [ECT]: [DEGMA] : [MAAm]= 1: 40: 30 (7h).

#### 1.15- Extraction experiment for macro-CTAs C0,D0,E0 and F0

The macro-CTA (25 mg) was dissolved in the water phase (1 mL) and top up with styrene (0.5 mL). Then, the solution was shaken for 10 seconds by hand, followed by centrifugation for 30 minutes at 8000 rpm to observe phase separation. Subsequently, the top layer and bottom layer (50 µL) were dissolved in 1 mL of DMAC and analyzed by SEC to quantify how much macro-CTA were dissolved in each phase.

### **1.16- RAFT miniemulsion polymerization of styrene with P(MAAm-*co*-DEGMA)-SC(=S)SC<sub>2</sub>H<sub>5</sub> (F0) as macro-CTA resulting in nanoparticles with different morphologies**

The macro-CTA (F0, 25 mg) was added in a 2 mL glass vial and was dissolved with an aqueous solution of SDS (0.25 mg of SDS in 2 mL of deionized water). In parallel, a stock solution was prepared containing 2 mg of AIBN dissolved in 1166  $\mu$ L of styrene. From this stock solution, 35  $\mu$ L (0.06 mg of AIBN) was transferred on the top of the SDS and macro-CTA solution. The vial was closed with a cap and shaken for 10 seconds by hand at room temperature. Then, the vial was placed in a preheated oven (70 °C). Polymerization was stopped, after 6 or 7 hours, by exposing the latex to air. Aliquots of the latex were analyzed by <sup>1</sup>H-NMR and SEC to determine conversion, molecular weight and dispersity. Conversion was calculated by the integral area of a peak at 5.8 ppm ( $I_{5.8}$ ) and a peak in the range of 6.5 to 7.7 ppm ( $I_{6.5-7.7}$ ) using the following equation: Conversion of Styrene =  $100 \times (1 - [(5 \times I_{5.8}) / (I_{6.5-7.7} - I_{5.8})])$ . In parallel, the hot latex (70 °C) was analyzed by DLS to determine the particle size and polydispersity. After polymerization and cooling down to room temperature, 100  $\mu$ L of latex was transferred in a 1.5 mL vials together with a small amount of toluene (10  $\mu$ L) to induce the shape transformation from emulsion spheres to vesicles. To obtain worms balls and worms like morphologies, other DP's for the polystyrene blocks were targeted by simply varying the amount of styrene to 10  $\mu$ L (DP(STY)=38), 14  $\mu$ L (DP(STY)=54) and adjusting the amount of added toluene (1  $\mu$ L).

Table S1. SEC,  $^1\text{H-NMR}$ , DLS, and inverse pendant drop tensiometry data of macro-CTA P(HPMA-*co*-DEGMA)-SC(=S)SC<sub>2</sub>H<sub>5</sub>, A0, A1, A2, A3, and A4 corresponding to 0, 10, 20, 30 and 43 % HPMA respectively.

Entry	macro-CTA	SEC		$^1\text{H-NMR}$			DLS	Inverse pendant drop tensiometry
		$M_{n,\text{exp}}$	$\bar{D}$	Repeat unit	HPMA	HPMA [%]	$T_{\text{cp}}$ [°C]	IFT between styrene and water + macro-CTA [mN/m]
				DEGMA	HPMA			
1	A0	6700	1.19	31	0	0	24	11.72 (+/-0.85)
2	A1	7900	1.17	31	3.5	10	30	4.29 (+/-0.10)
3	A2	8900	1.19	32	8	20	38	0.49 (+/-0.06)
4	A3	10700	1.19	30	13	30	46	1.15 (+/-0.11)
5	A4	13000	1.17	31	24	43	54	3.46 (+/-0.25)

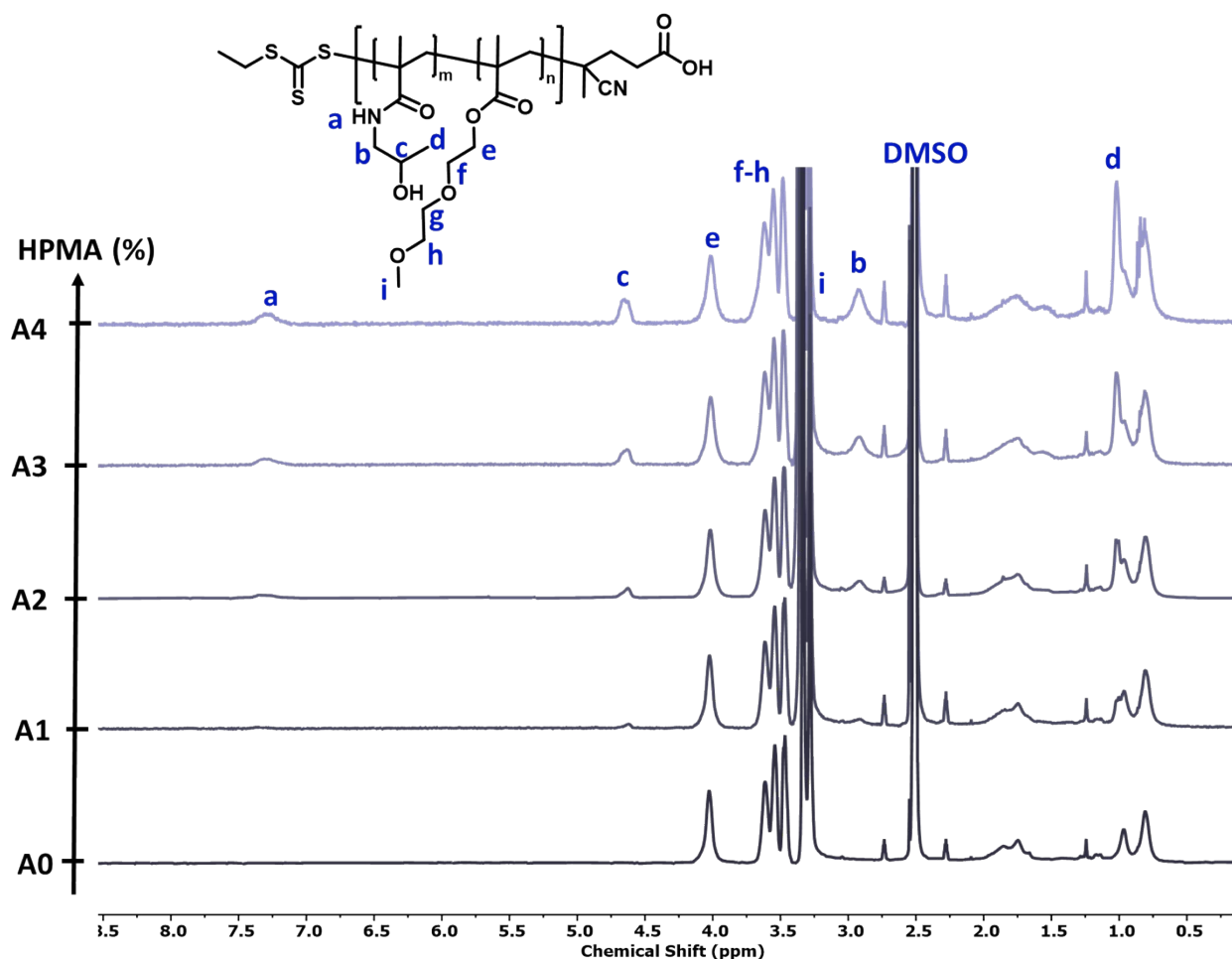


Figure S1.  $^1\text{H-NMR}$  spectrum in DMSO- $d_6$  of macro-CTA P(HPMA-*co*-DEGMA)-SC(=S)SC<sub>2</sub>H<sub>5</sub> A0, A1, A2, A3 and A4 - 0, 10, 20, 30 and 43 % HPMA respectively.

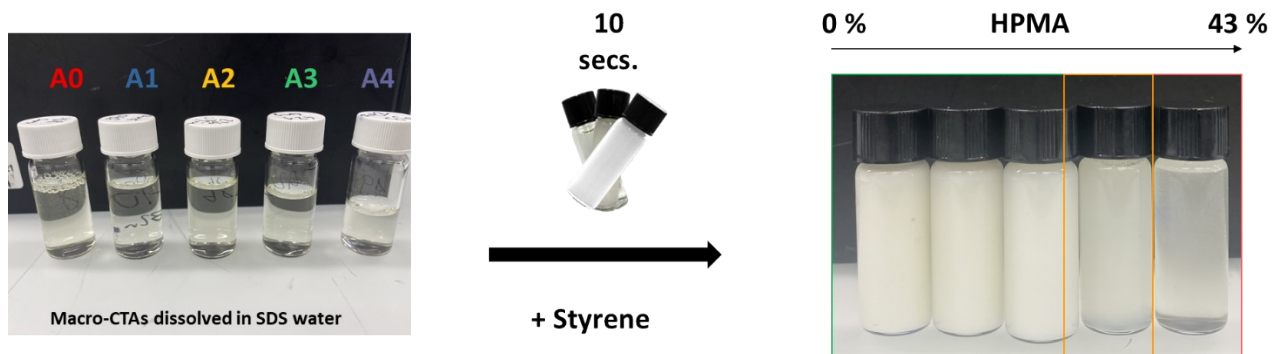


Figure S2. Digital pictures of macro-CTA P(HPMA-*co*-DEGMA)-SC(=S)SC<sub>2</sub>H<sub>5</sub> A0, A1, A2, A3 and A4 - 0, 10, 20, 30 and 43 % HPMA respectively dissolved in water at room temperature and after 10 seconds of manual shaking

Table S2. DLS data for styrene miniemulsion prepared simply by handshaking (10 seconds) with the following formulation (mass ratio constant): [macro-CTA] : [STY] : [SDS] = 25 mg : 35  $\mu$ L : 0.25 mg in 2 mL of deionized water using as macro-CTAs A0 (entry 1), A1 (entry 2), A2 (entry 3), A3 (entry 4) and A4 (entry 5).

Entry	macro-CTA	HPMA	DLS – 25 °C					DLS – 70 °C				
			Number Mean	$\sigma$	Z-average	$\sigma$	Pdl	Number Mean	$\sigma$	Z-average	$\sigma$	Pdl
		[ % ]	d [nm]					d [nm]				
1	A0	0	642	26	689	2	0.11	650	14	725	28	0.16
2	A1	10	321	7	373	6	0.15	296	7	416	22	0.17
3	A2	20	180	7	235	4	0.21	191	4	249	7	0.23
4	A3	30	169,3332	51,1583	4413	1469	0.71	351	105	2939	994	0.96
5	A4	43	3700	1868	3554	2656	0.27	435	15	613	1	0.27

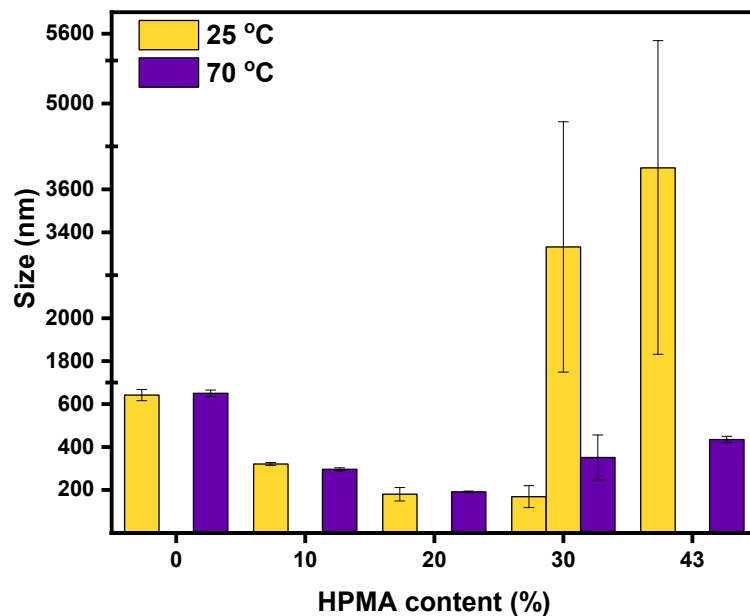


Figure S3. DLS size (number mean) of a styrene miniemulsion formed by handshaking (10 seconds) at room temperature (yellow) or at 70 °C (purple) with the following formulation (mass ratio constant): [macro-CTA] : [STY] : [SDS] = 25 mg : 35  $\mu$ L : 0.25 mg, in 2 mL of water where A0(0 % HPMA), A1(10 % HPMA), A2(20 % HPMA), A3(30 % HPMA) and A4(43 % HPMA) were utilized as macro-CTAs. It is noted that there are two size distributions for samples prepared at room temperature using A3.

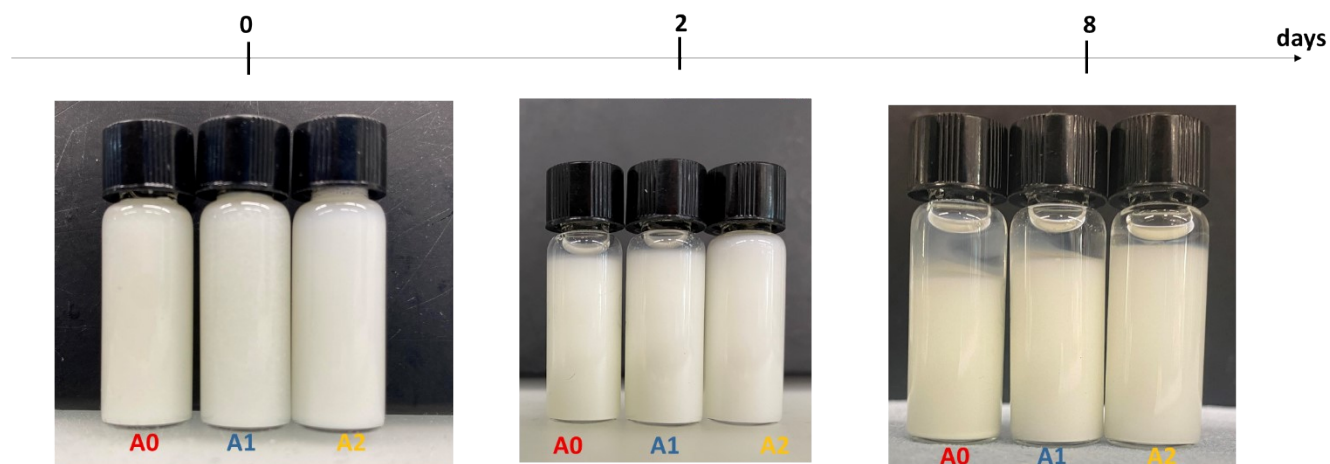


Figure S4. Digital pictures of the phase separation after 0, 2, and 8 days of the miniemulsions formed with macro-CTA P(HPMA-*co*-DEGMA)-SC(=S)SC<sub>2</sub>H<sub>5</sub> A0, A1, and A2 - 0, 10 and 20 % HPMA respectively.

Table S3. Summary of macro-CTAs (A0, A1, A2, A3, and A4) solubility in water (12.5 mg/ml) and in styrene (12.5 mg/ml).

Entry		macro-CTA				
		A0	A1	A2	A3	A4
1	Water	V> 5 min **	V 2 min	V 2 min	Soluble	Soluble
2	Styrene	Soluble	Soluble	V 2 min	V> 5 min	V> 5 min

\*V= vortex \*\* The sample was put in the fridge for 5 min

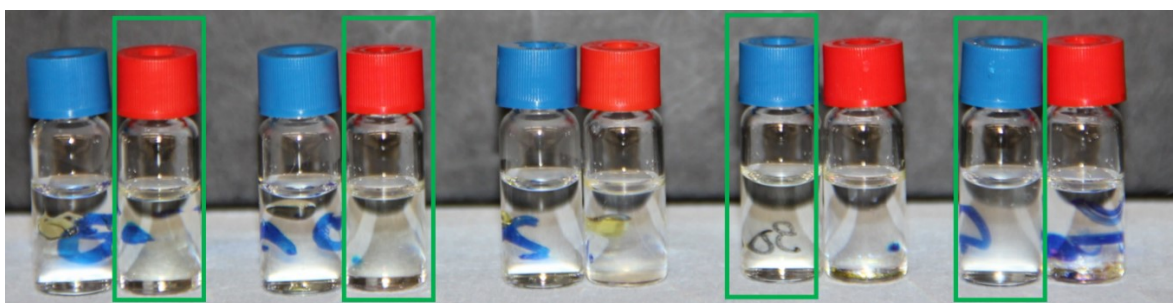


Figure S5. Digital picture of macro-CTAs A0, A1, A2, A3, and A4 dissolved in water (12.5 mg/ml, blue caps) and in styrene (12.5 mg/ml, red caps) before any vortexing. The green boxes represent the vials with immediate solubility in the phases.

Table S4. DLS data for styrene miniemulsion formed by handshaking (10 seconds) with the following formulation (molar ratio constant): [macro-CTA] : [STY] : [SDS] = 1 : 108 : 0.3 in 2 mL of

deionized water using as macro-CTAs A0 (entry 1), A1 (entry 2), A2 (entry 3), A3 (entry 4) and A4 (entry 5).

Entry	macro-CTA	HPMA [%]	DLS – 25 °C					DLS – 70 °C				
			Number Mean	$\sigma$	Z-average	$\sigma$	Pdl	Number Mean	$\sigma$	Z-average	$\sigma$	Pdl
			d [nm]					d [nm]				
1	A0	0	690	65	741	29	0.13	688	20	726	3	0.10
2	A1	10	322	7	377	1	0.13	312	17	414	3	0.19
3	A2	20	173	3	241	3	0.30	187	6	251	5	0.26
4	A3	30	61,514	41,503	2231	281	0.91	350	15	808	97	0.51
5	A4	43	3800	1200	6400	222	0.29	633	37	882	22	0.46

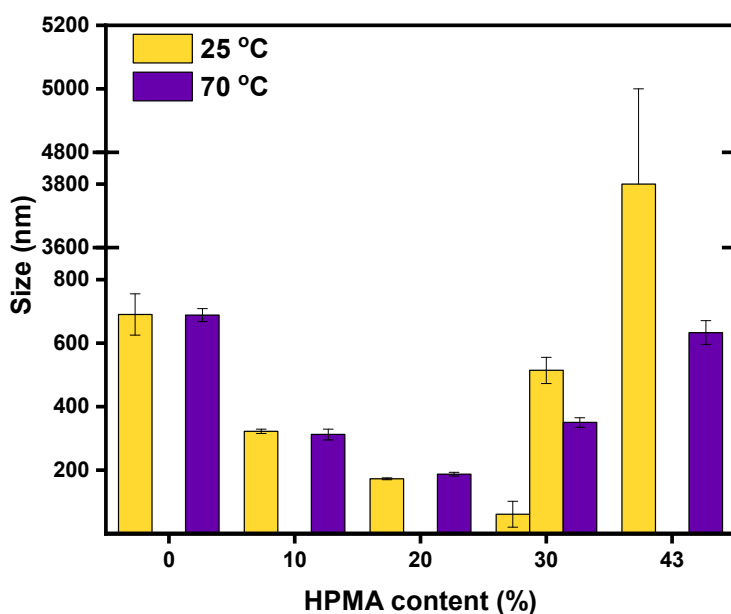


Figure S6. DLS size (number mean) of a styrene miniemulsion formed by handshaking (10 seconds) at room temperature (yellow) or at 70 °C (purple) with the following formulation (molar ratio constant): [macro-CTA] : [STY] : [SDS] = 1 : 108 : 0.3, in 2 mL of deionized water where A0 (0 % HPMA), A1(10 % HPMA), A2(20 % HPMA), A3(30 % HPMA) and A4(43 % HPMA) were utilized as macro-CTAs.

Table S5. SEC, <sup>1</sup>H-NMR, DLS, and inverse pendant drop tensiometry data of macro-CTAs P(HPMA-co-DEGMA)-SC(=S)SC<sub>2</sub>H<sub>5</sub>, B0, B1, B2, B3, and B4 corresponding to 0, 10, 18, 30, and 40 % HPMA respectively. The  $M_n$  was maintained to approximately ~ 8000.



Entry	macro-CTA	SEC		<sup>1</sup> H-NMR			DLS	Inverse pendant drop tensiometry
		<i>M<sub>n,exp</sub></i>	<i>D</i>	Repeat unit		HPMA	<i>T<sub>cp</sub></i>	IFT between styrene and water + macro-CTA
				DEGMA	HPMA	[%]	[°C]	[mN/m]
1	B0	7700	1.22	38	0	0	24	11.26 (+/-0.35)
2	B1	7900	1.17	31	3	10	30	4.29 (+/-0.10)
3	B2	8200	1.18	27	6	18	34	0.86 (+/-0.07)
4	B3	8300	1.19	22	10	30	46	1.20 (+/-0.18)
5	B4	8100	1.19	19	12.5	40	50	2.95 (+/-0.21)

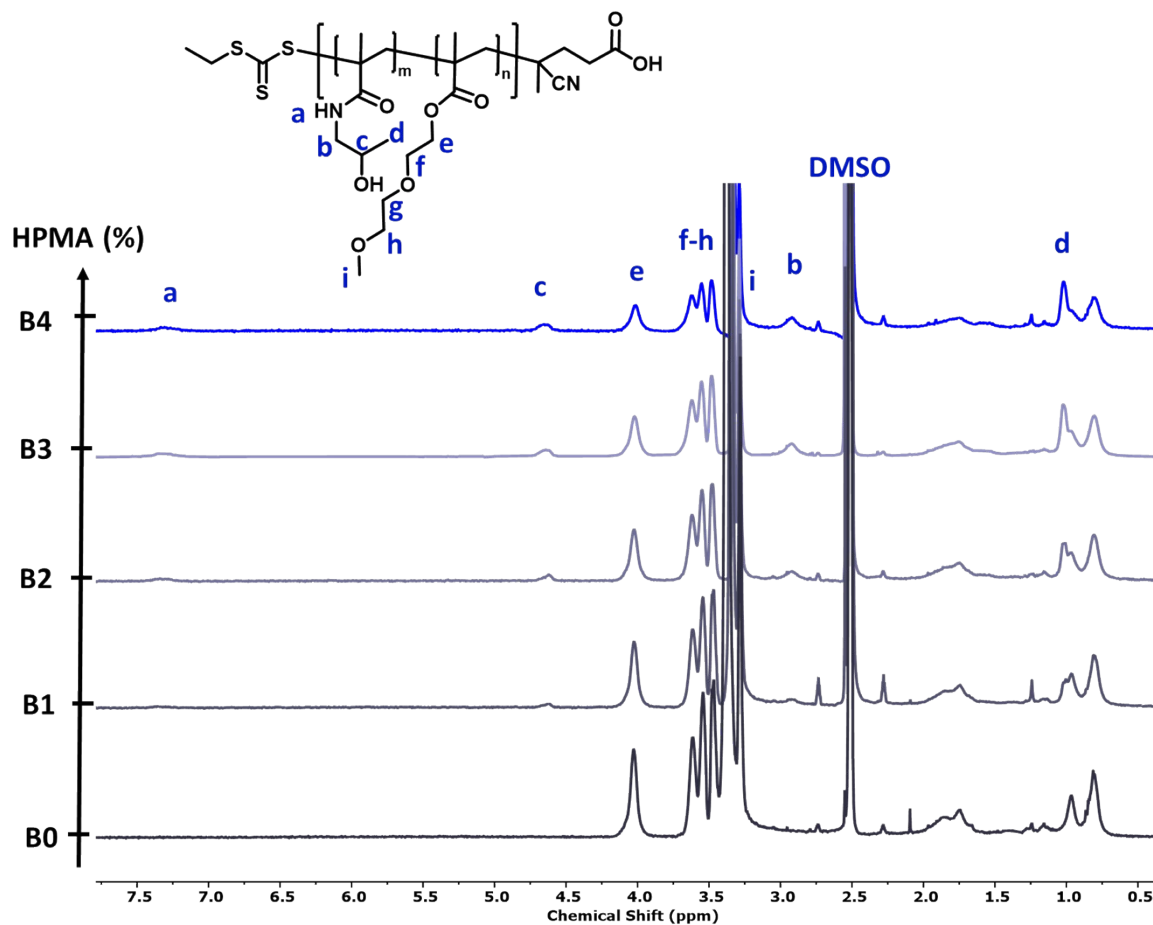


Figure S7. <sup>1</sup>H-NMR spectrum in DMSO-d<sub>6</sub> of macro-CTAs P(HPMA-co-DEGMA)-SC(=S)SC<sub>2</sub>H<sub>5</sub> B0, B1, B2, B3, and B4 - 0, 10, 18, 30, and 40 % HPMA respectively.

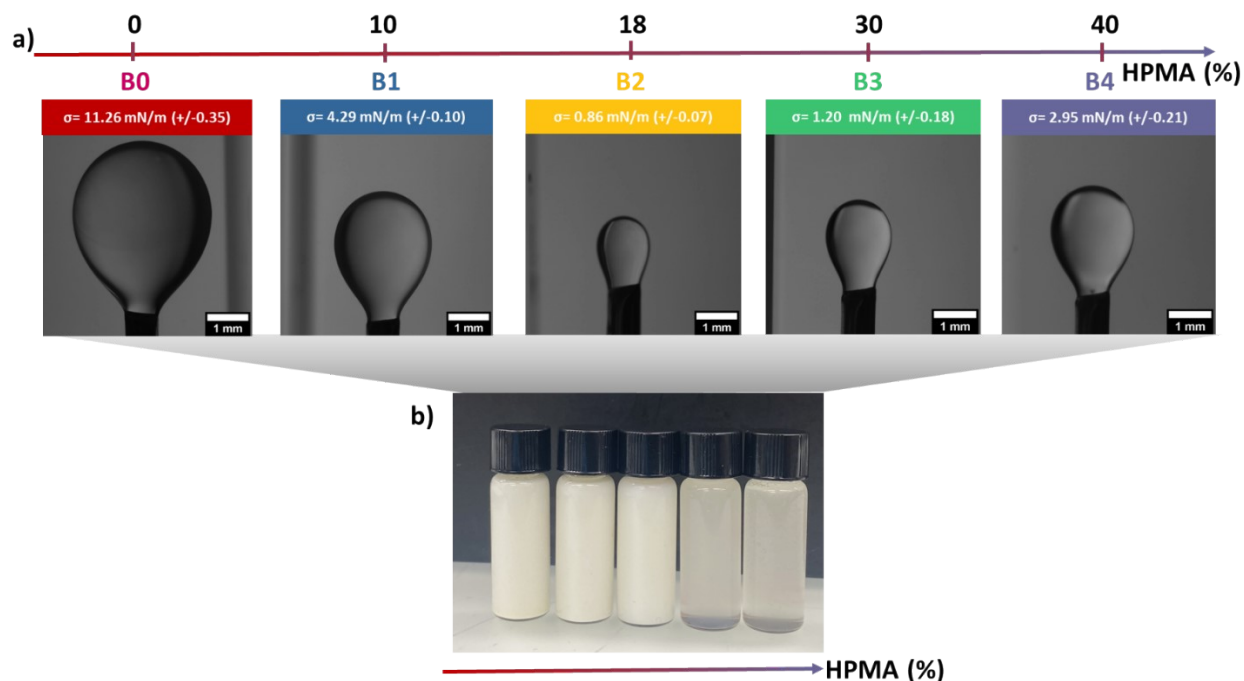


Figure S8. a) Example pictures of interfacial tension measured by inverse pendant drop of a styrene droplet in deionized water + macro-CTA B0 (red), B1 (blue), B2 (yellow), B3 (green), and B4 (purple, 12.5 mg/mL). The pictures were flipped before analyzing with the MATLAB code. b) Digital picture of styrene miniemulsion formed by handshaking (10 seconds) at room temperature with the following formulation (molar/mass ratio constant): [macro-CTA] : [STY] : [SDS] = 1 (25 mg): 97 (35  $\mu$ L) : 0.3 (0.25 mg), in 2 mL of deionized water. From left to right, B0 (0 % HPMA), B1 (10 % HPMA), B2 (18 % HPMA), B3 (30 % HPMA) and B4 (40 % HPMA) were utilized as macro-CTAs.

Table S6. DLS data of a styrene miniemulsion formed by handshaking (10 seconds), at room temperature (yellow) or at 70  $^{\circ}$ C (purple), with the following formulation (molar/mass ratio constant):

[macro-CTA] : [STY] : [SDS] = 1 (25 mg): 97 (35  $\mu$ L) : 0.3 (0.25 mg), in 2 mL of deionized water where B0 (entry 1), B1 (entry 2), B2 (entry 3), B3 (entry 4) and B4 (entry 5) were utilized as macro-CTAs.

Entry	macro-CTA	HPMA	DLS – 25 °C					DLS – 70 °C				
			Number Mean	$\sigma$	Z-average	$\sigma$	Pdl	Number Mean	$\sigma$	Z-average	$\sigma$	Pdl
		[ % ]	d [nm]					d [nm]				
1	B0	0	563	31	599	29	0.10	566	10	637	8	0.14
2	B1	10	321	7	373	6	0.15	296	7	416	22	0.17
3	B2	18	194	22	295	7	0.28	228	13	364	29	0.40
4	B3	30	140,2620	3400	3200	446	0.78	189,401	112	660	45	0.45
5	B4	40	2088	63	7535	219	0.08	501	34	875	38	0.53

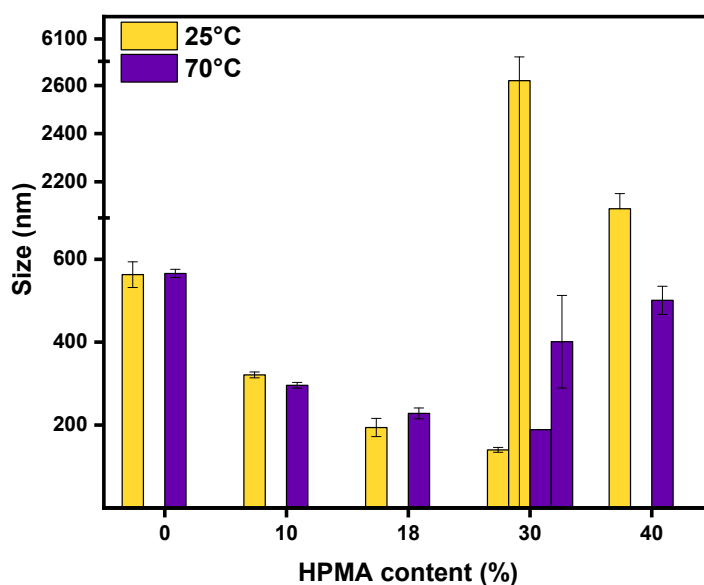


Figure S9. DLS size (number mean) of a styrene miniemulsion formed by handshaking (10 seconds) at room temperature (yellow) or at 70 °C (purple) with the following formulation (molar/mass ratio constant): [macro-CTA] : [STY] : [SDS] = 1 (25 mg): 97 (35  $\mu$ L) : 0.3 (0.25 mg), in 2 mL of deionized water where B0 (0 % HPMA), B1 (10 % HPMA), B2 (18 % HPMA), B3 (30 % HPMA) and B4 (40 % HPMA) were utilized as macro-CTAs.

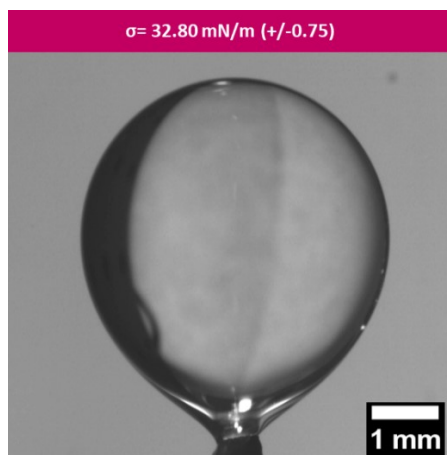


Figure S10. Example picture of IFT measured by inverse pendant drop of a styrene droplet in deionized water. The picture was flipped before analyzing with the MATLAB code.

Table S7.  $^1\text{H-NMR}$  data of RAFT miniemulsion *in situ* kinetic study of styrene using A2 as macro-CTAs. Polymerization conditions are the following (mass ratio constant): [macro-CTA] : [STY] : [AIBN] : [SDS] = 6.25 mg : 8.75  $\mu\text{L}$  : 0.015 mg : 0.06 mg in 0.5 mL of deuterium oxide. The polymerization was carried out in a 70  $^\circ\text{C}$  preheated NMR for 2 hours.

Entry	Time	NMR
		Conversion
	[min]	[%]
1	1	0.0
2	5	0.5
3	10	3.3
4	15	6.2
5	20	9.0
6	25	10.4
7	30	11.8
8	35	15.9
9	40	17.2
10	45	21.3
11	50	24.0
12	55	25.3
13	60	29.2
14	70	34.4
15	80	38.2
16	90	44.4
17	100	49.3
18	110	55.3
19	120	57.7

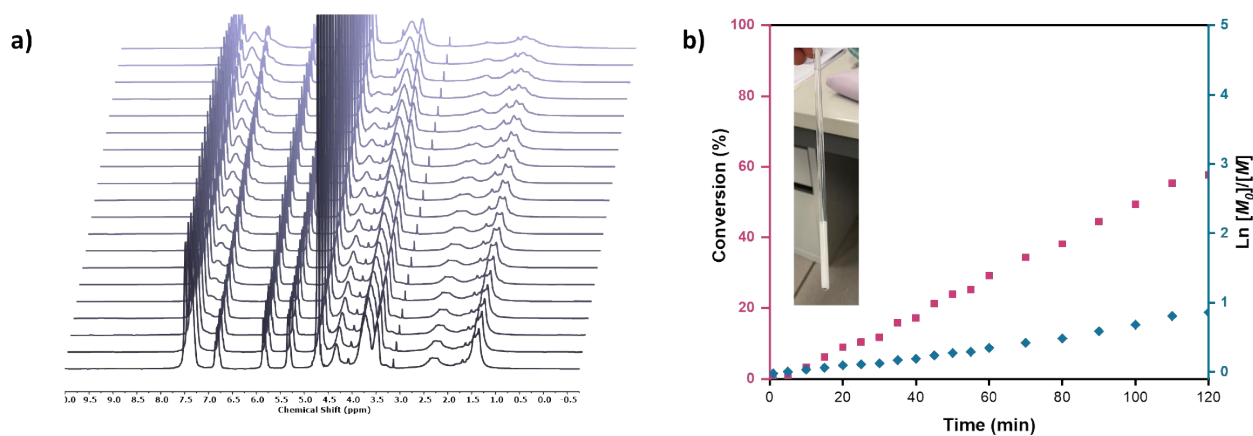


Figure S11. <sup>1</sup>H-NMR traces of RAFT miniemulsion *in situ* kinetic study of styrene using A2 as macro-CTA. Polymerization conditions are the following (mass ratio constant): [macro-CTA] : [STY] : [AIBN] : [SDS] = 6.25 mg : 8.75 μL : 0.015 mg : 0.06 mg in 0.5 mL of deuterium oxide. The polymerization was carried out in a 70 °C preheated NMR for 2 hours.

Table S8. SEC, <sup>1</sup>H-NMR, and DLS data of RAFT miniemulsion polymerization of styrene using A0 (entry 1), A1 (entry 2), A2 (entry 3), A3 (entry 4), and A4 (entry 5) as macro-CTAs. Polymerization conditions are the following (mass ratio constant): [macro-CTA] : [STY] : [AIBN] : [SDS] = 25 mg :

35  $\mu\text{L}$  : 0.06 mg : 0.25 mg in 2 mL of deionized water. All polymerizations were carried out in a 70 °C preheated oven for 6 hours.

Entry	macro-CTA	$M_n(\text{macro-CTA})$	HPMA	[Macro-CTA] : [STY] : [AIBN] : [SDS]	SEC			NMR	DLS – 70 °C				
					$M_{n,\text{th}}$	$M_{n,\text{exp}}$	$\bar{D}$	Conversion	Number mean	$\sigma$	Z-average	$\sigma$	PdI
			[ % ]				[ % ]	d [nm]					
1	A0	6700	0	1 : 81 : 0.1 : 0.2	10800	9500	1.21	48	467	9	564	6	0.13
2	A1	7900	10	1 : 96 : 0.1 : 0.3	14400	11500	1.30	65	272	31	395	8	0.24
3	A2	8900	20	1 : 108 : 0.1 : 0.3	19700	19400	1.33	96	183	2	232	1	0.10
4	A3	10700	30	1 : 130 : 0.2 : 0.4	17700	14300	1.66	52	290	23	390	7	0.24
5	A4	13000	43	1 : 158 : 0.2 : 0.4	19500	17200	2.40	40	85	16	255	9	0.45

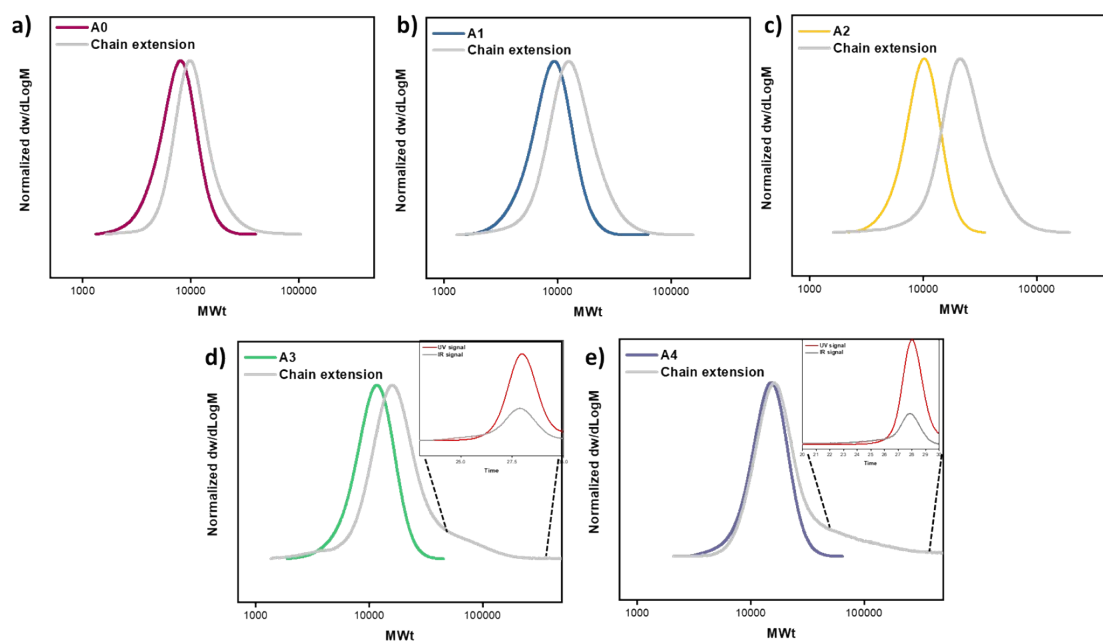


Figure S12. SEC traces (RI detector) of RAFT miniemulsion polymerization of styrene using a) A0, b) A1, c) A2, d) A3 and e) A4 as macro-CTAs. Polymerization conditions are the following (mass ratio constant): [macro-CTA] : [STY] : [AIBN] : [SDS] = 25 mg : 35  $\mu\text{L}$  : 0.06 mg : 0.25 mg in 2 ml of deionized water. All polymerizations were carried out in a 70 °C preheated oven for 6 hours. In panels d and e, SEC traces using UV detectors were compared with RI showing the high molecular weight distributions have little to no UV signals.

Table S9. SEC, <sup>1</sup>H-NMR, and DLS data of RAFT miniemulsion polymerization of styrene using A0 (entry 1) and A1 (entry 2) as macro-CTAs. Polymerization conditions are the following (mass ratio constant): [macro-CTA] : [STY] : [AIBN] : [SDS] = 25 mg : 35 μL : 0.06 mg : 0.25 mg, in 2 mL of deionized water. The polymerizations were carried out in a 70 °C preheated oven for 9 hours (entry 1) and 8 hours (entry 2).

Entry	macro-CTA	$M_n(\text{macro-CTA})$	HPMA	[Macro-CTA] : [STY] : [AIBN] : [SDS]	Time	SEC		NMR	DLS – 70 °C					
						$M_{n,\text{th}}$	$M_{n,\text{exp}}$	$\mathcal{D}$	C	Number mean	$\sigma$	Z-average	$\sigma$	PDI
			[ % ]					[ % ]	d [nm]					
1	A0	6700	0	1 : 81 : 0.1 : 0.2	9	14600	11700	1.34	94	337	13	483	1	0.18
2	A1	7900	10	1 : 96 : 0.1 : 0.3	8	17200	13400	1.24	94	262	12	345	1	0.16

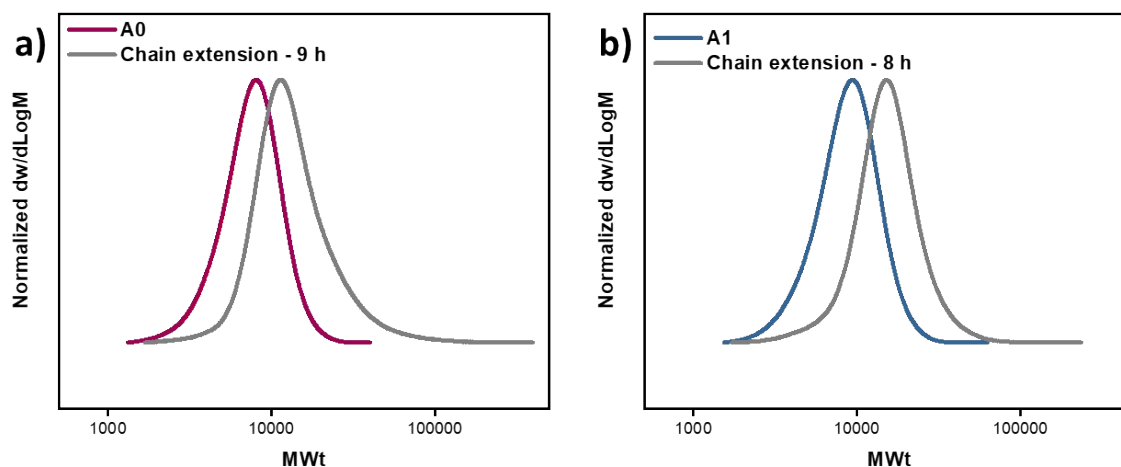


Figure S13. SEC traces of RAFT miniemulsion polymerization of styrene using a) A0 and b) A1 as macro-CTA. Polymerization conditions are the following (mass ratio constant): [macro-CTA] : [STY] : [AIBN] : [SDS] = 25 mg : 35 μL : 0.06 mg : 0.25 mg, in 2 ml of deionized water. The polymerizations were carried out in a 70 °C preheated oven for a) 9 hours and b) 8 hours.

Table S10. SEC, <sup>1</sup>H-NMR and DLS data of RAFT miniemulsion polymerization of styrene using A0 (entry 1), A1 (entry 2), A2 (entry 3), A3 (entry 4) and A4 (entry 5) as macro-CTAs. Polymerization

conditions are the following (molar ratio constant): [macro-CTA] : [STY] : [AIBN] : [SDS] = 1 : 108 : 0.1 : 0.3 in 2 ml of deionized water. All polymerizations were carried out in a 70 °C preheated oven for 6 hours.

Entry	macro-CTA	$M_n(\text{macro-CTA})$	HPMA	[Macro-CTA] : [STY] : [AIBN] : [SDS]	SEC			NMR	DLS – 70 °C				
					$M_{n,\text{th}}$	$M_{n,\text{exp}}$	$\bar{D}$	C	Number mean	$\sigma$	Z-average	$\sigma$	Pdl
			[ % ]				[ % ]	d [nm]	d [nm]				
1	A0	6700	0	1 (19 mg) : 108 : 0.1 : 0.3	10700	10500	1.74	43	490	29	599	9	0.19
2	A1	7900	10	1 (22.4 mg) : 108 : 0.1 : 0.3	14800	10700	1.37	62	280	13	359	3	0.19
3	A2	8900	20	1 (25 mg) : 108 : 0.1 : 0.3	19700	19400	1.33	96	183	2	232	1	0.10
4	A3	10700	32	1 (30 mg) : 108 : 0.1 : 0.3	10700	15800	1.60	62	271	3	390	12	0.22
5	A4	13000	43	1 (37 mg) : 108 : 0.1 : 0.3	13000	19600	3.2	63	79	17	239	7	0.38

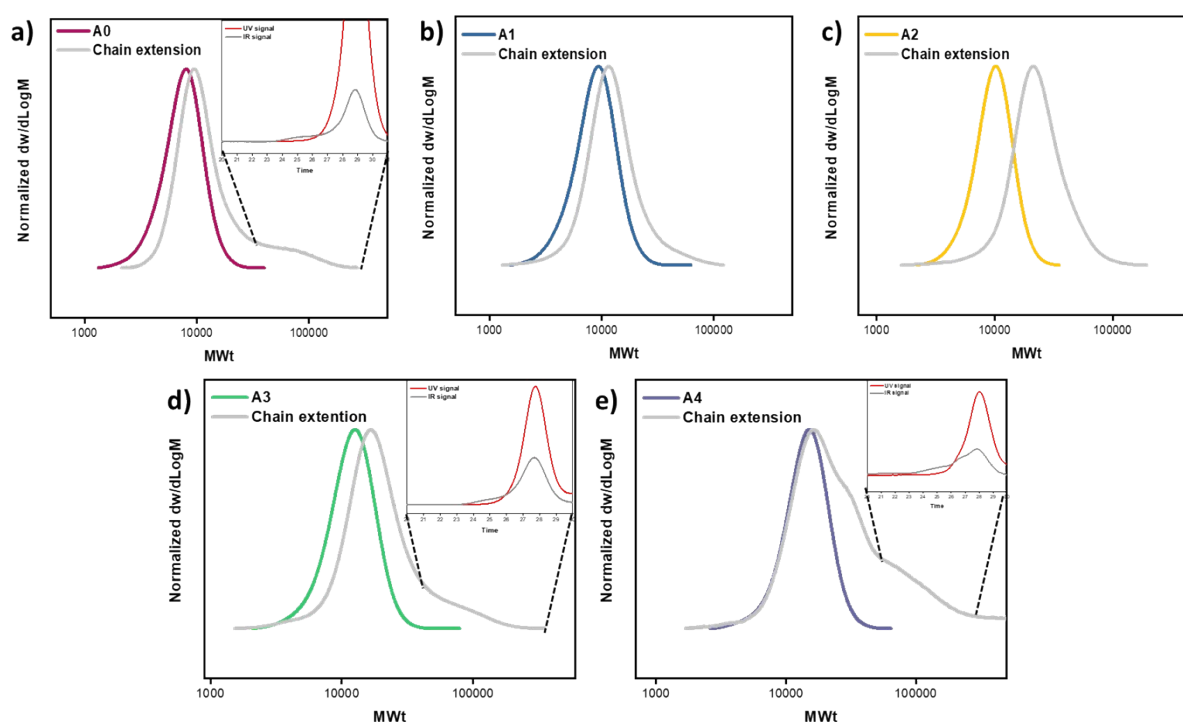


Figure S14. SEC traces (RI detector) of RAFT miniemulsion polymerization of styrene using a) A0, b) A1, c) A2, d) A3 and e) A4 as macro-CTA. Polymerization conditions are the following (molar ratio constant): [macro-CTA] : [STY] : [AIBN] : [SDS] = 1 : 108 : 0.1 : 0.3, in 2 ml of deionized water. All polymerizations were carried out in a 70 °C preheated oven for 6 hours. Small figures show SEC traces comparing UV and RI detectors indicating the high molecular weight distributions have little to no UV signals.



Table S11. SEC, <sup>1</sup>H-NMR, and DLS data of RAFT miniemulsion polymerization of styrene using B0 (entry 1), B1 (entry 2), B2 (entry 3), B3 (entry 4), and B4 (entry 5) as macro-CTA. Polymerization conditions are the following (molar/mass ratio constant): [macro-CTA] : [STY] : [AIBN] : [SDS] = 1 (25 mg) : 97 (35 μl) : 0.1 (0.07 mg) : 0.3 (0.25 mg) in 2 ml of deionized water. All polymerizations were carried out in a 70 °C preheated oven for 6 hours.

Entry	macro-CTA	M <sub>n</sub> (macro-CTA)	HPMA	[Macro-CTA] : [STY] : [AIBN] : [SDS]	SEC			NMR	DLS – 70 °C				
					M <sub>n,th</sub>	M <sub>n,exp</sub>	Đ	C	Number mean	σ	Z-average	σ	PdI
			[ % ]					[ % ]	d [nm]		d [nm]		
1	B0	7900	0	1 : 97 : 0.1 : 0.3	14800	11500	1.32	69	123,379	4,2	458	5	0.14
2	B1	7900	10	1 : 97 : 0.1 : 0.3	15300	11800	1.26	74	263	15	357	7	0.19
3	B2	8000	18	1 : 97 : 0.1 : 0.3	17000	16500	1.29	90	197	8	246	7	0.11
4	B3	8000	30	1 : 97 : 0.1 : 0.3	13000	10900	1.88	53	356	54	446	3	0.15
5	B4	8000	40	1 : 97 : 0.1 : 0.3	9100	11000	2.37	11	398,67	207,25	2209	432	0.88

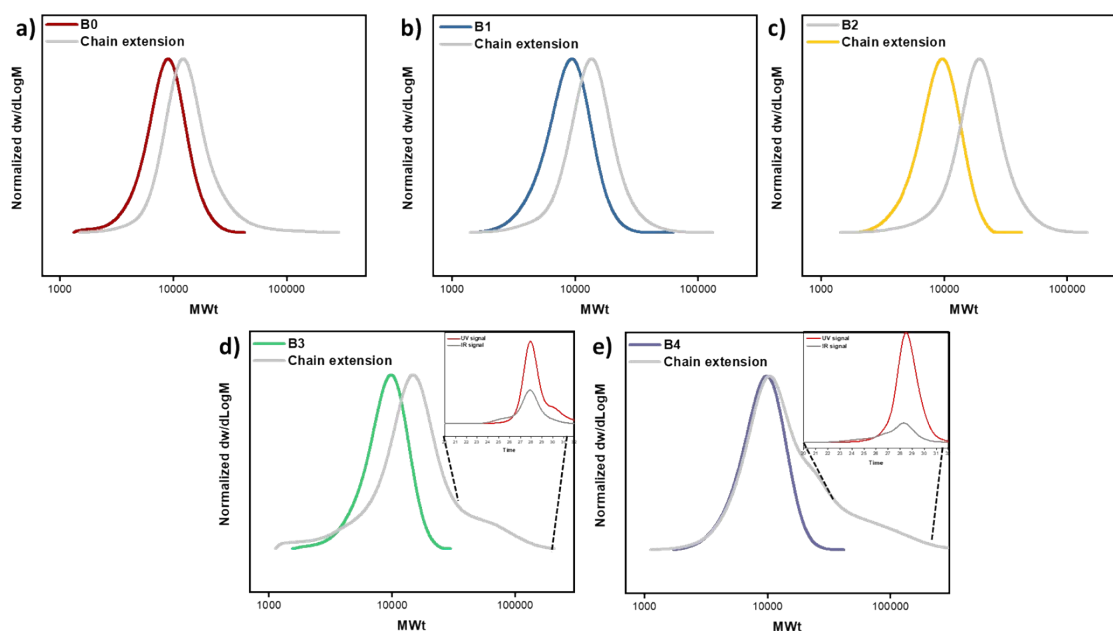


Figure S15. SEC traces (RI detector) of RAFT miniemulsion polymerization of styrene using a) B0, b) B1, c) B2, d) B3 and e) B4 as macro-CTAs. Polymerization conditions are the following (molar/mass ratio constant): [macro-CTA] : [STY] : [AIBN] : [SDS] = 1 (25 mg) : 97 (35 μl) : 0.1 (0.07 mg) : 0.3 (0.25 mg), in 2 ml of deionized water. All polymerizations were carried out in a 70 °C preheated oven for 6 hours. Small figures show SEC traces comparing UV and RI detectors indicating the high molecular weight distributions have little to no UV signals.

Table S12. SEC,  $^1\text{H-NMR}$ , DLS, and inverse pendant drop tensiometry data of macro-CTA P(HPMA-co-DEGMA)-SC(=S)SC<sub>2</sub>H<sub>5</sub>, A5 & A6, corresponding to ~ 20 % HPMA and presenting increased molecular weight.

Entry	macro-CTA	SEC		$^1\text{H-NMR}$			DLS	Inverse pendant drop tensiometry
		$M_{n,\text{exp}}$	$\bar{D}$	Repeat unit		HPMA	LCST	IFT between styrene and water + macro-CTA
				DEGMA	HPMA	[ % ]	[ °C ]	[ mN/m ]
1	A5	5200	1.17	15	3.8	20	32	1.65 (+/- 0.26)
2	A6	17100	1.17	61	15	20	38	0.12 (+/- 0.03)

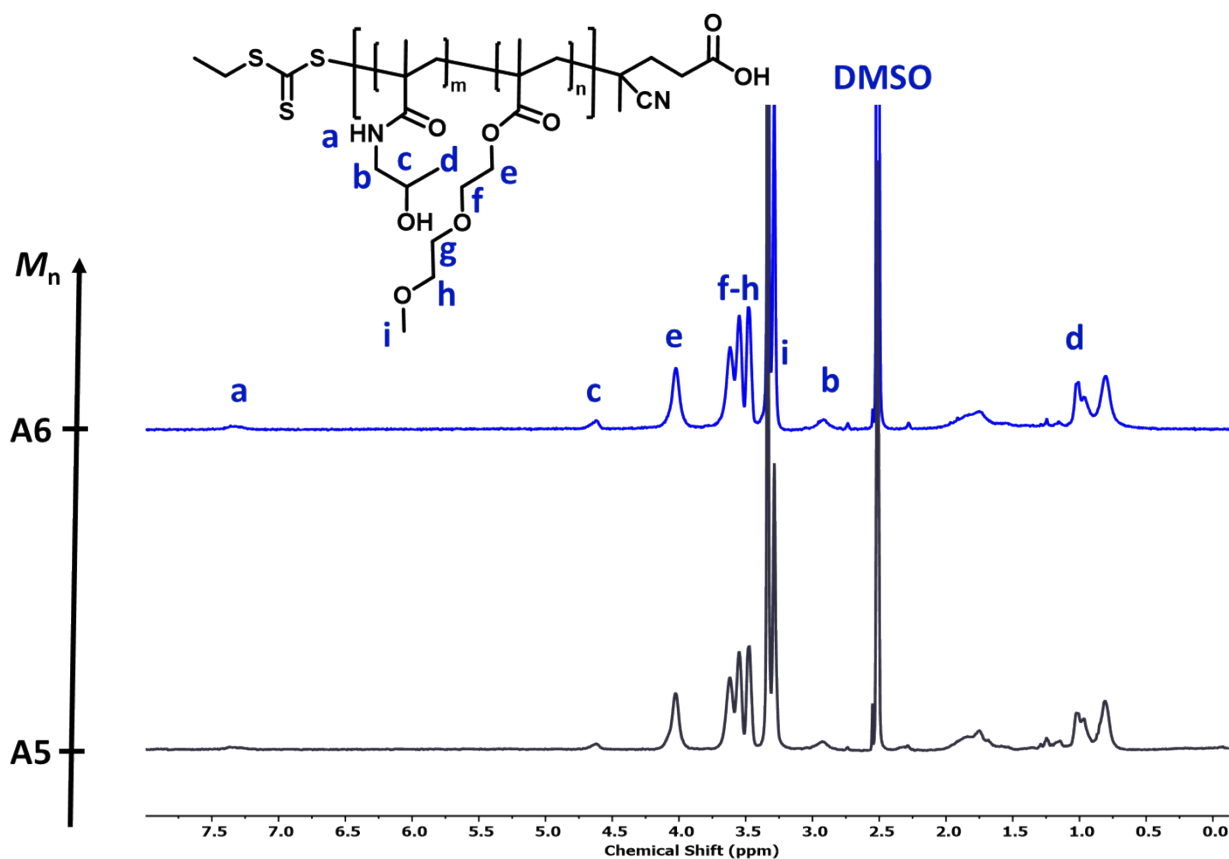


Figure S16.  $^1\text{H-NMR}$  spectrum in DMSO- $d_6$  of macro-CTA P(HPMA-co-DEGMA)-SC(=S)SC<sub>2</sub>H<sub>5</sub>, A5 & A6, corresponding to ~ 20 % HPMA and presenting increased molecular weight.



Figure S17. Digital pictures of miniemulsion formed with macro-CTAs A5, A2 and A6 by simple handshaking (10 seconds) with the following formulation (mass ratio constant): [macro-CTA] : [STY] : [SDS] = 25 mg : 35  $\mu$ L : 0.25 mg in 2 mL of deionized water.

Table S13. DLS data for styrene miniemulsion prepared simply by handshaking (10 seconds) with the following formulation (mass ratio constant): [macro-CTA] : [STY] : [SDS] = 25 mg : 35  $\mu$ L : 0.25 mg in 2 mL of deionized water using as macro-CTAs A5 (entry 1), A2(entry 2), A6 (entry 3).

Entry	macro-CTA	HPMA [%]	DLS – 25 °C					DLS – 70 °C				
			Number mean	$\sigma$	Z- average d [nm]	$\sigma$	Pdl	Number mean	$\sigma$	Z- average d [nm]	$\sigma$	Pdl
1	A5	19	445	59	803	172	0.47	385	21	816	235	0.46
2	A2	20	180	7	235	4	0.21	191	4	249	7	0.23
3	A6	20	105	9	178	7	0.37	108	9	176	5	0.30

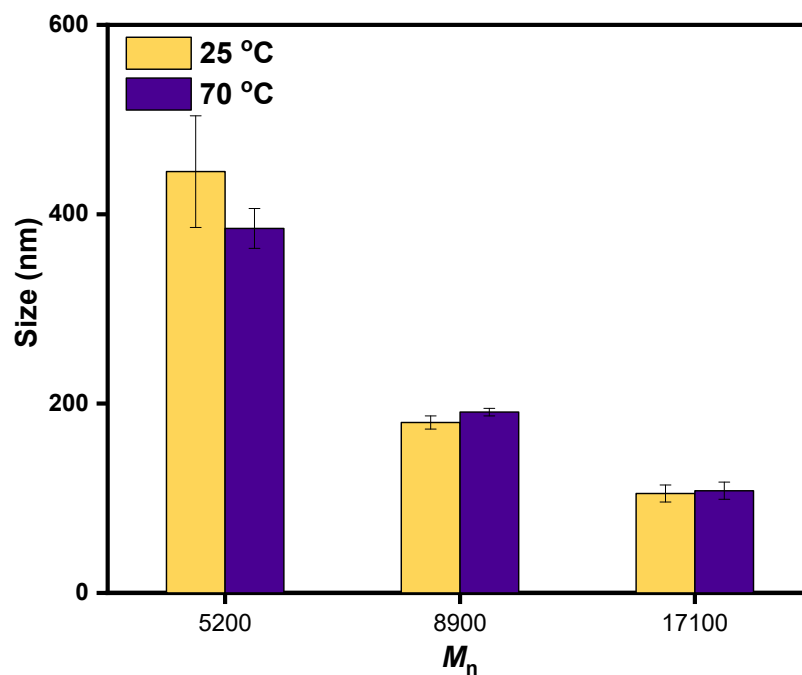


Figure S18. DLS size (by number) of styrene miniemulsion prepared simply by handshaking (10 seconds) with the following formulation (mass ratio constant): [macro-CTA] : [STY] : [SDS] = 25 mg : 35  $\mu$ L : 0.25 mg in 2 mL of deionized water using as macro-CTAs A5, A2, A6 at both 25°C and 70 °C.

Table S14. SEC, <sup>1</sup>H-NMR and DLS data of RAFT miniemulsion polymerizations of styrene using A5 (entries 1 & 2), A2 (entry 3), A6 (entry 4) as macro-CTAs with the following formulation (mass ratio constant): [macro-CTA] : [STY] : [AIBN] : [SDS] = 25 mg : 35 μL : 0.06 mg : 0.25 mg in 2 mL of deionized water. All polymerizations were conducted in a preheated oven (70 °C).

Entry	macro-CTA	$M_n(\text{macro-CTA})$	[macro-CTA] : [STY] : [AIBN] : [SDS]	Time [h]	SEC		NMR		DLS – 70 °C				
					$M_{n,\text{th}}$	$M_{n,\text{exp}}$	$\bar{D}$	C [%]	Number mean	$\sigma$	Z-average	$\sigma$	PDI
1	A5	5200	1:63:0.1:0.2	6	7800	6400	1.19	39	369	20	749	189	0.37
2	A5	5200	1:63:0.1:0.2	9	10000	7300	1.20	74	289	22	386	8	0.20
3	A2	8900	1:108:0.1:0.3	6	16600	19400	1.26	96	183	3	232	1	0.11
4	A6	17100	1:208:0.2:0.6	3.45	38200	33200	1.33	98	110	5	150	1	0.08

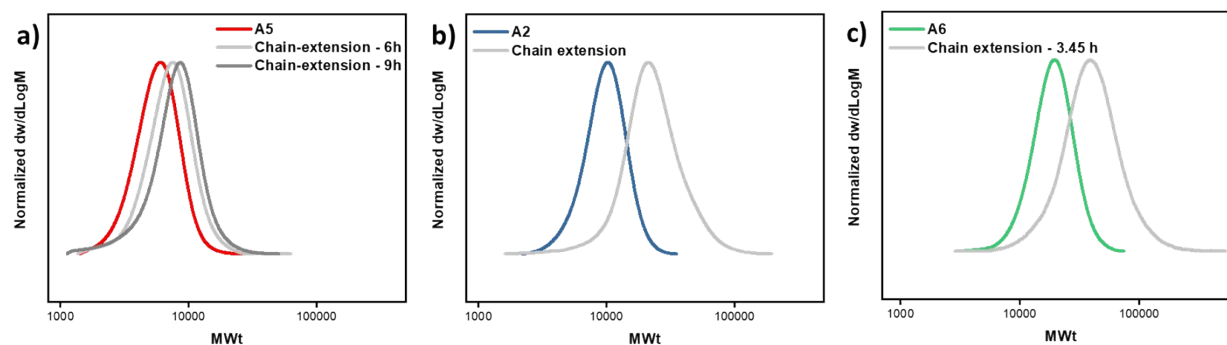


Figure S19. SEC traces of RAFT miniemulsion polymerization of styrene using a) A5, b) A2, c) A6 as macro-CTAs with the following formulation (mass ratio constant): [macro-CTA] : [STY] : [AIBN] : [SDS] = 25 mg : 35 μL : 0.06 mg : 0.25 mg in 2 mL of deionized water.

Table S15. SEC,  $^1\text{H-NMR}$ , DLS, and inverse pendant drop tensiometry data of macro-CTA P(TEGMA-*co*-DEGMA)-SC(=S)SC<sub>2</sub>H<sub>5</sub>, D0 (C0, entry 1), P(PEGMA-*co*-DEGMA)-SC(=S)SC<sub>2</sub>H<sub>5</sub> (D0, entry 2), P(HEMA-*co*-DEGMA)-SC(=S)SC<sub>2</sub>H<sub>5</sub> (E0, entry 3) and, P(MAAm-*co*-DEGMA)-SC(=S)SC<sub>2</sub>H<sub>5</sub> (F0, entry 4).

Entry	macro-CTA	monomer 1	monomer 2	SEC		$^1\text{H-NMR}$	DLS	Inverse pendant drop tensiometry
				$M_{n,\text{exp}}$	$\bar{D}$	monomer 1 [%]	$T_{\text{cp}}$ [°C]	IFT between styrene and water + macro-CTA mN/m
1	C0	TEGMA	DEGMA	8700	1.17	19	28	10.52 (+/-0.19)
2	D0	PEGMA	DEGMA	9000	1.19	19	34	9.27 (+/-0.33)
3	E0	HEMA	DEGMA	11000	1.19	19	24	2.6 (+/- 0.08)
4	F0	MAAm	DEGMA	11000	1.10	23	38	0.18 (+/-0.03)

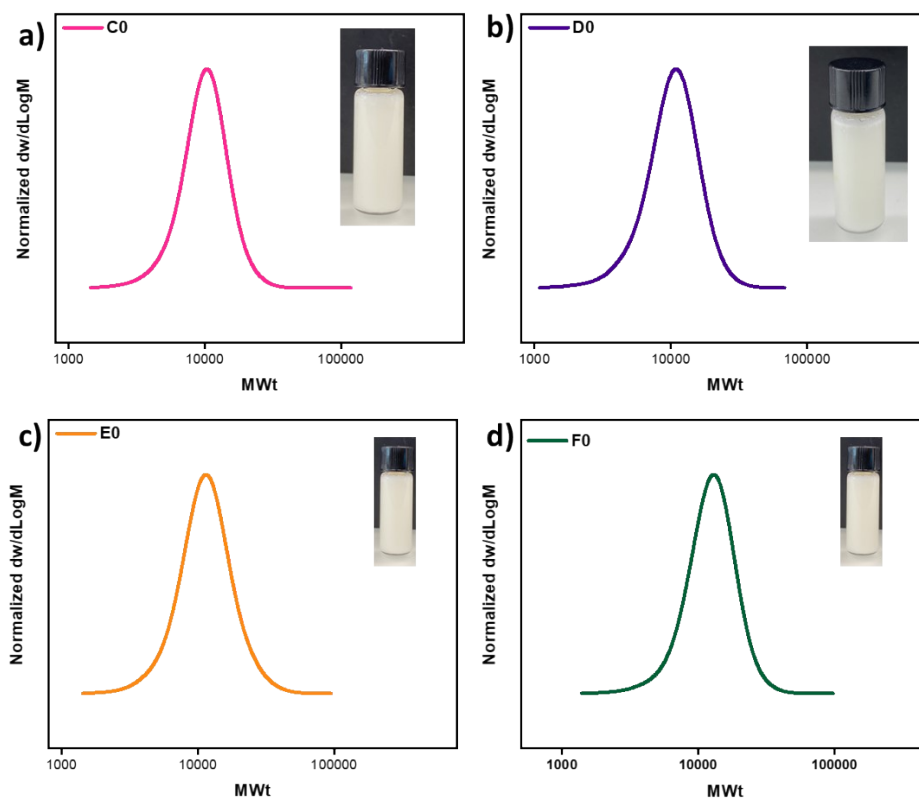


Figure S20. SEC traces of macro-CTA a) P(TEGMA-*co*-DEGMA)-SC(=S)SC<sub>2</sub>H<sub>5</sub> (C0), b) P(PEGMA-*co*-DEGMA)-SC(=S)SC<sub>2</sub>H<sub>5</sub> (D0), c) P(HEMA-*co*-DEGMA)-SC(=S)SC<sub>2</sub>H<sub>5</sub> (E0) and, d) P(MAAm-*co*-DEGMA)-SC(=S)SC<sub>2</sub>H<sub>5</sub> (F0) and digital pictures of the miniemulsion formed with the following conditions (mass ratio constant): [macro-CTA] : [STY] : [SDS] = 25 mg : 35  $\mu\text{L}$  : 0.25 mg in 2 mL of deionized water.

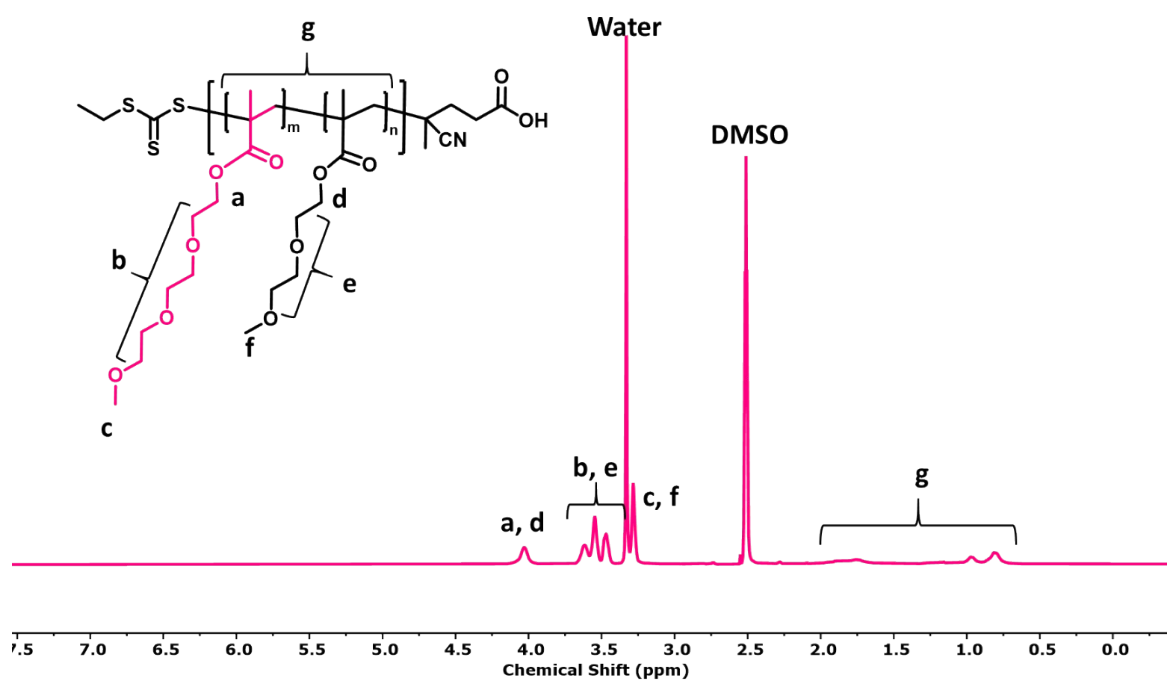


Figure S21. <sup>1</sup>H-NMR trace of macro-CTA P(TEGMA-*co*-DEGMA)-SC(=S)SC<sub>2</sub>H<sub>5</sub> (C0).

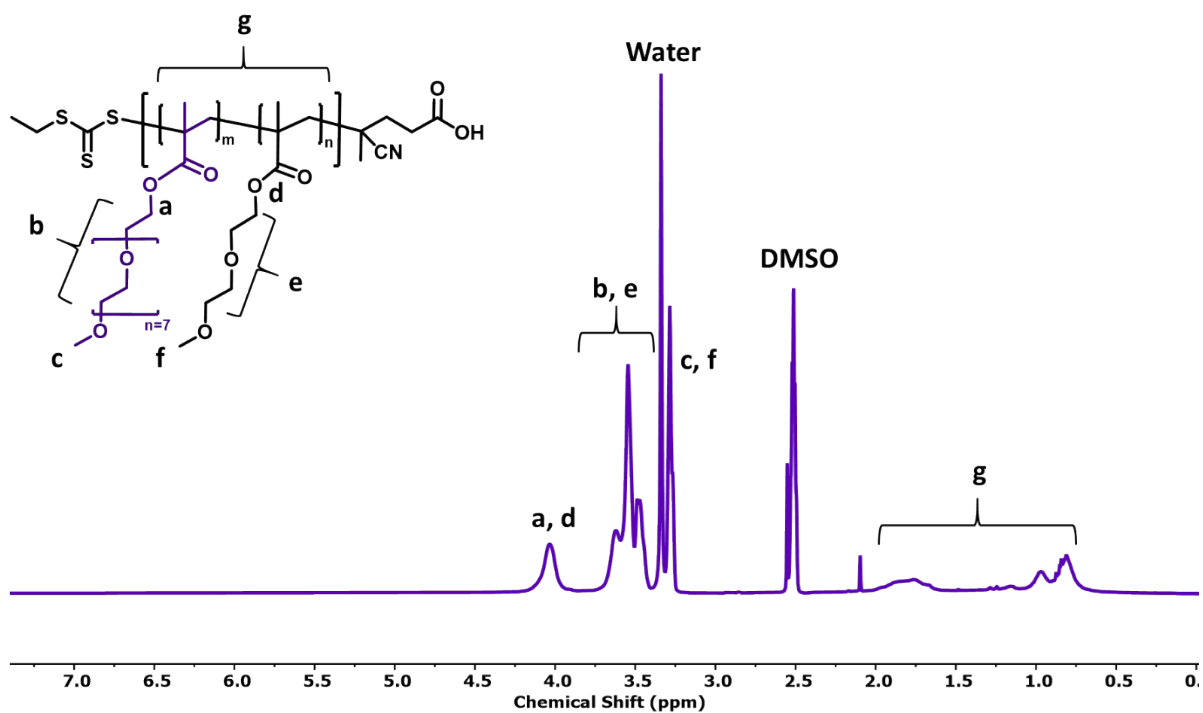


Figure S22. <sup>1</sup>H-NMR trace of macro-CTA P(PEGMA-*co*-DEGMA)-SC(=S)SC<sub>2</sub>H<sub>5</sub> (D0).

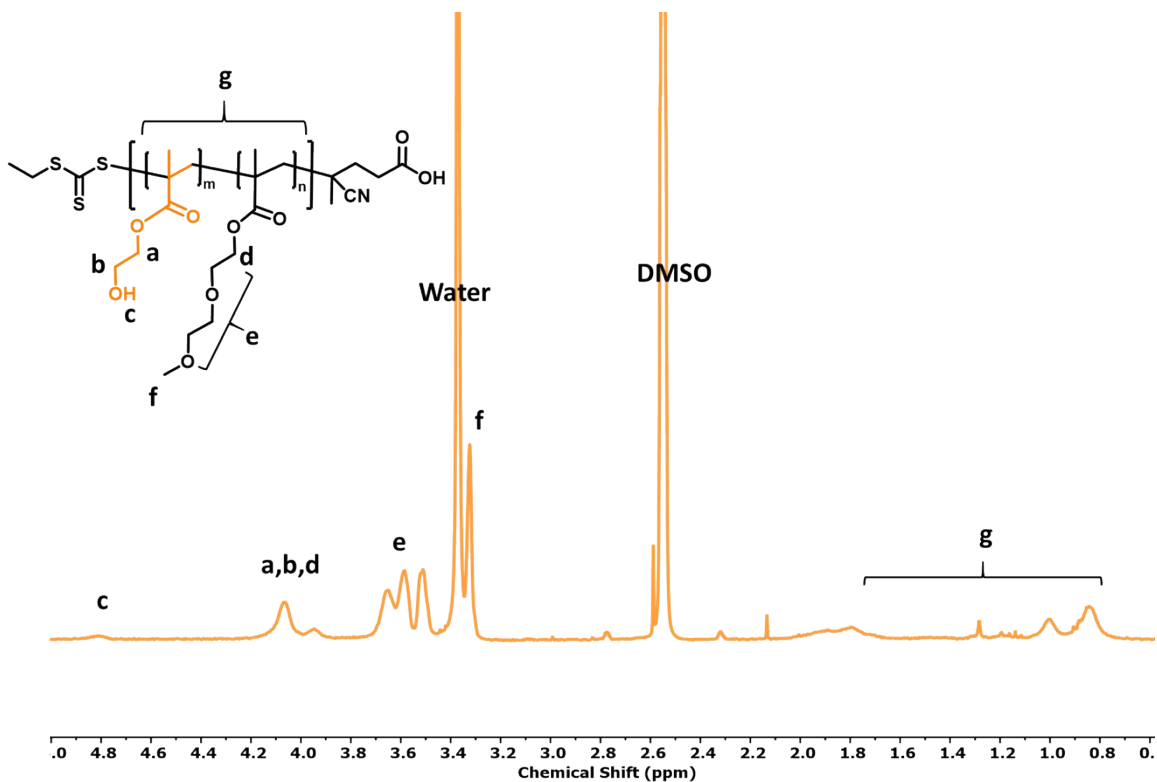


Figure S23. <sup>1</sup>H-NMR trace of macro-CTA P(HEMA-co-DEGMA)-SC(=S)SC<sub>2</sub>H<sub>5</sub> (E0).

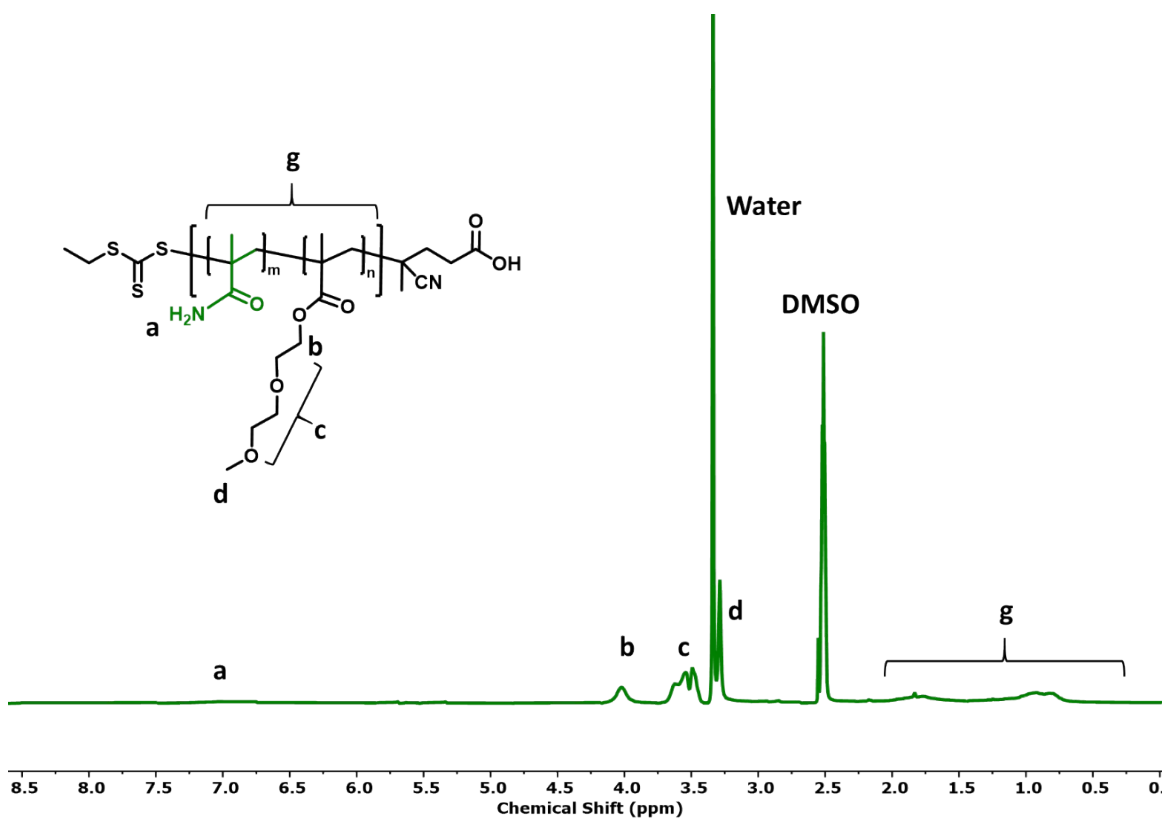


Figure S24. <sup>1</sup>H-NMR trace of macro-CTA P(MAAm-co-DEGMA)-SC(=S)SC<sub>2</sub>H<sub>5</sub> (F0).



Table S16. DLS data for styrene miniemulsion prepared simply by handshaking (10 seconds) with the following formulation (mass ratio constant): [macro-CTA] : [STY] : [SDS] = 25 mg : 35  $\mu$ L : 0.25 mg in 2 mL of deionized water using as macro-CTA C0 (entry 1-4), D0 (entry 5-8), E0 (entry 9-12) and F0 (entry 13-16).

Entry	macro-CTA	Repeat	DLS – 25 °C					DLS – 70 °C				
			Number Mean	$\sigma$	Z-average	$\sigma$	Pdl	Number Mean	$\sigma$	Z-average	$\sigma$	Pdl
			d [nm]					d [nm]				
1	C0	1	561,128	59,15	510	5	0.25	400,174	223	550	7	0.28
2	C0	2	526,195	72	509	1	0.42	361,165	238	481	4	0.27
3	C0	3	598,309	309,3	549	10	0.39	333,131	206	501	15	0.28
4	C0	Average	561,210	261,200	525	21	0.35	364,157	22,31	511	31	0.28
5	D0	1	484	5	540	13	0.16	494	19	565	15	0.14
6	D0	2	468	30	523	1	0.18	467	2	512	3	0.15
7	D0	3	488	13	553	4	0.18	459	57	587	18	0.18
8	D0	Average	492	32	536	12	0.17	473	31	555	35	0.17
9	E0	1	263	34	393	1	0.19	341	56	566	5	0.28
10	E0	2	278	8	493	15	0.32	358	13	456	3	0.24
11	E0	3	344	29	499	1	0.29	289	14	424	1	0.19
12	E0	Average	299	43	470	48	0.27	300	79	502	74	0.23
13	F0	1	145	10	316	78	0.39	201	3	271	8	0.32
14	F0	2	139	3	215	35	0.30	177	5	226	5	0.20
15	F0	3	146	3	278	37	0.41	191	4	263	8	0.33
16	F0	Average	144	6	270	63	0.36	190	11	252	21	0.28

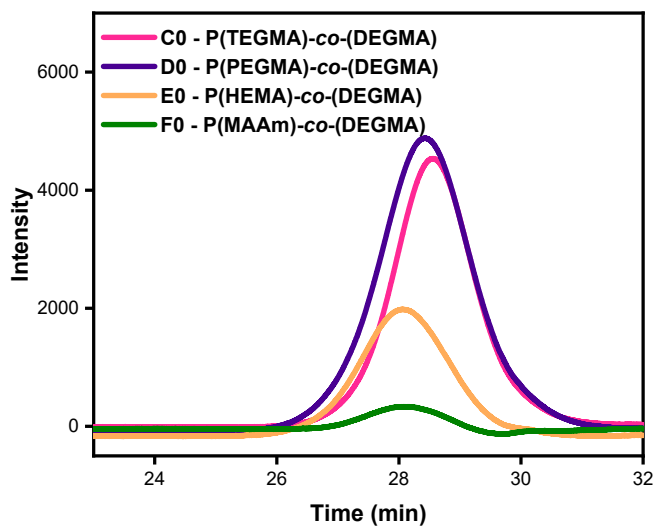


Figure S25. Miniemulsion formed by simple handshaking (10 seconds) with the following formulation: [macro-CTA] : [Water] : [Styrene]= 25 mg : 1 mL : 0.5 mL which has been dephased by centrifugation and the corresponding SEC traces not normalized of an aliquot of the styrene phase (50  $\mu$ L).

Table S17. SEC,  $^1\text{H-NMR}$ , DLS, and inverse pendant drop tensiometry data of macro-CTA P(MAAm-*co*-DEGMA)-SC(=S)SC<sub>2</sub>H<sub>5</sub> (F1 & F2).

Entry	macro-CTA	monomer 1	monomer 2	SEC		$^1\text{H-NMR}$	DLS	Inverse pendant drop tensiometry
				$M_{n,\text{exp}}$	$\bar{D}$	monomer 1 [%]	$T_{\text{cp}}$ [ $^{\circ}\text{C}$ ]	
1	F1	MAAm	DEGMA	7100	1.17	14	30	1.43 (+/- 1.43)
2	F2	MAAm	DEGMA	8800	1.18	35	44	1.32 (+/- 0.12)

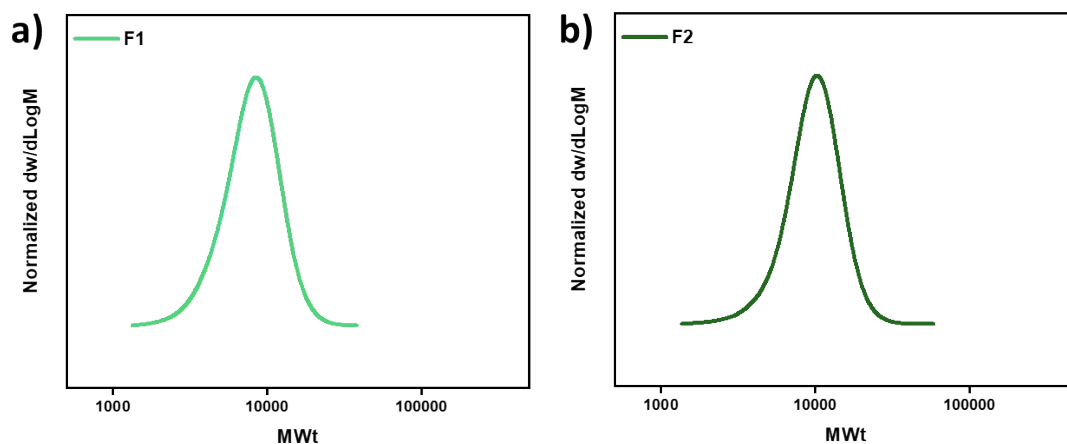


Figure S26. SEC traces and of macro-CTAs a) F1 and b) F2.

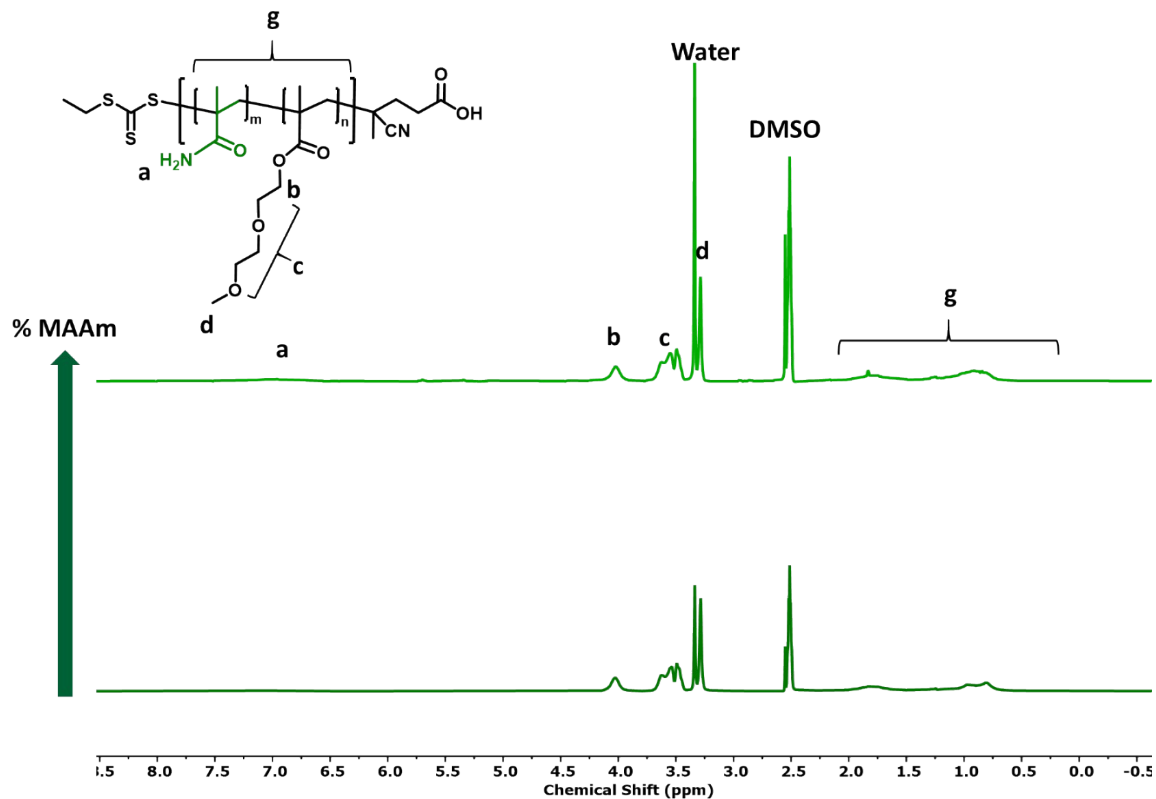


Figure S27.  $^1\text{H-NMR}$  of macro-CTA P(MAAm-co-DEGMA)-SC(=S)SC<sub>2</sub>H<sub>5</sub> (F1 & F2).

Table S18. DLS data of styrene miniemulsion formed by handshaking (10 seconds) at room temperature with the following formulation (mass ratio constant): [macro-CTA] : [STY] : [SDS] = 25 mg : 35  $\mu\text{L}$  : 0.25 mg, in 2 mL of deionized water with macro-CTA F1 (entry 1-4) and F2 (entry 5-8).

Entry	macro-CTA	Repeats	DLS – 25 °C					DLS – 70 °C				
			Number Mean	$\sigma$	Z-average	$\sigma$	Pdl	Number Mean	$\sigma$	Z-average	$\sigma$	Pdl
			d [nm]					d [nm]				
1	F1	1	253	32	480	39	0.33	312	5	500	117	0.34
2	F1	2	377	35	429	13	0.20	343	31	466	11	0.21
3	F1	3	300	21	389	25	0.24	270	15	398	19	0.25
4	F1	Average	352	50	433	50	0.25	310	42	455	69	0.28
5	F2	1	171,3789	39,63	6192	775	0.30	460	26	1041	124	0.52
6	F2	2	188,937	183,999	714	86	1	183	18	433	25	0.52
7	F2	3	159,1360	75,1357	6174	1006	0.63	266	48	2823	195	0.95
8	F2	Average	172,2028	14,1539	4360	3157	0.64	303	142	1432	1242	0.66

Table S19. SEC, <sup>1</sup>H-NMR and DLS data of RAFT miniemulsion polymerization of styrene using F0 as macro-CTA with the following formulation (mass ratio constant): [macro-CTA] : [STY] : [AIBN] : [SDS] = 25 mg : 35 μL : 0.06 mg : 0.25 mg in 2 mL of deionized water. The polymerization was conducted in a preheated oven (70 °C) for 7 hours.

Entry	macro-CTA	$M_n(\text{macro-CTA})$	[macro-CTA] : [STY] : [AIBN] : [SDS]	Time	SEC		NMR		DLS – 70 °C				
					$M_{n,th}$	$M_{n,exp}$	$\bar{D}$	C	Number Mean	$\sigma$	Z-average	$\sigma$	PDI
					[h]			[%]	d [nm]				
1	F0	11000	1:134:0.1:0.2	7	24600	21700	1.22	98	197	2	260	3	0.16

Table S20. SEC, <sup>1</sup>H-NMR, DLS and morphologies data of RAFT miniemulsion polymerization of styrene using F0 as macro-CTA with the following formulation: [macro-CTA] : [STY] : [AIBN] : [SDS] = 25 mg : vary (10, 14 and 35 μL) : 0.06 mg : 0.25 mg in 2 mL of deionized water, entry 1) worms balls, entry 2) worms and 3) vesicles.

Entry	macro-CTA	$M_n(\text{macro-CTA})$	[macro-CTA] : [STY] : [AIBN] : [SDS]	Time	SEC		NMR		Amount of added toluene	Morphologies	DLS - 70 °C				
					$M_{n,th}$	$M_{n,exp}$	$\bar{D}$	C			Number mean	$\sigma$	Z-average	$\sigma$	PDI
					[h]			[%]	μL						
1	F0	11000	1:38:0.1:0.4	6	14000	13200	1.23	76	0	Worms balls	146	9	186	2	0.19
2	F0	11000	1:54:0.1:0.4	6	15300	14000	1.30	70	1	Worms	201	14	232	1	0.12
3	F0	11000	1:134:0.1:0.4	6	21400	19700	1.29	80	10	Vesicles	197	17	309	42	0.25

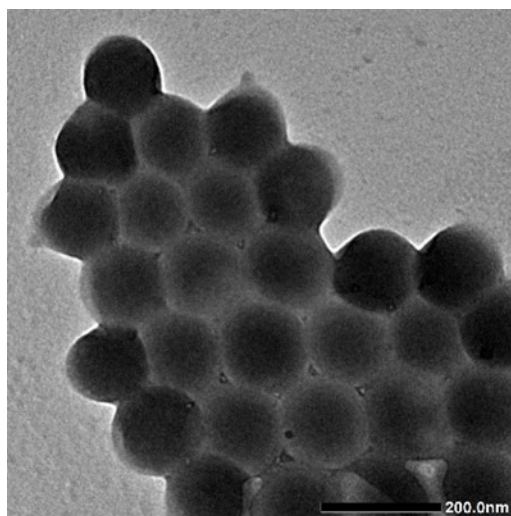


Figure S28. TEM pictures of the latex directly after polymerization with the following conditions: [macro-CTA] : [STY] : [AIBN] : [SDS] = 25 mg : 35 μL : 0.06 mg : 0.25 mg in 2 mL of deionized water for 6 hours with a final of  $M_n = 19700$ ,  $\bar{D} = 1.29$ .

