SUPPORTING INFORMATION:

SHAPE-CONTROLLED NANOPARTICLES FROM A LOW-ENERGY NANOEMULSION

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Materials

Methyl methacrylate (MMA, 99%) and 4-Cyano-4-[(ethylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (ECT, 95%) were 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%), 4,4'-Azobis(4-cyanovaleric acid) (ACPA, >= 98%), Sodium dodecyl sulfate, (SDS, >= 99.0%), Sodium chloride (NaCl, >= 99.5%), Calcium chloride anhydrous ($CaCl_2$, >= 93%), Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Pluronic F108, average M_n ~14,600), Ethyl acrylate (EA, 99%) were obtained from Sigma Aldrich. 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-d6 (99.8%), Chloroform-d ($CDCl_3$, 99.8%), Dimethyl sulfoxide-d6 (DMSO-d6, 99.8%) 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 nanoemulsion experiments. All monomers were purified through basic alumina before being used. Other chemicals were used as received.

Instrumentations

Edmund Bühler TH-30 shaker or specific industry, vortex genie, or IKA, magnetic stirrer or manual shaking by hand were utilized to form the nanoemulsion.

^{1}H nuclear magnetic resonance (^{1}H-NMR) spectra were measured in DMSO-d6 or in a mixture of Acetone-d6 : Chloroform-d (5:1, *v*/*v*) on a Bruker Avance-300 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^{-1}), 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 1.5×10^6 g mol^{-1} (Agilent Technology). Before injection, all samples were passed through 0.45 μm filters and water was removed by drying sample under air (only for nanoemulsion experiments).

Transmission electron microscopy (TEM) images were taken without staining for polystyrene and with Uryl acetate staining (2% concentrated in aqueous, 30 seconds) for PMMA using Jeol JEM 1400 (High Voltage: 80 kV, 120 kV, Emitter: LaB6 crystal) or TF20 Cryo FEI Tecnai (High Voltage: 200 kV, Emitter: Schottky Type) 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.

Cryogenic electron microscopy (Cryo-EM) images were taken on a 120 kV Tecnai Spirit G2 (FEI) TEM under low dose utilizing a 2k x 2k UltraScan CCD camera. Samples were prepared for cryo-EM using a Vitrobot (Thermo Fisher). Briefly, 3.5 μL of sample was placed on a glow-discharged Quantifoil R 3.5/1 holey carbon grid within a humidified chamber at 4 °C, blotted for 3s with a blotting force of -3 before being plunged into liquid ethane. Vitrified samples were transferred to liquid nitrogen for storage prior to imaging.

Dynamic light scattering (DLS) measurements were carried out using a Malvern Zetasizer Nano Series ZS, employing a backscatter detection system at 173 °C angle and a standard laser (4 mW, 633 nm) or using Malvern Zetasizer Advance Series-Pro (Red Label, 10 mW, 633 nm). The sample refractive index (RI) was set at 1.59 for

styrene and 1.49 for methyl methacrylate latexes. The dispersant viscosity and RI were set to 0.89 Ns m^{-2} and 1.33, respectively. To determine particle size, all measurements were carried out without dilution whereas solutions were diluted ten times before running zeta potential analysis.

Inverse Pendant and Sessile Drop 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). The experimental setup is detailed in Figure S4a for the inverse pendant drop and in Figure S4b for the sessile drop measurement.

Study of worms degradation was performed using Sonicator Bandelin- SONOREX (U= 230 V, 60 Hz, I= 0.6 A, P= 480W, f= 35 kHz).

Table S1: ^{1}H-NMR and SEC data of macro-CTA P(DEGMA-*co*-HPMA)-SC(=S)SC_2H_5.

			SEC		Conversion (%) by NMR		Repeat unit (n)			
Entry	[ECT] : [DEGMA] : [HPMA] : [ACPA]	Time (h)	$M_{n(SEC)}$	Đ	DEGMA	HPMA	DEGMA	HPMA	% HPMA	$M_{n(Theo)}$
1	1 : 40 : 20 : 0.08	8.5	8900	1.15	78	33	31	7	18	7000

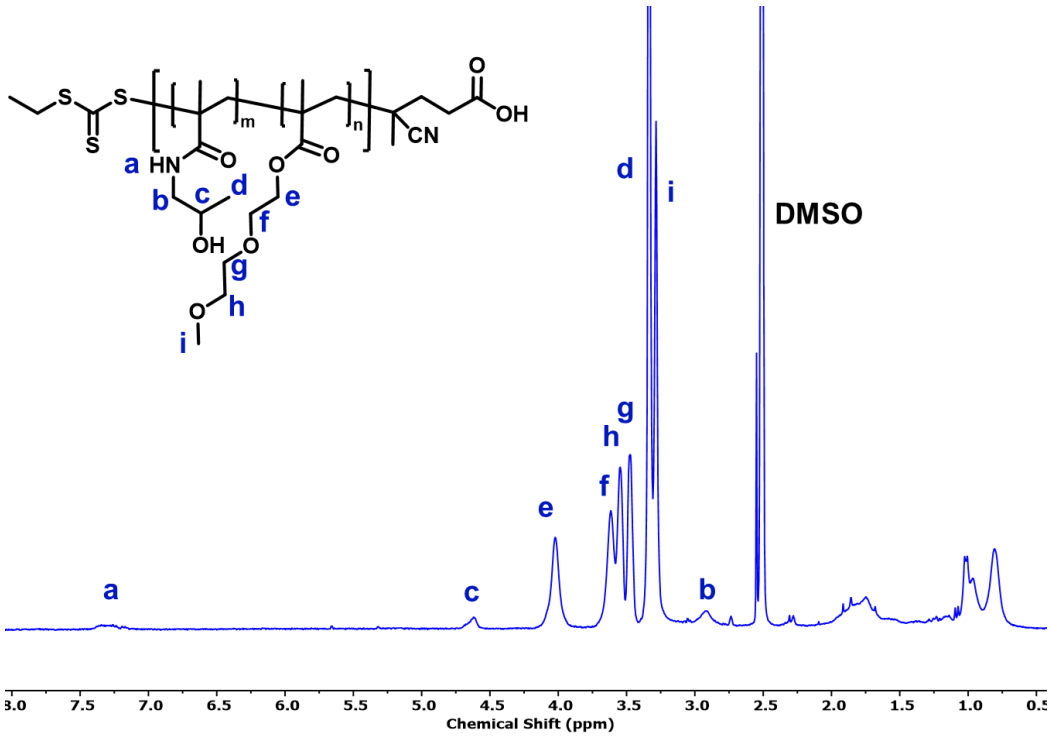

Figure S1: ^{1}H-NMR spectrum of macro-CTA P(DEGMA-*co*-HPMA)-SC(=S)SC_2H_5 in DMSO-d6.

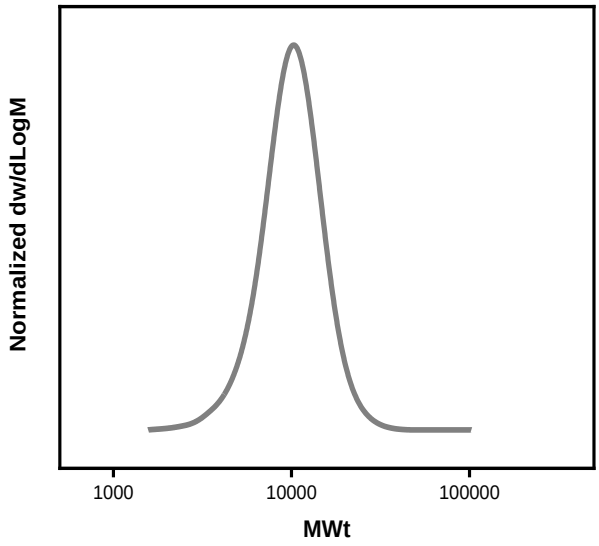

Figure S2: SEC trace of the macro-CTA P(DEGMA-*co*-HPMA) SC(=S)SC_2H_5.

Table S2: DLS data for styrene nanoemulsion prepared simply by shaking by hand (10 seconds, entry 1, 2, 3), vortexing/vibrating (10 seconds, speed 10, entry 4), stirring (10 seconds, 300 rpm, entry 5) or using a mechanical shaker (entry 6, 300 rpm) with the following formulation: [Macro-CTA] : [STY] : [SDS] = 25 mg : 35 µL : 0.25 mg in 2 mL of water.

Entry	Mixing method	Temperature	DLS		
			Number Mean	Z-Average	PdI
		[°C]	d [nm]	d [nm]	
1	Shake	25	183	251	0.21
2	Shake	25	173	250	0.25
3	Shake	25	180	268	0.22
4	Vortexer/Vibrator	25	170	251	0.37
5	Stir	25	179	264	0.19
6	Mechanical Shaker	25	172	267	0.22

Table S3: DLS data for styrene nanoemulsion prepared simply by shaking (2 seconds, entry 1 and 1 minute, entry 2) with the following formulation: [Macro-CTA] : [STY] : [SDS] = 25 mg : 35 μL : 0.25 mg in 2 mL of water.

Entry	Shaking Time	Temperature	DLS		
			Number Mean	Z-Average	PdI
		°C	d [nm]	d [nm]	
1	2 secs	25	214	309	0.37
2	1 min	25	179	242	0.42

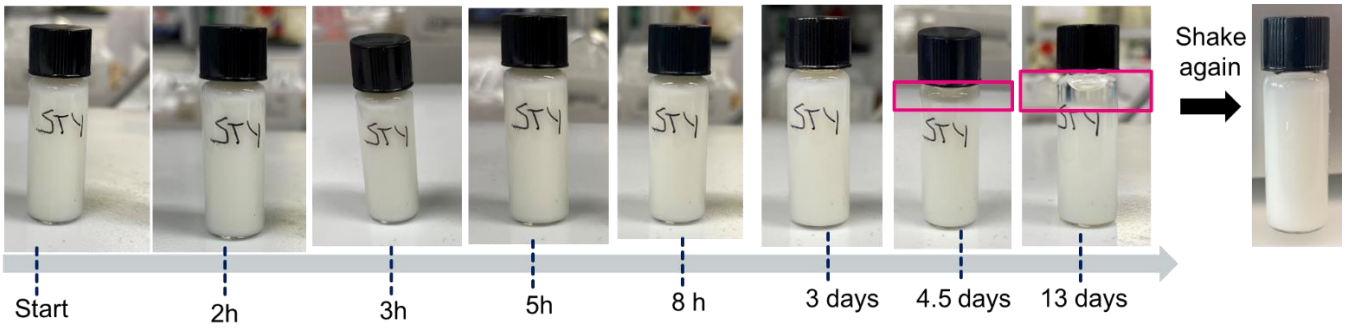

Figure S3: Styrene nanoemulsion stability study with the following formulation: [Macro-CTA] : [STY] : [SDS] = 25 mg : 35 μL : 0.25 mg in 2 mL of water, shaken for 10 seconds at room temperature. The vial was left on the bench for 13 days in total and shaken again after 13 days.

Table S4: DLS data for styrene nanoemulsion prepared simply by shaking (10 seconds) with the following formulation: [Macro-CTA] : [STY] : [SDS] = 25 mg : 35 μL : 0.25 mg in 2 mL of water. The vial was left on the bench for 13 days and then, shaken again by hand for 10 seconds.

Entry	Temperature	DLS		
		Number Mean	Z-Average	PdI
	°C	d [nm]	d [nm]	
1	25	157	197	0.19

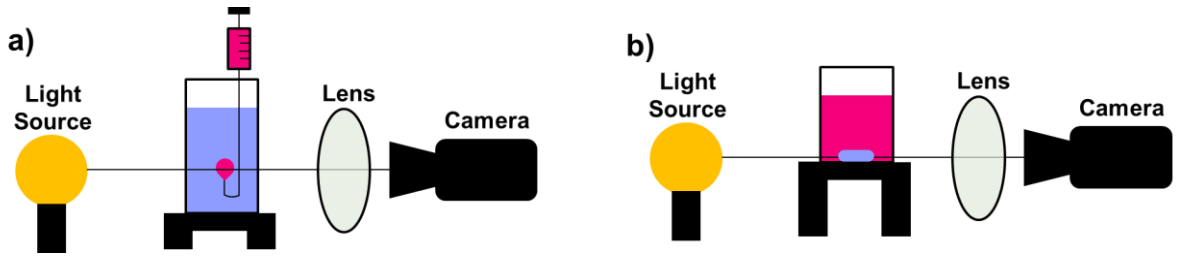

Figure S4: Experimental set-up for a) the inverse pendant drop method where a styrene droplet (pink) is stabilized at the end of a flat needle tip immersed in aqueous solution (blue) and b) the sessile drop measurement where an aqueous droplet (blue) is stabilized on a glass surface and immersed in styrene. It is noted that for the inverse pendant drop method, the droplets were imaged upside down and the resulting pictures were flipped before analysis with the MATLAB code.

Table S5: Summary of interfacial tension data obtained by the inverse pendant drop measurement as described in Figure S4a.

	Continuous phase				Droplet	Interfacial Tension	
Entry	Macro-CTA		SDS			(mN/m)	
	mg/mL	mM	mg/mL	mM			
1	0	0	0	0	Styrene	32.000	(+/-0.668)
2	12.5	1.50	0	0	Styrene	0.338	(+/-0.990)
3	12.5	1.50	0.125	0.43	Styrene	0.577	(+/-0.071)
4	*Pluronic F108 12.5	0.86	0	0	Styrene	9.24	(+/-0.430)
5	0	0	0.125	0.43	Styrene	26.012	(+/-0.0354)

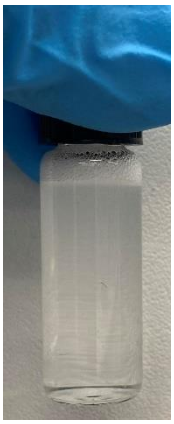

Figure S5: Digital photo showing phase separation between styrene (35 μL) and an aqueous solution of SDS (25 mg of SDS in 2 mL of deionized water), after shaking for 10 seconds, at room temperature. Phase separation was observed within 20 seconds.

Table S6: DLS data of styrene emulsion formed without SDS at room temperature, simply by shaking (10 seconds) with the following formulation: [Macro-CTA] : [STY] : [SDS] = 25 mg : 35 μL : 0, in 2 mL of deionized water. In this special case, a range of sizes are given per the poor reproducibility of the measurement.

Entry	Temperature	DLS		
		Number Mean	Z-Average	PdI
	°C	d [nm]	d [nm]	
1	25	Range 399 to 559	Range 580 to 796	Range 0.34 to 0.39

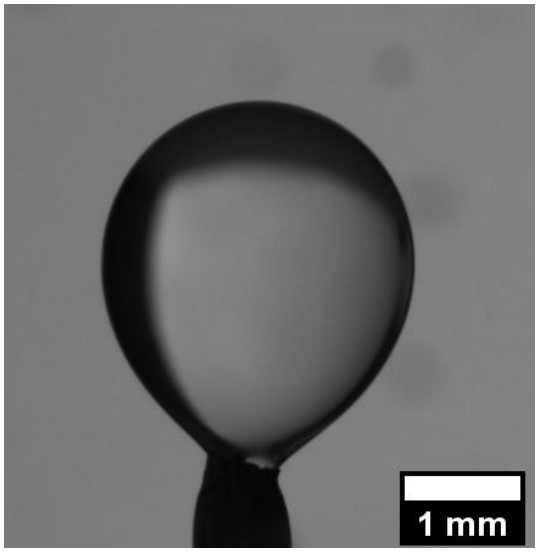

Figure S6: Inverse pendant drop example picture utilized to determinate interfacial tension for a styrene droplet in deionized water + Pluronic F108 (0.86 mM). The picture was taken as described in Figure S4a and flipped before analyzing with the MATLAB code.

Figure S7: Picture illustrating a styrene droplet in deionized water + Pluronic F108 (0.86 mM). Phase separation was observe after 2 hours and no latex was formed upon shaking.

Table S7: Summary of interfacial tension obtained with the sessile drop measurement as described in figure S4b.

	Continuous phase				Droplet	Interfacial Tension	
Entry	Macro-CTA		SDS			(mN/m)	
	mg/mL	mM	mg/mL	mM			
1	12.5	1.50	0	0	Styrene	0.150	(+/-0.048)
2	12.5	1.50	0.125	0.43	Styrene	0.149	(+/-0.072)

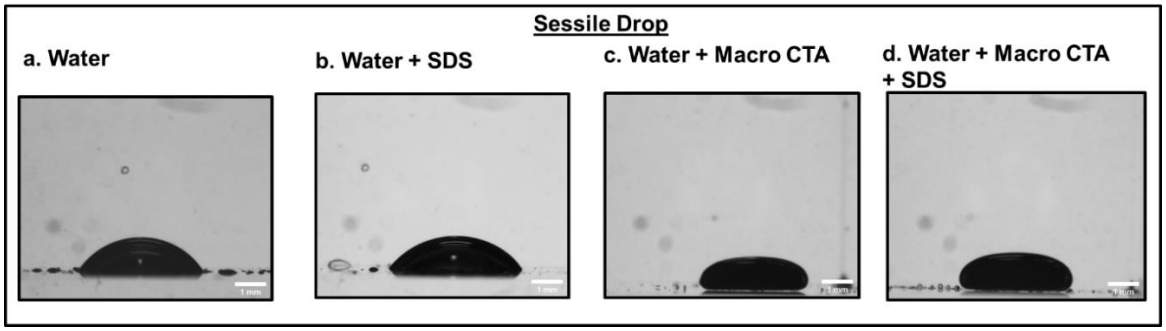

Figure S8: Pictures obtained with the sessile drop measurement as described in figure S4b. a) water droplet and b) water + styrene, c) water + macro-CTA, d) water + macro-CTA + SDS. Interfacial tension was measured only for c & d with the sessile drop method and a & b are used for direct visual comparison.

Table S8: Zeta potential data by DLS for styrene nanoemulsion prepared simply by shaking (10 seconds).

			DLS	
Entry	[Macro-surfactant] : [STY] : [SDS]	Temperature	Zeta potential	Std. deviation
		°C	mV	mV
1	25 mg : 35 µL: 0.25 mg	25	-53.3	-10.4
2	25 mg : 35 µL: 0 mg	25	-20 .3	-5.2

Table S9: DLS data (Zetasizer Pro, red label) for the subsequent addition of monovalent, NaCl, and divalent $CaCl_2$ salts into a nanoemulsion of styrene prepared at room temperature, simply by shaking (10 seconds), with the following formulation: [Macro-CTA] : [STY] : [SDS] = 25 mg : 35 μL : 0.25 mg, in 2 mL of water.

					DLS		
Entry	**Salt**	**Salt concentration**			**Number mean**	**Z-Average**	**PDI**
		[mM]	[mg/2mL]	[mg/mL]	d [nm]	d [nm]	
1		0	0	0	189	248	0.25
2	NaCl	0.9	0.1	0.05	181	289	0.45
3	NaCl	4.3	0.5	0.25	172	281	0.40
4	NaCl	8.5	1	0.5	185	263	0.34
5	NaCl	21.1	2.5	1.25	177	268	0.33
6	NaCl	25.3	3	1.5	79, 254	389	0.50
7	NaCl	41.7	5	2.5	165, 623, 4900	782	0.68
8	NaCl	81.5	10	5	4500	5200	0.12
8	$CaCl_2$	0	0	0	194	275	0.27
9	$CaCl_2$	0.5	0.1	0.05	196	286	0.26
10	$CaCl_2$	2.2	0.5	0.25	210	316	0.33
11	$CaCl_2$	4.5	1	0.5	238	338	0.24
12	$CaCl_2$	6.7	1.5	0.75	399, 5000	714	0.47
13	$CaCl_2$	8.9	2	1	1400, 5500	2300	0.42

Table S10: DLS data of a styrene nanoemulsion formed by shaking (10 seconds) at room temperature and then measured at room temperature (entry 1), 70 °C (entry 2), 80 °C (entry 3), 90 °C (entry 4), with the following formulation: [Macro-CTA] : [STY] : [SDS] = 25 mg : 35 µL : 0.25 mg, in 2 mL of water.

Entry	Temperature	DLS		
		Number Mean	Z-Average	PdI
	°C	d [nm]	d [nm]	
1	25	171	272	0.31
2	70	181	264	0.27
3	80	224	359	0.47
4	90	223	935	0.59

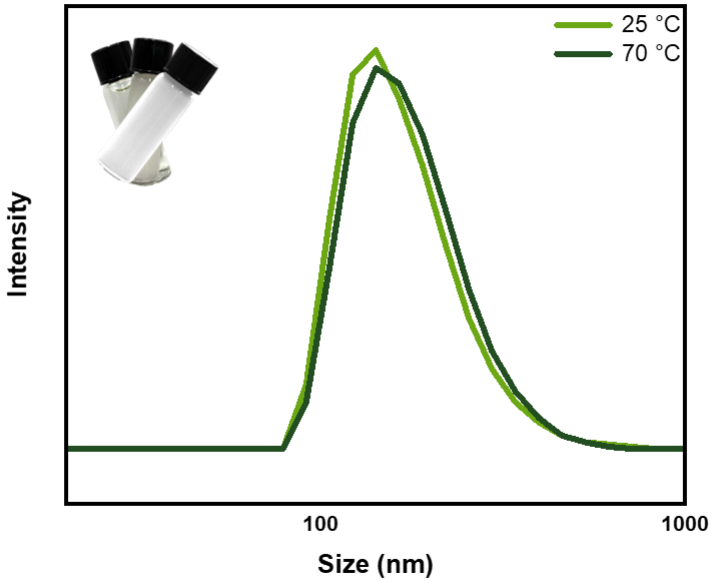

Figure S9: DLS size (number mean) of a styrene nanoemulsion formed by shaking (10 seconds) at room temperature then measured at room temperature (light green) or at 70 °C (dark green) with the following formulation: [Macro-CTA] : [STY] : [SDS] = 25 mg : 35 µL : 0.25 mg, in 2 mL of water.

Figure S10: Digital photo of an aqueous solution of SDS (0.25 mg of SDS in 2 mL of deionized water) and macro-CTA (25 mg) with styrene (35 µL) on the top (without shaking).

Table S11: DLS data of styrene (nano)emulsion with the following formulation: [Macro-CTA] : [STY] : [SDS] = 25 mg : 200 µL : 0.25 mg, in 1.8 mL of water. In entry 1, SDS is dissolved together with macro-CTA in the aqueous phase before shaking. In entry 2, only SDS is dissolved in the aqueous phase and macro-CTA in the oil phase (styrene) before shaking.

Entry	Aqueous phase (AP) or Oil phase (Ol)	Temperature	DLS		
			Number Mean	Z-Average	PdI
		°C	d [nm]	d [nm]	
1	Maco-CTA + SDS in AP	25	142	234	0.36
2	SDS in AP and macro-CTA in OP	25	4400	4500	0.26

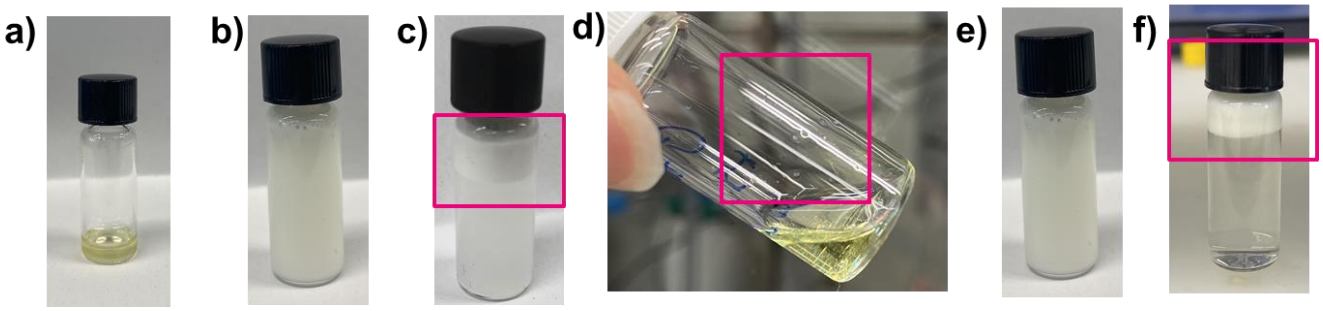

Figure S11: Pictures of a) macro-CTA (25mg) dissolved in styrene (200 µL) at room temperature, b) the resulting emulsion after adding an aqueous solution of SDS (0.25 mg in 1.8 mL of deionized water) to the previous vial (Picture a)) and shaking for 10 seconds, c) the creamed emulsion after 1 hours d) macro-CTA (25mg) + SDS (0.25 mg) dissolved in styrene (200 µL) at room temperature where solid particle were observed, e) the resulting emulsion after adding water (1.8 mL of deionized water) to a 2 ml vial containing SDS, macro-CTA and styrene (Picture d) and shaking for 10 seconds, e) the creamed emulsion after 1 hours.

Table S12: Inverse pendant drop example picture utilized to determinate interfacial tension for a styrene (100 µL/mL) + macro-CTA (12.5 mg/mL) droplet in deionized water + SDS (0.125 mg/mL). The picture was taken as described in Figure S4a and flipped before analyzing with the MATLAB code.

	Continuous phase		Droplet			Interfacial Tension	
Entry	SDS		Macro CTA		Styrene	(mN/m)	
	mg/mL	mM	mg/mL	mM	µL/mL		
1	0.125	0.43	12.5	1.5	100	0.565	(+/-0.440)

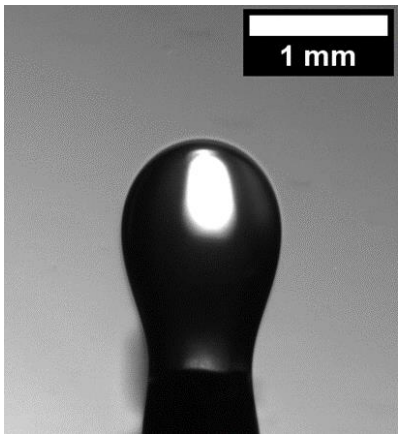

Figure S12: Inverse pendant drop example picture utilized to determinate interfacial tension for a styrene + macro-CTA (1.5 mM) droplet in deionized water + SDS (0.43 mM). The picture was taken as described in Figure S4a and flipped before analyzing with the MATLAB code.

Table S13: DLS data of a styrene nanoemulsion formed by shaking (10 seconds) at room temperature with the following formulation: [Macro-CTA] : [STY] : [SDS] = (entry 1) 12.5 mg, (entry 2) 25 mg, (entry 3), 50 mg : 35 μL : 0.25 mg, in 2 mL of water.

Entry	Amount of CTA	Temperature	DLS		
			Number Mean	Z-Average	PdI
		[°C]	d [nm]	d [nm]	
1	12.5 mg	25	186	276	0.41
2	25 mg	25	187	274	0.34
3	50 mg	25	206	311	0.32

Table S14: DLS data of a styrene nanoemulsion formed by shaking (10 seconds) at room temperature with decreasing amount of SDS while the ratio between [Macro-CTA] : [STY] was maintained to 25 mg: 35 µL in 2 mL of water.

Entry		SDS	SDS	Temperature	DLS		
					Number	Z-Average	PDI
		mM	mg/2mL	[°C]	d [nm]	d [nm]	d [nm]
1	CMC	8.5	4.9	25	1022	3200	0.7
2		6.94	4	25	97	159	0.34
3		4.34	2.5	25	131	179	0.14
4		1.74	1	25	150	214	0.28
5		0.87	0.5	25	172	244	0.23
6		0.43	0.25	25	185	265	0.22
7		0.04	0.025	25	301	402	0.22
8		0.00	0.0025	25	322	447	0.28

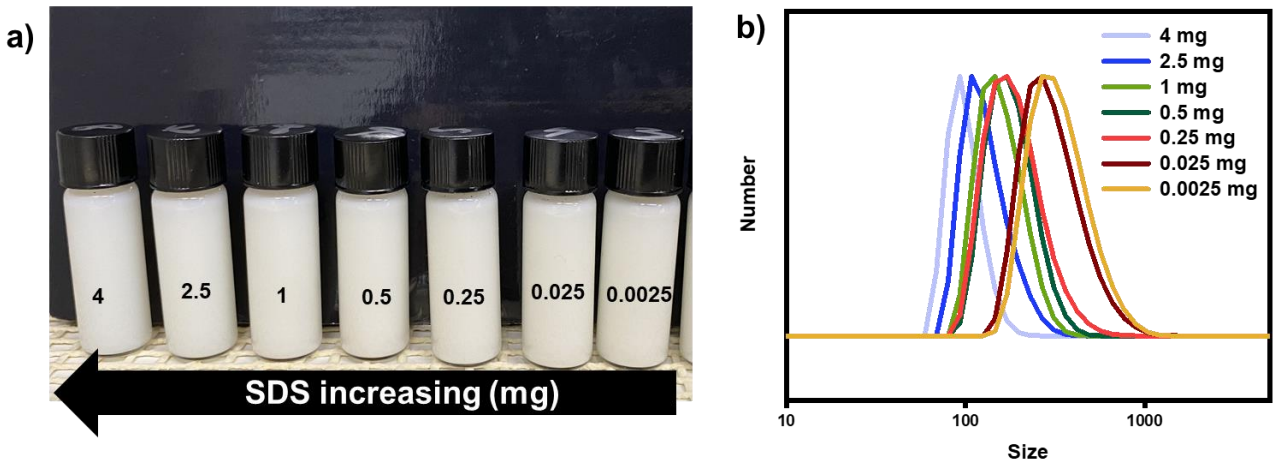

Figure S13: a) Pictures illustrating styrene nanoemulsion with decreasing amount of SDS, b) DLS traces (number) of a styrene nanoemulsion formed by shaking (10 seconds) at room temperature with decreasing amount of SDS while the ratio between [Macro-CTA] : [STY] was maintained to 25 mg: 35 µL in 2 mL of water.

Table S15: DLS data of a styrene nanoemulsion formed by shaking (10 seconds) at room temperature and then measured at room temperature (entry 1) and at 70 °C (entry 2) with the following formulation: [Macro-CTA] : [STY] : [SDS] : [AIBN] = 1 : 108 : 0.3 : 0.1, in 2 mL of water.

Entry	Temperature	DLS		
		Number Mean	Z-Average	PdI
	°C	d [nm]	d [nm]	
1	25	188	246	0.26
2	70	182	271	0.26

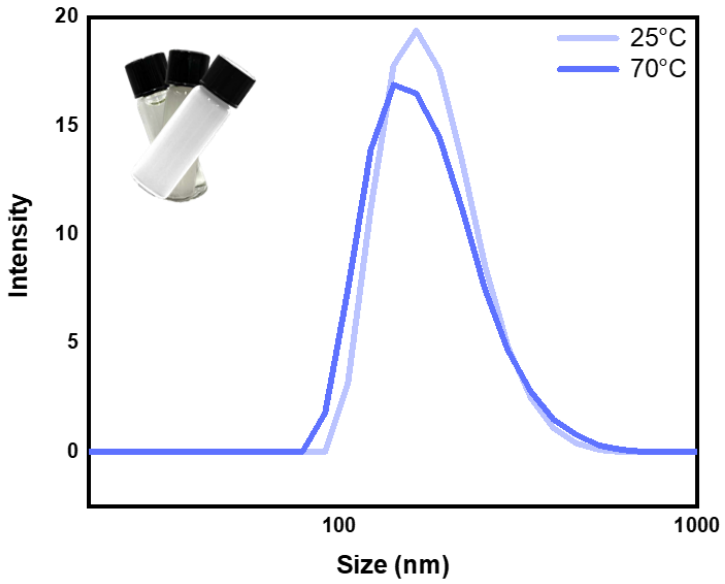

Figure S14: DLS size (number mean) of a styrene nanoemulsion formed by shaking (10 seconds) at room temperature then measured at room temperature (light blue) or at 70 °C (dark blue) with the following formulation: [Macro-CTA] : [STY] : [SDS] : [AIBN] = 1 : 108 : 0.3 : 0.1 in 2 mL of water.

Table S16: SEC, ^{1}H-NMR, DLS (number mean) and TEM data of RAFT nanoemulsion polymerization of styrene using P(DEGMA-*co*-HPMA)-SC(=S)SC_2H_5 as macro-CTA. Polymerization conditions are the following: [Macro-CTA] : [STY] : [SDS] : [AIBN] = 1 : 108 : 0.3 : 0.1 in 2 ml water. All polymerizations were carried out in a 70 °C preheated oven.

		SEC		NMR	DLS		TEM
Entry	**Time (h)**	$M_{n,exp}$	$Đ$	**C(%)**	**d [nm]**	**PdI**	**d [nm]**
1	0	8900	1.15	--	181	0.27	--
2	1	8900	1.19	<1	175	0.20	--
3	2	10200	1.18	11	161	0.16	--
4	3	11900	1.25	34	181	0.10	--
5	4	13800	1.23	56	172	0.11	--
6	5	16300	1.29	76	170	0.13	--
7	6	18400	1.28	99	176	0.12	180

Table S17: SEC and DLS of RAFT (nano)emulsion polymerization of styrene using P(DEGMA-*co*-HPMA)-SC(=S)SC_2H_5 as macro-CTA and without SDS. Polymerization conditions are the following: [Macro-CTA] : [STY] : [SDS] : [AIBN] = 1 : 108 : 0 : 0.1 in 2 ml water. Polymerization was carried out in a 70 °C preheated oven.

		SEC		DLS	
Entry	Time (h)	$M_{n,exp}$	$Đ$	d [nm]	PdI
1	6	13000	1.25	561	0.24

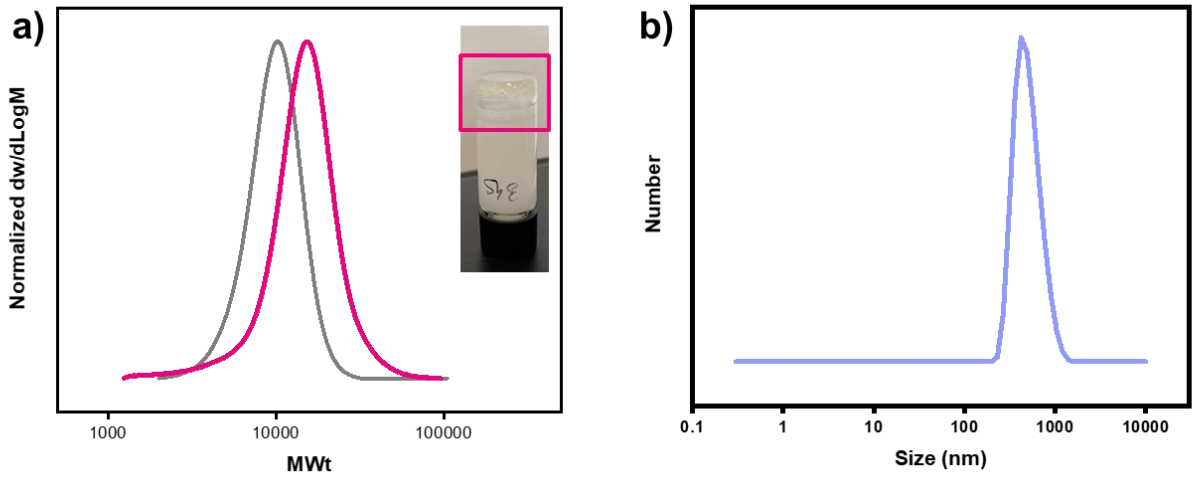

Figure S15: a) SEC and b) DLS traces of RAFT (nano)emulsion polymerization of styrene using P(DEGMA-*co*-HPMA)-SC(=S)SC_2H_5 as macro-CTA and without SDS. Polymerization conditions are the following: [Macro-CTA] : [STY] : [SDS] : [AIBN] = 1 : 108 : 0 : 0.1 in 2 ml water. Polymerization was carried out in a 70 °C preheated oven.

Table S18: SEC data of RAFT nanoemulsion polymerization of styrene using P(DEGMA-*co*-HPMA)-SC(=S)SC_2H_5 as macro-CTA performed with three different headspaces (entry 1, a sixth, entry 2, a third and entry 3, half). Polymerization conditions are the following: [Macro-CTA] : [STY] : [SDS] : [AIBN] = 1 : 108 : 0.3 : 0.1 in 2 ml water. Polymerization was carried out in a 70 °C preheated oven.

Entry	Headspace	[Macro-CTA] : [STY] : [AIBN] : [SDS]	Time (h)	$M_{n(SEC)}$	$Đ$
1	1/6	1 : 108 : 0.1 : 0.3	8	20000	1.40
2	1/3	1 : 108 : 0.1 : 0.3	8	20300	1.36
3	1/2	1 : 108 : 0.1 : 0.3	8	19700	1.38

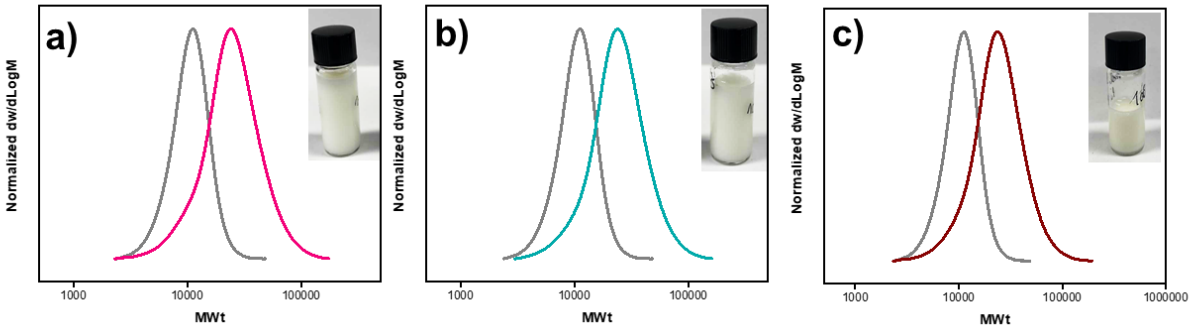

Figure S16: SEC traces of RAFT nanoemulsion polymerization of styrene using P(DEGMA-*co*-HPMA)-SC(=S)SC_2H_5 as macro-CTA performed with three different headspaces a) a sixth, b) a third and c) half. Polymerization conditions are the following: [Macro-CTA] : [STY] : [SDS] : [AIBN] = 1 : 108 : 0.3 : 0.1 in 2 ml water. Polymerization was carried out in a 70 °C preheated oven.

Table S19: SEC traces of RAFT nanoemulsion polymerization of styrene using P(DEGMA-*co*-HPMA)-SC(=S)SC_2H_5 as macro-CTA. The vial was not shaken before polymerization and placed for 6 hours in a pre-heated oven (70 °C).

			SEC	
Entry	**[Macro-CTA] : [STY] : [AIBN] : [SDS]**	**Time (h)**	$M_{n,exp}$	$Đ$
1	1 : 108 : 0.1 : 0.3	6	9000	1.17

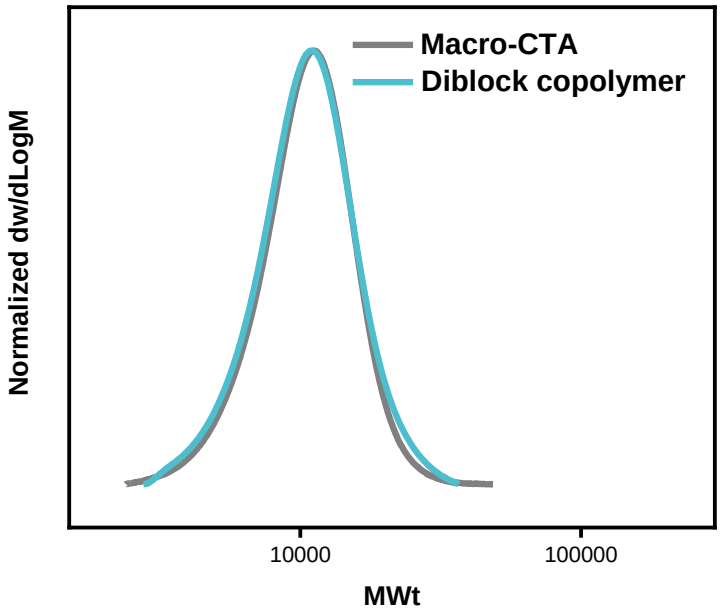

Figure S17: SEC traces of RAFT nanoemulsion polymerization of styrene using P(DEGMA-*co*-HPMA)-SC(=S)SC_2H_5 as macro-CTA. Polymerization conditions are the following: [Macro-CTA] : [STY] : [SDS] : [AIBN] = 1 : 108 : 0.3 : 0.1 in 2 ml deionized water. The vial was not shaken before polymerization.

Table S20: SEC and DLS (number mean) data of RAFT emulsion polymerization of styrene using P(DEGMA-*co*-HPMA)-SC(=S)SC_2H_5 as macro-CTA. The vial was not shaken before placing in a preheated oil bath (70 °C) and stirred at 300 rpm for 6 hours.

			SEC		DLS	
Entry	[Macro-CTA] : [STY] : [AIBN] : [SDS]	Time (h)	$M_{n,exp}$	Đ	d [nm]	PDI
1	1 : 108 : 0.1 : 0.3	6	13400	1.99	630	0.22

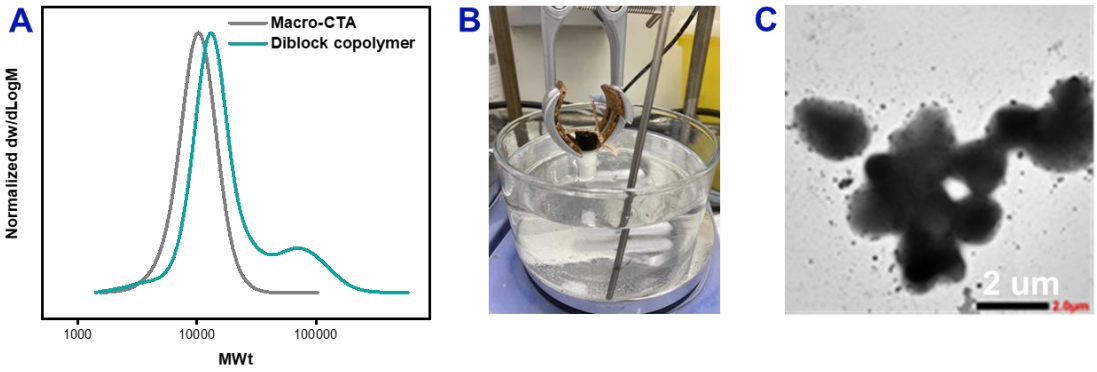

Figure S18: RAFT emulsion polymerization of styrene using P(DEGMA-*co*-HPMA)-SC(=S)SC_2H_5 as macro-CTA. Polymerization conditions are the following: [Macro-CTA] : [STY] : [SDS] : [AIBN] = 1 : 108 : 0.3 : 0.1 in 2 ml deionized water. The vial was not shaken before placing in a preheated oil bath (70 °C) and stirred at 300 rpm for 6 hours. A) SEC traces, B) experimental set up, C) TEM of the final latex.

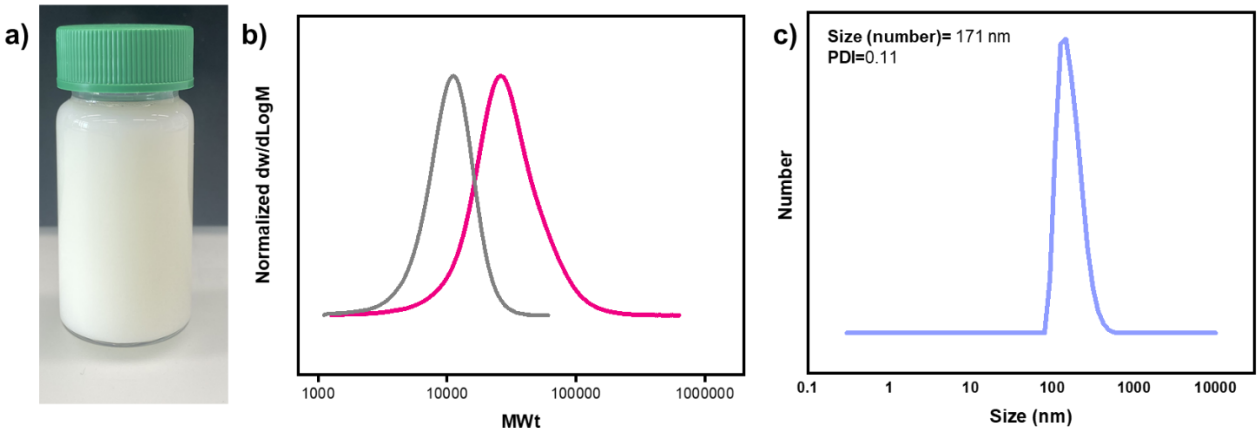

Figure S19: a) Scale up of the nanoemulsion in a 20 mL vial photo, b) SEC trace of RAFT (nano)emulsion scaled up polymerization of styrene using P(DEGMA-*co*-HPMA)-SC(=S)SC_2H_5 as macro-CTA. Polymerization conditions are the following: [Macro-CTA] : [STY] : [SDS] : [AIBN] = 1 : 108 : 0 : 0.1 in 20 ml water. Polymerization was carried out in a 70 °C preheated oven, c) DLS trace of the resulting nanoemulsion at 25 degrees.

Table S21: DLS data of RAFT nanoemulsion polymerization of styrene using P(DEGMA-*co*-HPMA)-SC(=S)SC_2H_5 as macro-CTA with different amount of styrene. Polymerization conditions are the following, entries 1 & 4, [Macro-CTA] : [STY] : [SDS] : [AIBN]= 1 : 22 : 0.3 : 0.1, entries 2 & 5, [Macro-CTA] : [STY] : [SDS] : [AIBN] = 1 : 44 : 0.3 : 0.1 and entries 3 & 6, [Macro-CTA] : [STY] : [SDS] : [AIBN] = 1 : 108 : 0.3 : 0.1 in 2 ml of deionized water. The vials were shaken at room temperature for 10 seconds.

Entry	Amount of styrene	Temperature	DLS		
			Number Mean	Z-Average	PdI
	[µL]	[°C]	d [nm]	d [nm]	
1	7	25	184	226	0.11
2	14	25	181	243	0.23
3	35	25	174	272	0.31
4	7	70	200	263	9.14
5	14	70	192	249	0.18
6	35	70	181	264	0.27

Table S22: TEM Morphologies and SEC data of RAFT nanoemulsion polymerization of styrene using P(DEGMA-*co*-HPMA)-SC(=S)SC_2H_5 as macro-CTA. The vials were shaken at room temperature for 10 seconds before polymerization. All polymerizations were carried out for 6 hours in a preheated oven (70 °C).

				SEC		Amont of toluene added	TEM
Entry	Time (h)	Name	[Macro-CTA] : [STY] : [AIBN] : [SDS]	$M_{n,exp}$	Đ	(for 100 uL of latex)	Morphologies
1	6	B1	1 : 22 : 0.1 : 0.3	10800	1.18	0.5	Small spheres
2	6	B2	1 : 44 : 0.1 : 0.3	12100	1.19	0.1	Worms balls
3	6	B2	1 : 44 : 0.1 : 0.3	12100	1.19	0.8	Worms
4	6	B3	1: 108 : 0.1: 0.3	18300	1.28	10	Vesicles

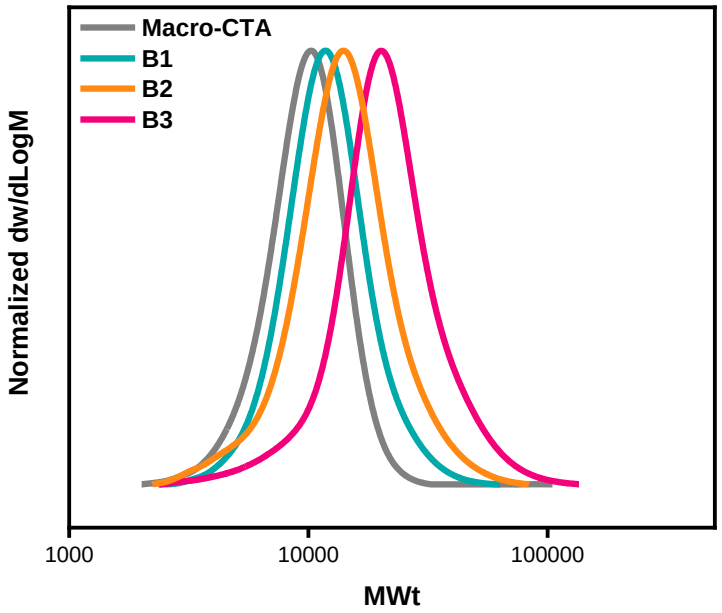

Figure S20: SEC traces of RAFT nanoemulsion polymerization of styrene using P(DEGMA-*co*-HPMA)-SC(=S)SC_2H_5 as macro-CTA. The vials were shaken at room temperature for 10 seconds before polymerization. All polymerizations were carried out for 6 hours in a preheated oven (70 °C). Polymerization conditions are the following, green trace [Macro-CTA] : [STY] : [SDS] : [AIBN]= 1 : 22 : 0.3 : 0.1, orange trace, [Macro-CTA] : [STY] : [SDS] : [AIBN] = 1 : 44 : 0.3 : 0.1 and pink trace [Macro-CTA] : [STY] : [SDS] : [AIBN] = 1 : 108 : 0.3 : 0.1 in 2 ml of deionized water.

Table S23: TEM Morphologies and SEC data of RAFT nanoemulsion polymerization of styrene using P(DEGMA-*co*-HPMA)-SC(=S)SC_2H_5 as macro-CTA. The vials were shaken at room temperature for 10 seconds before polymerization. Polymerization conditions are the following, entry 1, [Macro-CTA] : [STY] : [SDS] : [AIBN]= 1 : 50 : 0.3 : 0.1, entry 2, [Macro-CTA] : [STY] : [SDS] : [AIBN] = 1 : 61 : 0.3 : 0.1 and entry 3, [Macro-CTA] : [STY] : [SDS] : [AIBN] = 1 : 263 : 0.3 : 0.1 in 2 ml of deionized water. All polymerizations were carried out in a preheated oven (70 °C).

		Amont of Styrene	SEC		NMR	TEM
Entry	Time (h)		$M_{n,exp}$	$Đ$	C(%)	d [nm]
1	4	16	10400	1.21	58	Worms balls
2	5	20	11600	1.28	79	Worms
3	5	85	19500	1.29	56	Vesicles

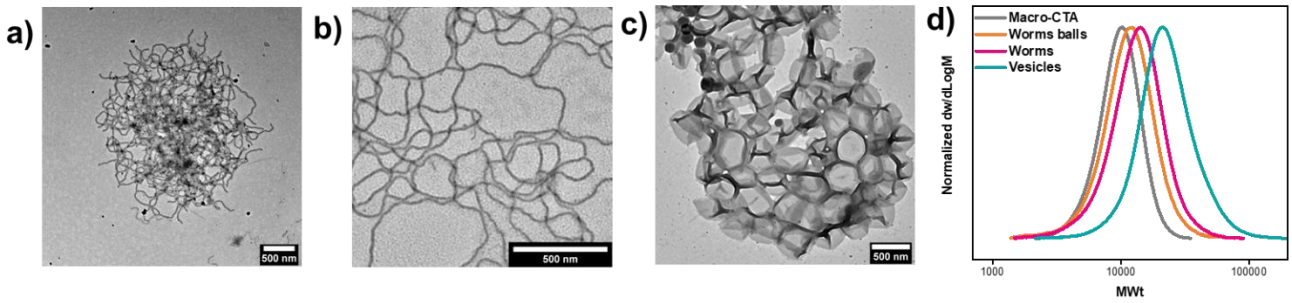

Figure S21: SEC traces of RAFT nanoemulsion polymerization of styrene using P(DEGMA-*co*-HPMA)-SC(=S)SC_2H_5 as macro-CTA. The vials were shaken at room temperature for 10 seconds before polymerization. All polymerizations were carried out in a preheated oven (70 °C). Polymerization conditions are the following, orange trace [Macro-CTA] : [STY] : [SDS] : [AIBN]= 1 : 50 : 0.3 : 0.1, pink trace, [Macro-CTA] : [STY] : [SDS] : [AIBN] = 1 : 61 : 0.3 : 0.1 and green trace [Macro-CTA] : [STY] : [SDS] : [AIBN] = 1 : 263 : 0.3 : 0.1 in 2 ml of deionized water.

Table S24: SEC data of nanoworms reproducibility via RAFT nanoemulsion polymerization of styrene using P(DEGMA-*co*-HPM)-SC(S)SC_2H_5 as macro-CTA. The vials were shaken at room temperature for 10 seconds before polymerization. All polymerizations were carried out for 6 hours in a preheated oven (70 °C).

				SEC		Amont of toluene added	TEM
Entry	Time (h)	Name	[Macro-CTA] : [STY] : [AIBN] : [SDS]	$M_{n,exp}$	Đ	(for 100uL of latex)	Morphology
1	6	B4	1 : 44 : 0.1 : 0.3	12200	1,31	1	Worms
2	6	B5	1 : 44 : 0.1 : 0.3	12200	1,27	1	Worms
3	6	B6	1 : 44 : 0.1 : 0.3	12600	1.23	1	Worms

Table S25: SEC data of RAFT nanovesicles reproducibility via nanoemulsion polymerization of styrene using P(DEGMA-*co*-HPM)-SC(S)SC_2H_5 as macro-CTA. The vials were shaken at room temperature for 10 seconds before polymerization. All polymerizations were carried out for 6 hours in a preheated oven (70 °C).

				SEC		Amont of toluene added	TEM
Entry	Time (h)	Name	[Macro-CTA] : [STY] : [AIBN] : [SDS]	$M_{n,exp}$	Đ	(for 100uL of latex)	Morphology
1	6	B7	1 : 108 : 0.1 : 0.3	18900	1.36	10	Vesicles
2	6	B8	1 : 108 : 0.1 : 0.3	18300	1.26	10	Vesicles
3	6	B9	1 : 108: 0.1 : 0.3	18500	1.28	10	Vesicles

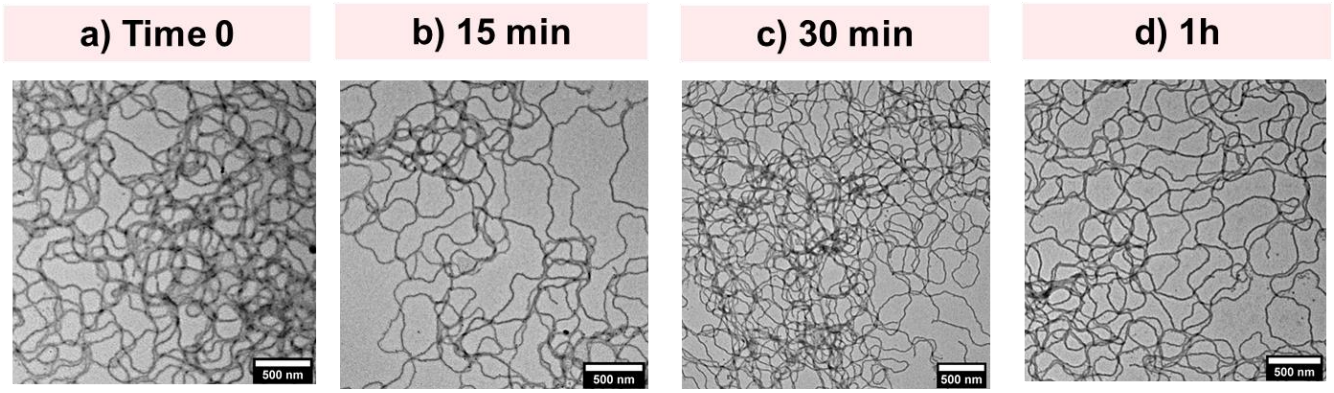

Figure S22: Picture of worms (Polymer B2)obtained by RAFT nanoemulsion polymerization of styrene (STY) using P(DEGMA-co-HPMA)-SC(S)SC_2H_5 as macro-CTA. a) time 0, b) after 15 min of sonication, c) after 30 min of sonication, d) after 1 hour of sonication.

Table S26: SEC data of RAFT nanoemulsion polymerization of methyl methacrylate (MMA) using P(DEGMA-*co*-HPMA)-SC(S)SC_2H_5 as macro-CTA. The vials were shaken at room temperature for 10 seconds before polymerization.

				SEC		DLS		Amont of MMA added	TEM
Entry	Name	Time (h)	[Macro-CTA] : [MMA] : [AIBN] : [SDS]	$M_{n,exp}$	$Đ$	PdI	d [nm]	(for 100 uL of Latex)	Morphologies
1	B10	2.00	1 : 100 : 0.06 : 0.4	10300	1.20	--	--	0.2	Nanomicelles
2	B11	2.25	1 : 100 : 0.06 : 0.4	13600	1.11	0.199	351.2	0.2	Worms balls
3	B12	2.33	1 : 100 : 0.06 : 0.4	15100	1.13	0.199	305.6	1.5	Nanoworms
4	B12	2.33	1 : 100 : 0.06 : 0.4	15100	1.13	0.186	305.6	5	Nanovesicles

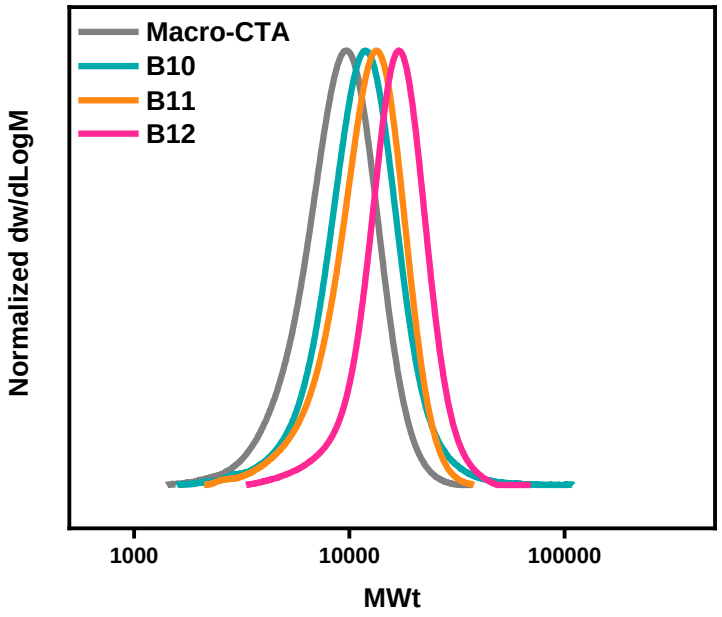

Figure S23: SEC traces of RAFT nanoemulsion polymerization of methyl methacrylate (MMA) using P(DEGMA-co-HPMA)-SC(S)SC_2H_5 as macro-CTA. Polymerization conditions are the following: [Macro-CTA] : [MMA] : [SDS] : [AIBN] = 1 : 100 : 0.4 : 0.06 in 2 ml deionized water. Traces corresponds to 2 hours (green), 2 hours 15 min (orange) and 2 hours 20 min (pink) of polymerization.

Table S27: SEC and DLS data (before polymerization) of RAFT nanoemulsion polymerization of ethyl acrylate (EA) using P(DEGMA-*co*-HPMA)-SC(S)SC_2H_5 as macro-CTA. The vial was shaken at room temperature for 10 seconds.

			SEC		DLS	
Entry	Time (h)	[Macro-CTA] : [EA] : [AIBN] : [SDS]	$M_{n,exp}$	$Đ$	PdI	d [nm]
1	5.00	1 : 50 : 0.06 : 0.4	14100	1.32	0.08	406

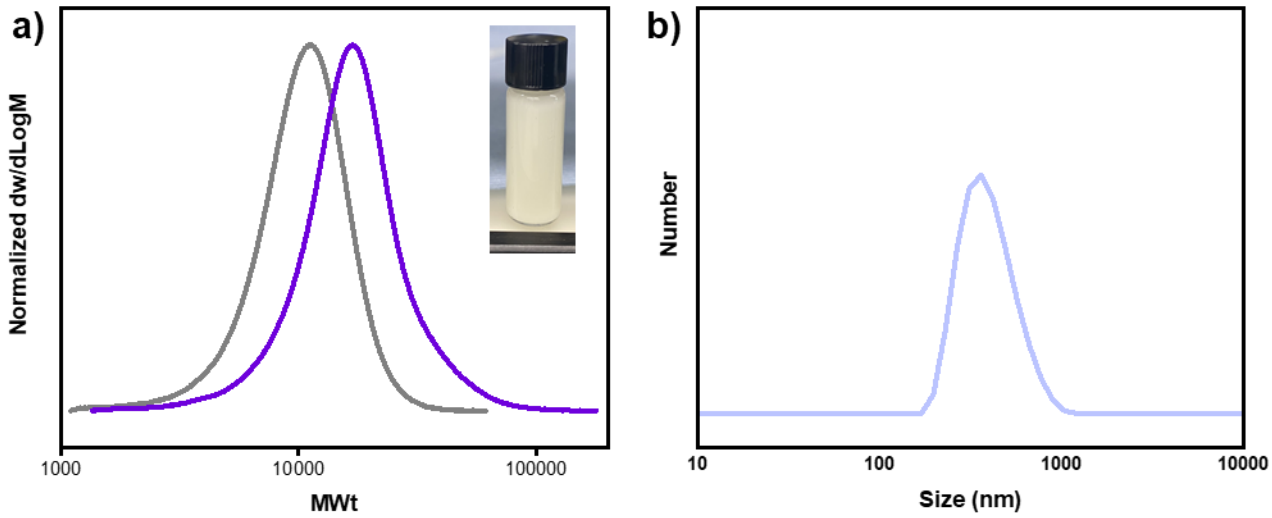

Figure S24: a) SEC and b) DLS traces of RAFT nanoemulsion polymerization of ethyl acrylate (EA) using P(DEGMA-*co*-HPMA)-SC(S)SC_2H_5 as macro-CTA. The vial was shaken at room temperature for 10 seconds.