Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information for

A Mild and Quantitative Route Towards Well-Defined Strong Anionic/Hydrophobic Diblock Copolymers: Synthesis and Aqueous Self-Assembly

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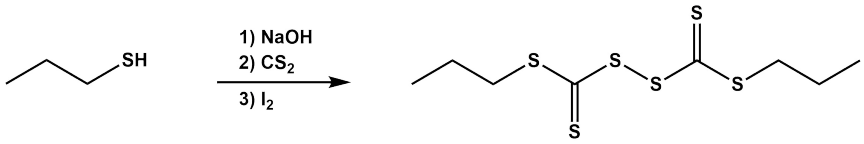
1 Experimental section

1.1 Materials

Reagent grade chemicals were obtained from either Sigma-Aldrich, TCI or Acros Organics in the highest purity available. Analytical grade solvents were purchased from Biosolve and were used as received. Deuterated solvents were acquired from Eurisotop. Anhydrous *N,N*-dimethylformamide (DMF, 99.8%) that was used for both the monomer synthesis and RAFT polymerizations was obtained from Sigma-Aldrich. Methyl methacrylate (MMA) was passed over a short basic alumina column to remove the inhibitor, and subsequently vacuum distilled from finely ground calcium hydride. Azobisisobutyronitrile (AIBN) was recrystallized twice from methanol.

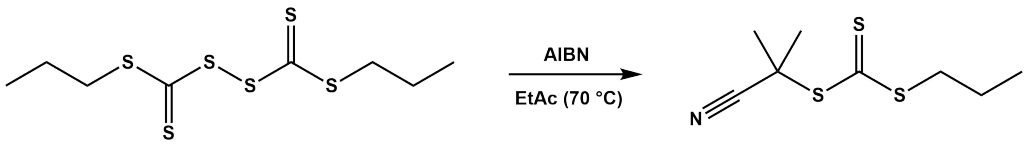
1.2 Synthesis

1. Synthesis of 2-cyanopropan-2-yl propyl trithiocarbonate (CPP-TTC)



CPP-TTC was synthesized according to a slightly modified two-step literature procedure.[1,2] Propanethiol (3.21 g; 42.1 mmol) was dissolved in 30 ml diethyl ether under a nitrogen atmosphere. 7.77 g of a 22 wt% sodium hydroxide solution (42.8 mmol) was added dropwise at room temperature and subsequently stirred for approximately 30 min. Next, three drops Aliquat 336 (phase-transfer catalyst) were added to the clear two-layer system, followed by slow addition of 3.56 g (46.8 mmol) carbon disulfide in 10 ml diethyl ether. The solution turned bright yellow instantaneously (predominantly the aqueous layer), and was left to stir for another 30 min. The reaction mixture was diluted with a portion of diethyl ether (10 ml). Iodine flakes (5.96 g; 23.5 mmol) were added in small quantities, and caused the almost colorless organic layer to slowly turn yellow/orange. After having stirred for 90 min, the now dark brown solution (due to the slight excess of iodine) was diluted with 20 ml diethyl ether, transferred to a separation funnel, and was washed with two portions 5 wt% aqueous sodium thiosulfate (70 ml each) and 70 ml water. The orange organic layer was dried over magnesium sulfate and concentrated in vacuo to give bis(propylsulfanylthiocarbonyl) disulfide as a bright orange oil (5.27 g) that was used in the next step without further purification (yield: 83%).

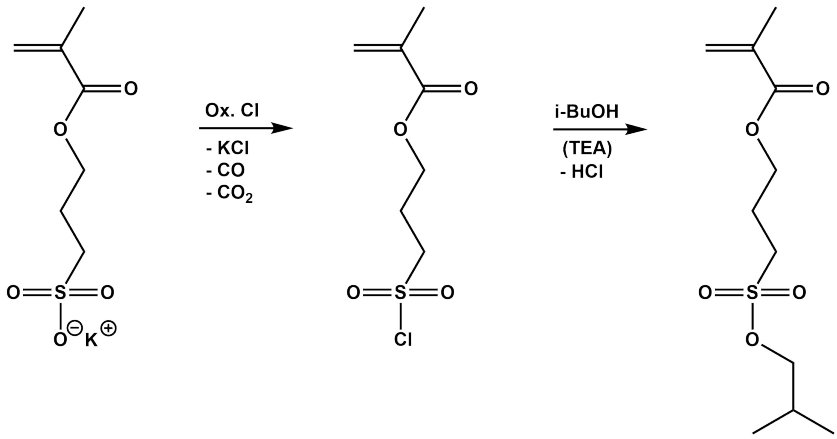
^{1}H-NMR ($CDCl_3$): δ (ppm) = 1.02 (t, CH_3), 1.74 (sextet, CH_2), 3.29 (t, CH_2).
^{13}C-NMR ($CDCl_3$): δ (ppm) = 13.6, 21.1, 40.2, 221.7.



In a 100 ml three-neck round-bottom flask under nitrogen atmosphere, bis(propylsulfanylthiocarbonyl) disulfide (2.02 g; 6.68 mmol) and AIBN (not recrystallized; 1.73 g; 10.5 mmol) were dissolved in 30 ml ethyl acetate. The clear orange solution was subjected to three freeze-pump-thaw cycles, and was subsequently heated to 70 °C for 19 h. Ethyl acetate was carefully removed in vacuo to give an orange suspension. The product was separated from the excess AIBN and its decomposition product tetramethylsuccinonitrile via extraction with hexane (25 ml).[3] Hexane was removed under reduced pressure to afford an orange oil (2.05 g) that was purified by silica gel column chromatography using hexane/ethyl acetate (20/1) as eluent. Only the purest fractions were collected, which slightly lowered the overall yield. CPP-TTC was obtained as a bright orange oil (0.65 g) that was stored in the fridge until further use (yield: 22%).

^{1}H-NMR ($CDCl_3$): δ (ppm) = 1.02 (t, CH_3), 1.74 (sextet, CH_2), 1.87 (s, 2 CH_3), 3.33 (t, CH_2) (Figure S3a). ^{13}C-NMR ($CDCl_3$): δ (ppm) = 13.6, 21.5, 27.2, 38.9, 42.5, 120.6, 218.0 (Figure S3b).

2. Synthesis of 3-(*i*-butoxysulfonyl)propyl methacrylate (BSPMA)



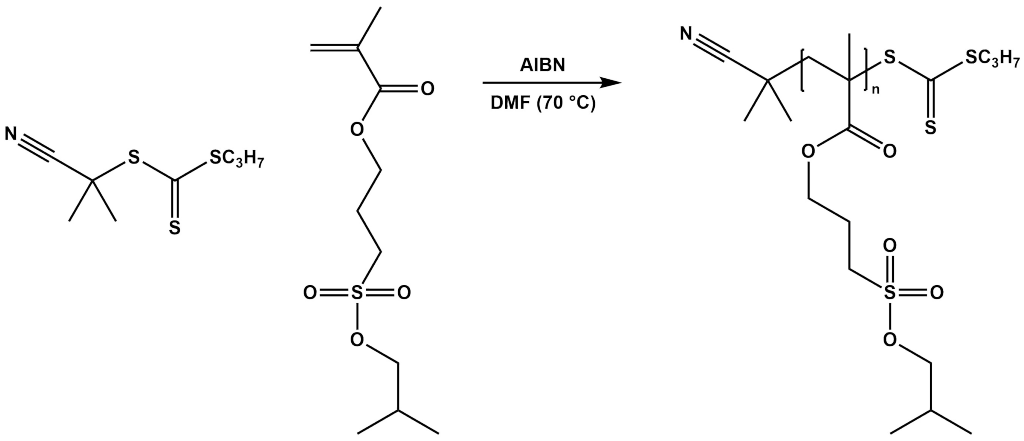
To a 100 ml two-neck round-bottom flask was added 10.3 g (41.8 mmol) 3-sulfopropyl methacrylate (SPMA) potassium salt, and was subsequently subjected to three vacuum/nitrogen cycles to remove residual traces of water. After putting the flask back under a nitrogen atmosphere, the salt was suspended in 30 ml anhydrous DMF and cooled to 0 °C using an ice bath. A solution of oxalyl chloride (5.90 g; 46.5 mmol) in 20 ml dichloromethane was added dropwise to the viscous white suspension using a glass Pasteur pipette under a nitrogen outflow. Instantaneous release of gas (CO_2/CO) from the reaction mixture was observed due to formation of the Vilsmeier reagent. ^{1}H-NMR confirmed

complete conversion of the SPMA potassium salt into the sulfonyl chloride within 30 min (Figure S1). Note: in contrast to *p*-styrene sulfonyl chloride the sulfonyl chloride of SPMA cannot be isolated via extraction; hydrolysis of SPMA-Cl is already observed in wet $CDCl_3$.

In a separate 250 ml three-neck round-bottom flask, a solution of 3.80 g (51.3 mmol) anhydrous isobutanol and 8.53 g (84.3 mmol) triethylamine in 30 ml dichloromethane was prepared under nitrogen atmosphere and was cooled to 0 °C using an ice bath. The now significantly less viscous white SPMA-Cl/KCl suspension was warmed up to room temperature, carefully transferred to a dropping funnel and added dropwise to the alcohol solution over a period of approximately 15 min. The turbid yellowish solution was stirred for 1 h at 0 °C, followed by stirring at room temperature overnight. The next morning this reaction mixture was transferred to a separation funnel, 300 ml water was added, and was extracted with three portions of diethyl ether (200 ml each). The organic fraction was dried over magnesium sulfate, and subsequently concentrated in vacuo to give 13.7 g dark yellow oil that was purified by silica gel column chromatography using hexane/ethyl acetate (2/1) as eluent. 9.25 g BSPMA was finally obtained as a clear colorless oil (yield: 84%). The monomer was stored in the fridge until further use.

^{1}H-NMR ($CDCl_3$): δ (ppm) = 0.98 (d, 2 CH_3), 1.94 (s, CH_3), 2.03 (m, CH), 2.25 (m, CH_2), 3.21 (t, CH_2), 4.00 (d, CH_2), 4.28 (t, CH_2), 5.60 (s, CH), 6.11 (s, CH). Purity >98% (Figure S2a). ^{13}C-NMR ($CDCl_3$): δ (ppm) = 18.4, 18.8, 23.5, 28.4, 47.4, 62.2, 75.7, 126.2, 136.0, 167.1 (Figure S2b).

3. Polymerization of BSPMA by RAFT

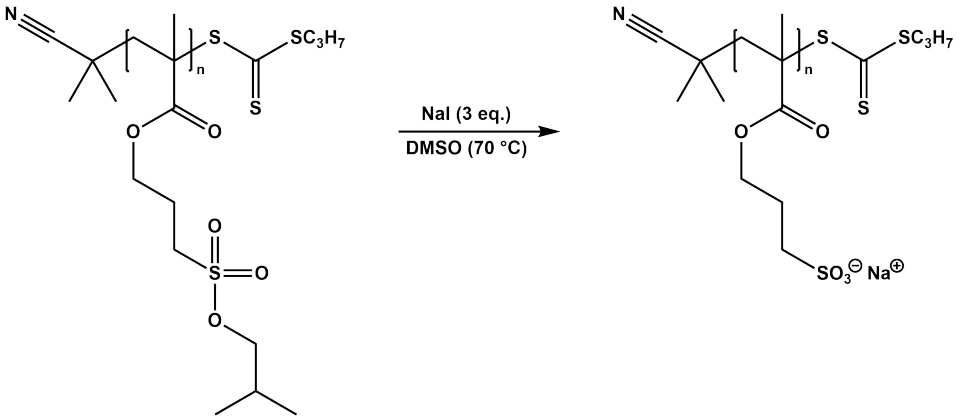


A typical RAFT polymerization of BSPMA is as following (PBSPMA-1): in a 50 ml two-neck round-bottom flask, 3.66 g (13.9 mmol) BSPMA and 29.2 mg (0.133 mmol) CPP-TTC were dissolved in 2.8 ml anhydrous DMF. Then 1.3 ml of a 1.95 mg ml^{-1} stock solution of AIBN (2.54 mg; 0.0155 mmol) in anhydrous DMF was added via a syringe. The clear

yellow reaction mixture was sparged with nitrogen for approximately 1 h, closed and submerged in a thermostated oil bath at 70 °C. The polymerization was carried out for 21 h, quenched by placing the flask in an ice bath and the conversion was calculated by using ^{1}H-NMR ($CDCl_3$; conv. = 99.6%). Next, the viscous yellow solution was diluted by addition of 5 ml acetone and precipitated into 175 ml hexane/ethanol (6/1). The sticky yellow polymer was washed with hexane/ethanol (2/1) and hexane inside the glass beaker. PBSPMA was dried in a vacuum oven (40 °C) overnight after having removed the supernatant. For further purification, the polymer was redissolved in 10 ml acetone and reprecipitated into 200 ml hexane. The sticky yellow polymer chunks were thoroughly washed with hexane, and subsequently dried in a vacuum oven (30 °C) overnight. The obtained yellow foam was crushed with a spatula to give 2.57 g fine yellow powder that was stored in the fridge until further use (yield: 71%). Reaction conditions for the synthesis of the other PBSPMA homopolymers are provided in Table S1.

^{1}H-NMR ($CDCl_3$): δ (ppm) = 0.8-1.1 (br, CH_3), 1.00 (d, 2 CH_3), 1.2-2.0 (br, CH_2), 2.05 (m, CH), 2.2 (br, CH_2), 3.2 (br, CH_2), 4.02 (d, CH_2), 4.1 (br, CH_2). GPC (0.02 M KTFA in HFIP): M_n = 31.2 kg mol^{-1}, $Đ$ = 1.28. DSC: $T_g \approx 15$ °C (Figure S5).

4. Deprotection of PBSPMA

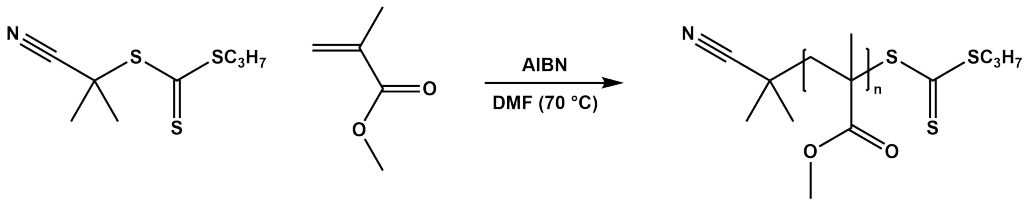


In a glass vial that contained a stirring bar, 332 mg PBSPMA-1 (1.26 mmol BSPMA) and 582 mg (3.88 mmol; 3 eq.) sodium iodide were dissolved in 5 ml DMSO. After having dissolved both components at room temperature, the clear and slightly yellow solution was heated to 70 °C for 22 h. Next, the dark brown solution was diluted with 2 ml DMSO and precipitated into 300 ml ethanol/hexane (2/1). The yellow supernatant was removed, and the off-white precipitate was subsequently washed inside the glass beaker with 200 ml ethanol/hexane (1/1). The suspension was filtered using a glass filter funnel (pore size 4). In order to remove side products and the excess sodium iodide, the residue was washed with large amounts of ethanol/hexane (1/1) until the filtrate became colorless. The product was finally washed with one portion hexane, dried in a vacuum oven overnight (40 °C)

and shortly heated to 120 °C (15 min) to give 0.23 g PSPMA sodium salt as an off-white powder (yield: 80%).

^{1}H-NMR (D_2O): δ (ppm) = 0.8-2.0 (br, CH_2 and CH_3 - backbone), 2.2 (br, CH_2), 3.0 (br, CH_2), 3.4 (br, CH_2, CTA), 4.2 (br, CH_2). (Figure S6a, deprotection = 100%).

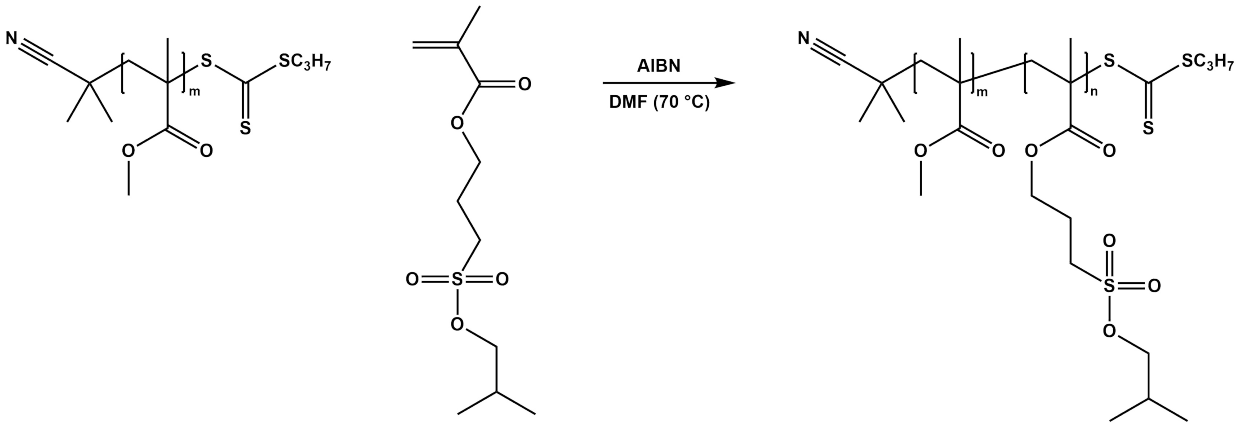
5. Synthesis of PMMA macro-CTAs by RAFT



A typical procedure for the synthesis of a PMMA macro-CTA is following (PMMA-1). In a 50 ml two-neck round-bottom flask that was equipped with a stirring egg, 6.06 g (60.5 mmol) MMA and 43.0 mg (0.196 mmol) CPP-TTC were dissolved in 11.0 ml anhydrous DMF. AIBN (2.4 mg; 0.0146 mmol) was added via a freshly prepared stock solution in DMF (1.2 ml; 2.0 mg ml^{-1}). The bright yellow reaction mixture was sparged with nitrogen for 45 min. RAFT polymerization of MMA was started by submerging the flask into a thermostated oil bath at 70 °C. The reaction was stopped after 21 h by placing the flask into an ice bath, and the conversion was subsequently determined by ^{1}H-NMR (conv. = 74.8%). The yellow solution was precipitated in undiluted form into 300 ml hexane/ethanol (2/1), filtered using a glass filter (pore size 4), washed with hexane and dried in a vacuum oven overnight (40 °C). The off-white powder was redissolved in 18 ml acetone and re-precipitated into 350 ml hexane/ethanol (2.5/1), filtered, washed with hexane and finally dried in a vacuum oven overnight to give PMMA-1 as a fine yellowish powder (3.3 g; yield: 73%). The reaction conditions for the synthesis of the other PMMA macro-CTAs can be found in Table S1.

^{1}H-NMR ($CDCl_3$): δ (ppm) = 0.7-1.1 (br, CH_3), 1.2-2.1 (br, CH_2), (3.2, CH_2, CTA), 3.6 (br, CH_3). GPC (0.02 M KTFA in HFIP): M_n = 24.5 kg mol^{-1}, $Đ$ = 1.24.

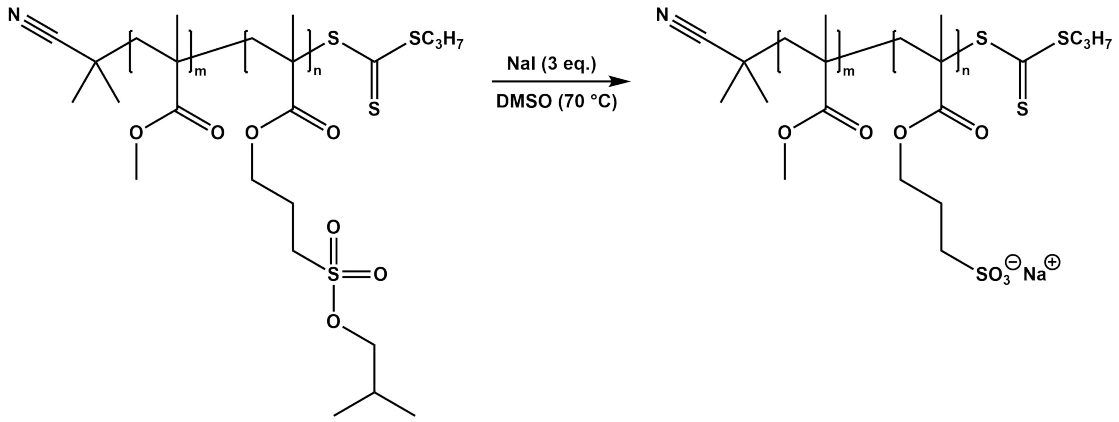
6. Synthesis of PMMA-*b*-PBSPMA



A typical procedure for the synthesis of a PMMA-*b*-PBSPMA diblock copolymer is as following, taking BCP-3 as an example. In a 50 ml two-neck round-bottom flask, PMMA-2 (616 mg; 0.0540 mmol) was dissolved in 4.0 ml anhydrous DMF. BSPMA (1.91 g; 7.23 mmol) was added using a glass Pasteur pipette and AIBN via a stock solution (1.94 mg ml^{-1}) using a syringe (0.4 ml; 0.78 mg; 0.0047 mmol). The bright yellow solution was sparged with nitrogen for 1 h. RAFT polymerization of BSPMA was started by placing the flask in an oil bath (70 °C) for 17 h. Next, the reaction was quenched by placing the flask in an ice bath, and after the conversion had been determined by ^{1}H-NMR (conv. = 98.1%), the reaction mixture was diluted with 5 ml acetone and precipitated into 300 ml hexane/ethanol (5/1). The yellow polymer chunks were washed with hexane/ethanol (5/1) and hexane. The copolymer was dried in a vacuum oven overnight (40 °C). For further purification, the polymer was redissolved in 8 ml acetone and reprecipitated into 300 ml hexane/ethanol (5/1). The obtained yellow polymer chunks were washed with hexane/ethanol (5/1) and with hexane, cut into smaller pieces and finally dried in a vacuum oven overnight. The protected block copolymer (2.10 g) was stored in the fridge until further use. Reaction conditions for the preparation of the other five diblock copolymers are given in Table S2.

^{1}H-NMR ($CDCl_3$): $f_{\mathrm{PMMA}} = 0.25$, $x_{\mathrm{PMMA}} = 0.47$ (Figure S11). GPC (0.02 M KTFA in HFIP): $M_{n,\mathrm{GPC+NMR}} = 44.8$ kg mol^{-1}, $Đ = 1.18$.

7. Deprotection of PMMA-*b*-PBSPMA



BCP-3 was deprotected under similar conditions as the PBSPMA homopolymers. In a small vial 625 mg BCP-3 (466 mg, 1.76 mmol BSPMA) and 817 mg (5.45 mmol; 3 eq.) sodium iodide were dissolved in 6 ml DMSO. The clear reaction mixture was stirred at 70 °C for 22 h. Afterwards, the dark brown solution was precipitated into 200 ml ethanol/hexane (1/1), decantated, filtered, washed with more ethanol/hexane (1/1) and finally with hexane. The copolymer was dried in a vacuum oven overnight (40 °C) and heated to 120 °C for 15 min to remove traces of organic solvent to give BCP-3 as a yellowish powder (0.44 g). In order to quantitatively deprotect the other diblock copolymers the ratio NaI / BSPMA / DMSO was kept approximately constant (i.e., 3 eq. NaI, ∼60 mg/ml PBSPMA).

^{1}H-NMR (DMSO-d_6): $x_{\mathrm{PMMA}} = 0.49$. (Deprotection = 100%).

1.3 Sample preparation

Micellar aggregates of the PMMA-*b*-PSPMA(Na) hydrophobic/strong anionic diblock copolymers were prepared by directly dissolving the copolymers in water containing 10 mM KNO_3 to obtain solutions with a copolymer concentration of 1.0 mg ml^{-1}. After stirring for a few hours at room temperature, the homogeneous and clear solutions were shortly heated to the boiling point by using a heat gun. Since BCP-6 turned out to be insoluble in water, 18 mg material was first dispersed in 2 g DMSO/H_2O (1/1, 10 mM KNO_3; still a non-solvent for PMMA) and subsequently diluted by dropwise addition of more water (16 ml, 10 mM KNO_3) to obtain a final polymer concentration of 1.0 mg ml^{-1}. For light scattering experiments the viscosity and refractive index of this particular dispersion were manually corrected using literature values (6 wt% DMSO: $\eta = 0.96$ cP, $n = 1.34$).[4] To remove dust, all samples for DLS and zeta potential measurements were filtered over 0.45 μm cellulose acetate filters.

To prepare negatively stained TEM samples, a drop of the same, but unfiltered solution was deposited onto a carbon-coated and glow-discharged 400 mesh copper grid. The excess

liquid was removed after 1 min using well-absorbing filter paper. The wet sample was washed with a few μl of a 2 wt% uranyl acetate aqueous solution, immediately blotted, and subsequently stained for 1 min with a drop of the same uranyl acetate solution. After blotting with filter paper, the sample was dried at ambient conditions.

1.4 Characterization

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a 400 MHz Bruker Avance III spectrometer operating at room temperature using deuterated chloroform ($CDCl_3$), dimethyl sulfoxide (DMSO-d_6) or deuterium oxide (D_2O) as a solvent.

Fourier-transform infrared spectroscopy (FT-IR) was carried out on a Bruker Tensor 27 instrument at room temperature.

Gel permeation chromatography (GPC) was performed on a Viscotek HP-SEC system equipped with a TDA 305 triple detector array (refractive index, viscosity and light scattering detectors), two PSS PFG analytical columns and a PSS PFG guard column. Both the columns and detectors were held at 30 °C. Hexafluoroisopropanol (HFIP) containing 0.02 M potassium trifluoroacetate (KTFA) was used as eluent at a flow rate of 0.7 ml min^{-1}. The system was calibrated with narrow PMMA standards and samples were filtered over a 0.2 μm PTFE filter prior to injection. Molecular weights were calculated by applying a triple detection method (refractive index, viscosity and light scattering) using Viscotek OmniSEC software. A predetermined refractive index increment (dn/dc) of 0.195 ml g^{-1} was applied for the PMMA macro-CTAs, while molecular weights of the protected diblock copolymers ($M_{n,\mathrm{GPC+NMR}}$) were determined by combining the molecular weight of the PMMA or PBSPMA macro-CTA (GPC) and the composition of the copolymer (^{1}H-NMR in $CDCl_3$). $M_{n,\mathrm{calc}}$ is the calculated molecular weight based on the monomer conversion (^{1}H-NMR) and the theoretical maximum molecular weight (CPP-TTC and monomer concentration).

Thermogravimetric analysis (TGA) was performed on a Perkin Elmer STA 6000 under a continuous nitrogen flow (30 ml min^{-1}). Samples were heated from 30 to 900 °C at a heating rate of 10 °C min^{-1}. For isothermal measurements the samples were heated to the indicated temperature (10 °C min^{-1}) and subsequently maintained at this particular temperature. The sample weight was recorded for 2 h.

Differential scanning calorimetry (DSC) measurements were conducted on a TA Instruments DSC Q1000 under nitrogen atmosphere in the modulated mode (0.5 °C, period 60 s). The samples were heated to 130 °C and cooled back to −80 °C at a rate of 2 °C min^{-1}, with the second heating cycle being used for analysis.

Dynamic light scattering (DLS) experiments were carried out on an ALV/CGS-3 compact goniometer system equipped with a JDSU 1145P HeNe 22 mW laser (λ = 632.8 nm), an

ALV/LSE-5004 goniometer and an ALV7004 external correlator. The temperature was kept constant at 25 °C by using a Julabo CF41 thermostat. Multi-angle DLS was performed by varying the detector angle from 30° to 130° in steps of 5°. Intensity correlation functions were recorded for 15 s and were averaged over 5 runs per angle. Hydrodynamic radii (R_h) and polydispersity indices (PDIs) were acquired through a second order cumulant analysis, while size distribution plots were obtained via the CONTIN algorithm using AfterALV software (at 90°).

Zeta potentials (ζ) of the micellar aggregates were determined at 25 °C using a Malvern Zetasizer Nano ZS. This instrument is equipped with a 4 mW HeNe laser ($\lambda = 632.8$ nm) with the scattering being detected at a fixed backscatter angle of 173°. Acquisition times were determined automatically and recorded zeta potentials were averaged over three consecutive runs.

Negatively stained samples were analyzed on a Philips CM120 transmission electron microscope (TEM) that was equipped with a LaB_6 filament and operated at an accelerating voltage of 120 kV. Images were recorded on a Gatan slow-scan 4K CCD camera.

2 Polymer synthesis

Polymer	[CTA]	[AIBN]	[AIBN]/[CTA]	[M]	t_R	conv.	$M_{n,\mathrm{calc}}$	$M_{n,\mathrm{GPC}}$	$Đ$
PBSPMA-1	17.1	1.98	1/8.6	1.78	21	99.6	27.6	31.2	1.28
PBSPMA-2	31.5	1.14	1/27.7	1.49	19	96.9	12.3	13.5	1.41
PMMA-1	10.5	0.79	1/13.4	3.25	21	74.8	23.3	24.5	1.24
PMMA-2	24.0	0.92	1/26.2	3.51	21	76.6	11.4	11.4	1.27

Table S1: Reaction conditions for the synthesis of PBSPMA and PMMA homopolymers by RAFT polymerization. Concentrations of CTA and AIBN are in mM, and monomer in M. Reaction times (t_R) are in h, conversions were determined by ^{1}H-NMR (%), and molecular weights are reported in kg mol^{-1}. $M_{n,\mathrm{calc}}$ is the calculated molecular weight based on the initial concentrations and monomer conversion.

BCP	[CTA]	[AIBN]	[AIBN]/[CTA]	[M]	t_R	conv.	$M_{n,\mathrm{GPC+NMR}}$	$Đ$
BCP-1	8.29 (PMMA-1)	0.97	1/8.5	0.91	21	99.5	52.4	1.16
BCP-2	4.95 (PMMA-1)	0.60	1/8.2	1.22	19	95.3	83.3	1.20
BCP-3	8.58 (PMMA-2)	0.75	1/11.4	1.15	17	98.1	44.8	1.18
BCP-4	4.76 (PMMA-2)	0.41	1/11.6	1.25	18	93.4	74.3	1.27
BCP-5	8.99 (PBSPMA-2)	0.72	1/12.4	3.61	20	66.9	31.0	1.29
BCP-6	6.25 (PBSPMA-2)	0.60	1/10.6	5.55	21	90.0	71.7	1.21

Table S2: Reaction conditions for the preparation of PMMA-*b*-PBSPMA diblock copolymers by RAFT. Concentrations of CTA and AIBN are in mM, and monomer in M. Reaction times (t_R) are in h, conversions were determined by ^{1}H-NMR (%), and molecular weights are given in kg mol^{-1}.

3 Results and discussion

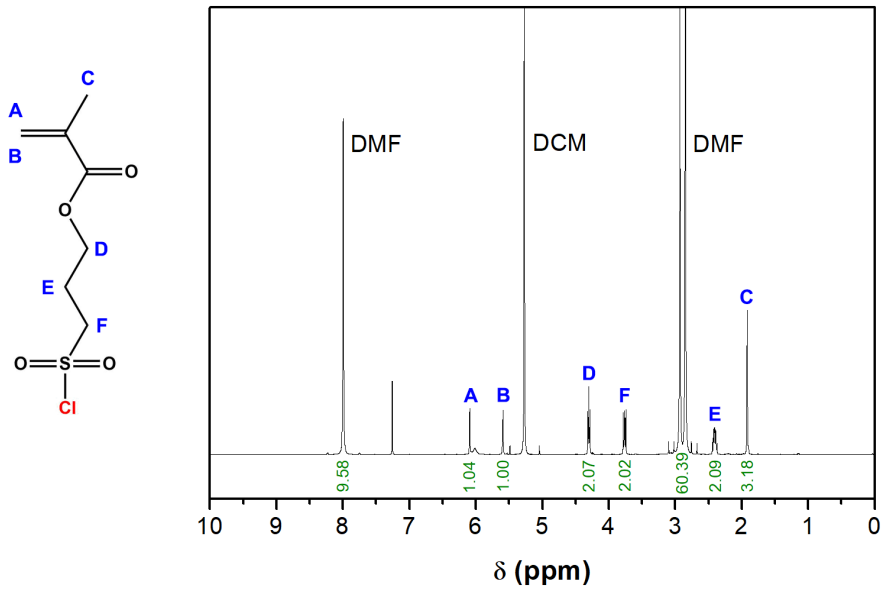


Figure S1: Synthesis of 3-(chlorosulfonyl)propyl methacrylate (SPMA-Cl). ^{1}H-NMR spectrum of the reaction mixture in $CDCl_3$ after addition of oxalyl chloride. Based on the ratio DMF/SPMA (9.6/1) SPMA(K) had been fully converted into SPMA-Cl (starting materials: 9.3/1). Due to its insolubility in $CDCl_3$, unreacted SPMA(K) is not visible in ^{1}H-NMR.

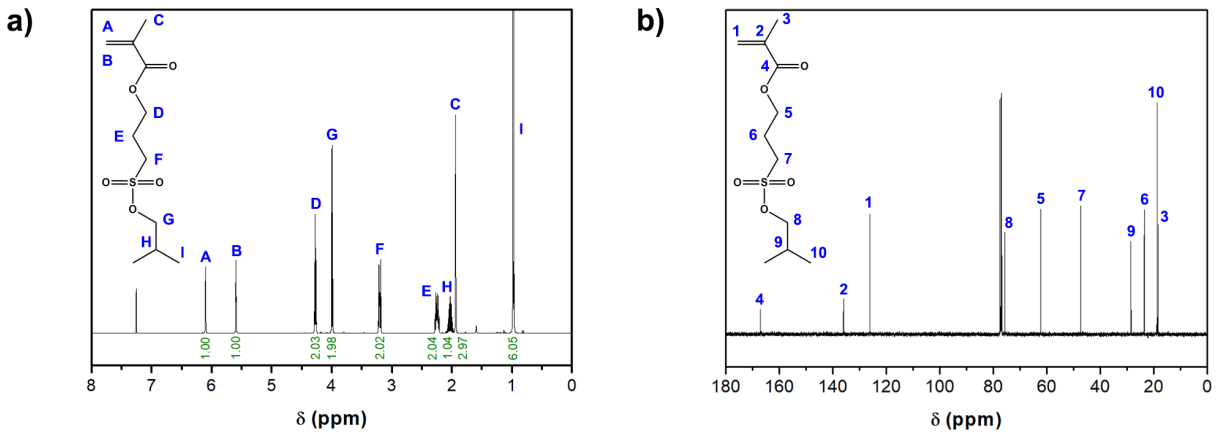


Figure S2: ^{1}H-NMR (a) and ^{13}C-NMR (b) spectra of purified 3-(*i*-butoxysulfonyl)propyl methacrylate (BSPMA) in $CDCl_3$.

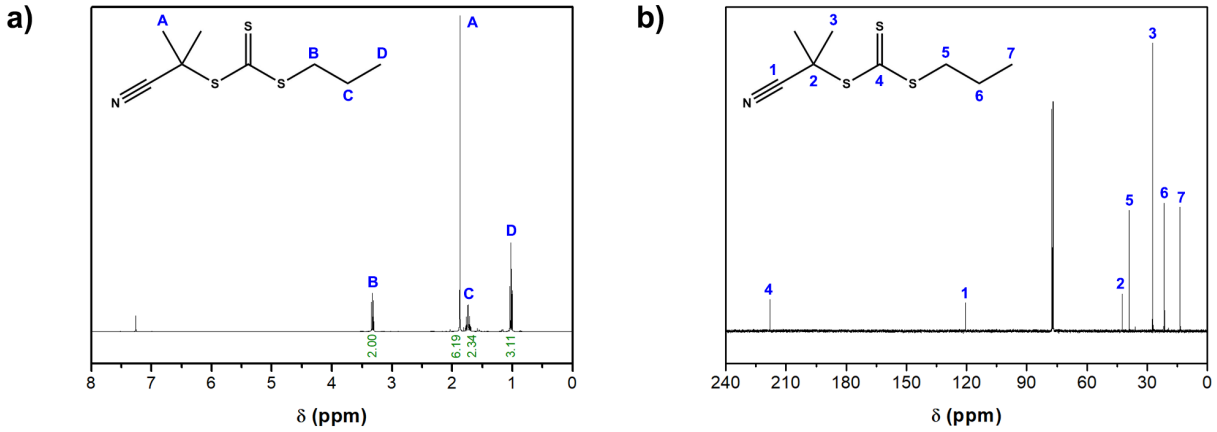


Figure S3: ^{1}H-NMR (a) and ^{13}C-NMR (b) spectra of purified 2-cyanopropan-2-yl propyl trithiocarbonate (CPP-TTC) RAFT agent in $CDCl_3$.

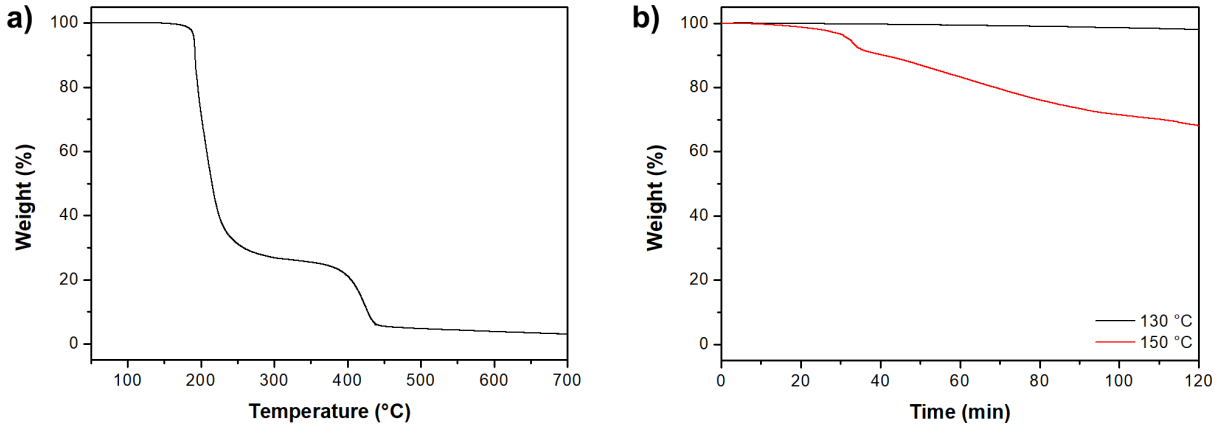


Figure S4: Thermogravimetric analysis of PBSPMA homopolymers. (a) PBSPMA-1 heated to 900 °C at 10 °C min^{-1}, and (b) PBSPMA-1 kept isothermal at 130 °C and 150 °C for 2 h.

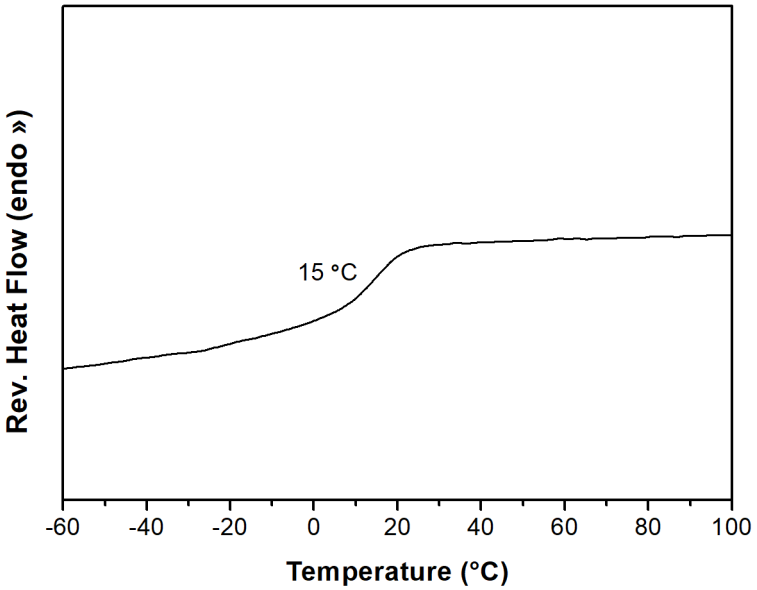


Figure S5: DSC thermogram of PBSPMA-1 recorded at 2 °C min^{-1} in the modulated mode. The second heating cycle is shown ($T_g \approx 15$ °C).

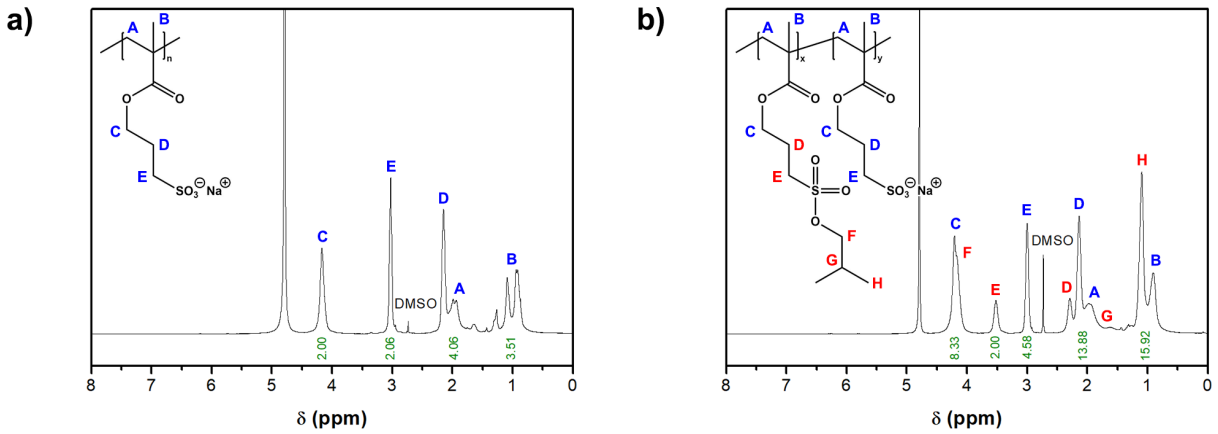


Figure S6: (a) ^{1}H-NMR spectrum of PSPMA-1(Na) recorded in D_2O demonstrating quantitative deprotection of PBSPMA-1 (3 eq. NaI, 70 °C). (b) Incomplete deprotection (70%) was obtained in the presence of 1.5 eq. NaI (60 °C).

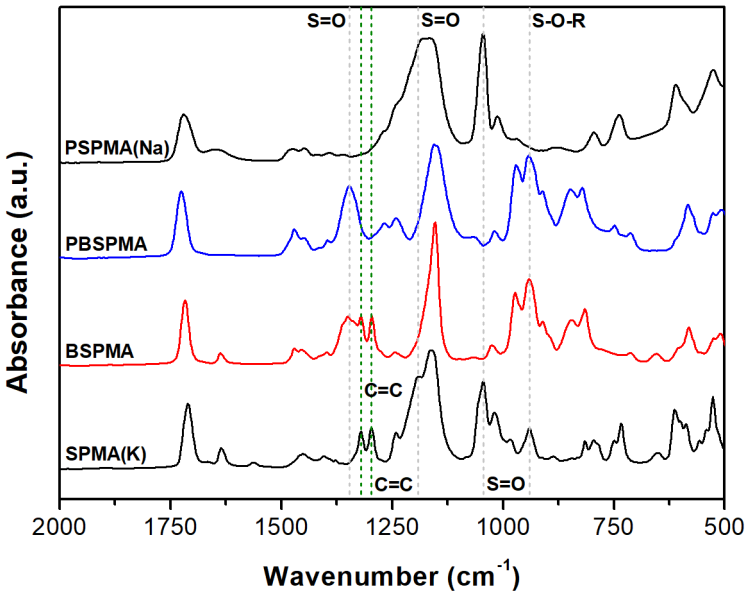


Figure S7: FT-IR spectra of SPMA(K), BSPMA, PBSPMA and PSPMA(Na). Protection, polymerization and deprotection can be followed qualitatively by monitoring the vinyl (1298 and 1320 cm^{-1}), sulfonate (1045, 1192 and 1347 cm^{-1}) and sulfonic ester (941 cm^{-1}) stretching modes.

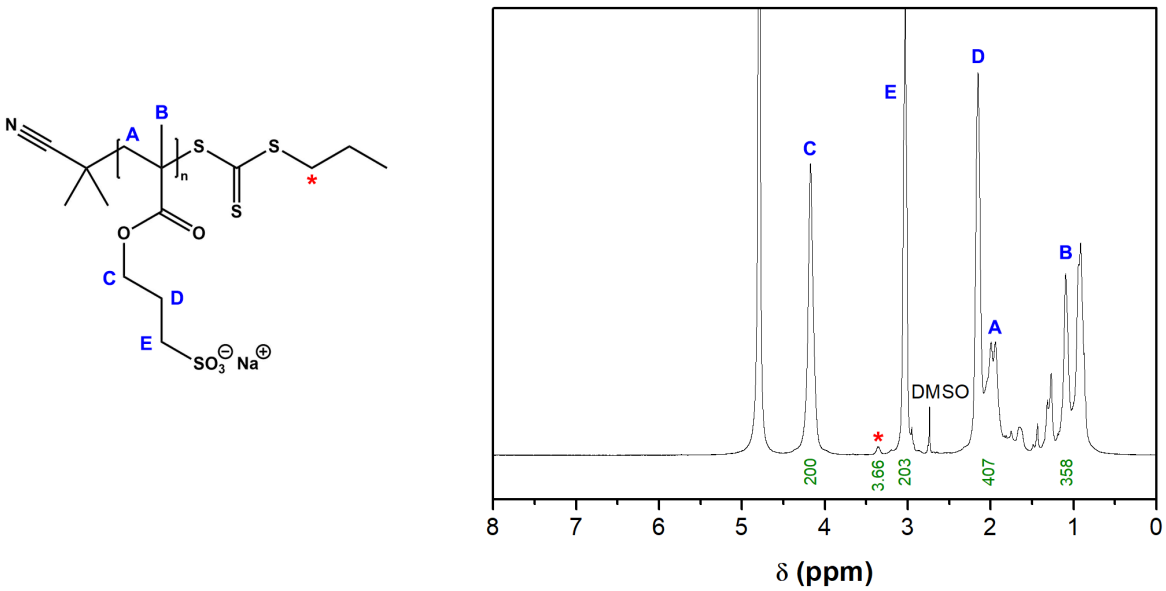


Figure S8: ^{1}H-NMR spectrum of PSPMA-2(Na) recorded in D_2O. The trithiocarbonate functional group (*) remained intact under the employed reaction conditions for the deprotection of PBSPMA-2. $P_{n,\mathrm{NMR}} = 55$ (PSPMA-2(Na)), $P_{n,\mathrm{GPC}} = 51$ (PBSPMA-2).

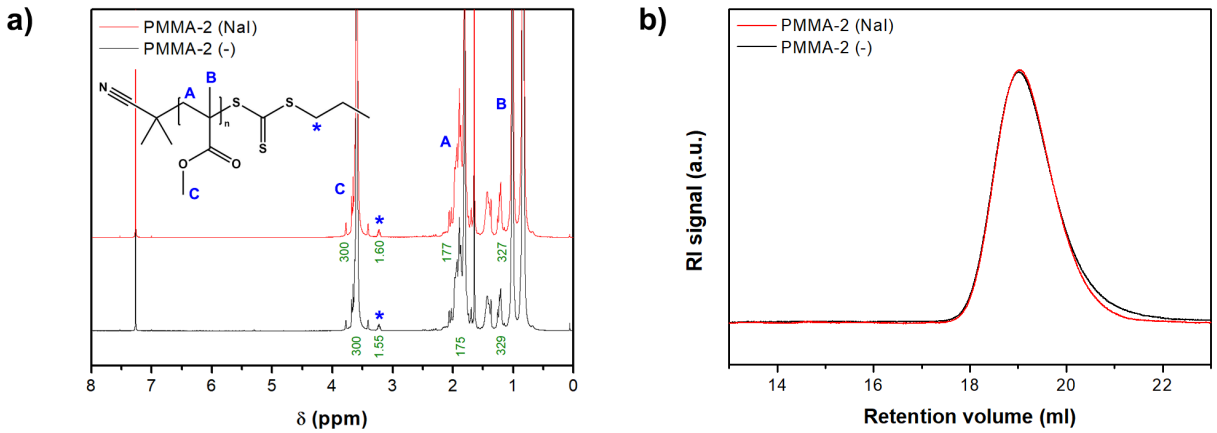


Figure S9: ^{1}H-NMR spectra (a) and GPC chromatograms (b) of PMMA-2 recorded before and after a deprotection model reaction ([MMA] = 0.61 M, [NaI] = 0.66 M, 70 °C, 20 h). Before NaI treatment: $P_{n,\mathrm{NMR}} = 129$, $P_{n,\mathrm{GPC}} = 114$ ($Đ = 1.24$). After: $P_{n,\mathrm{NMR}} = 125$, $P_{n,\mathrm{GPC}} = 118$ ($Đ = 1.24$).

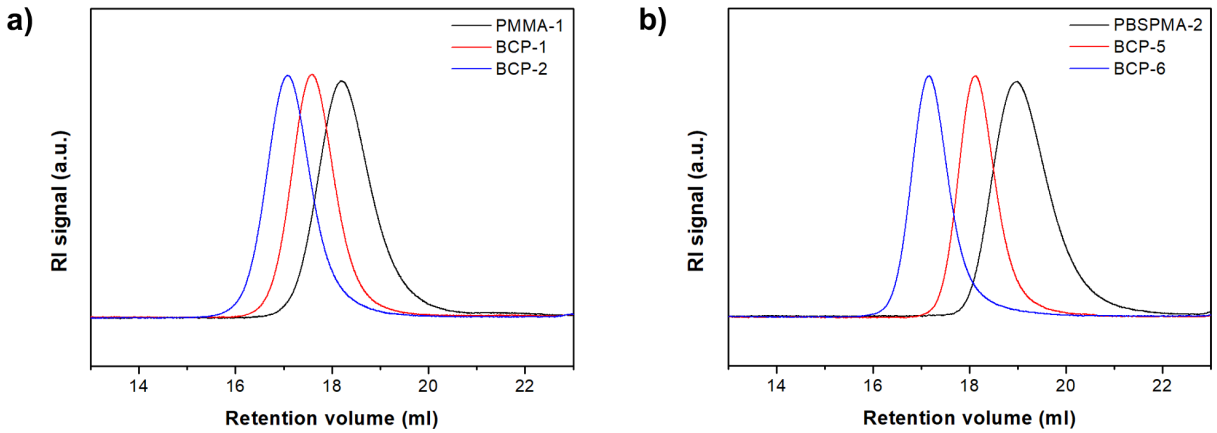


Figure S10: GPC chromatograms of macro-CTAs before and after chain extension with BSPMA or MMA: (a) PMMA-1/BCP-1/BCP-2 and (b) PBSPMA-2/BCP-5/BCP-6.

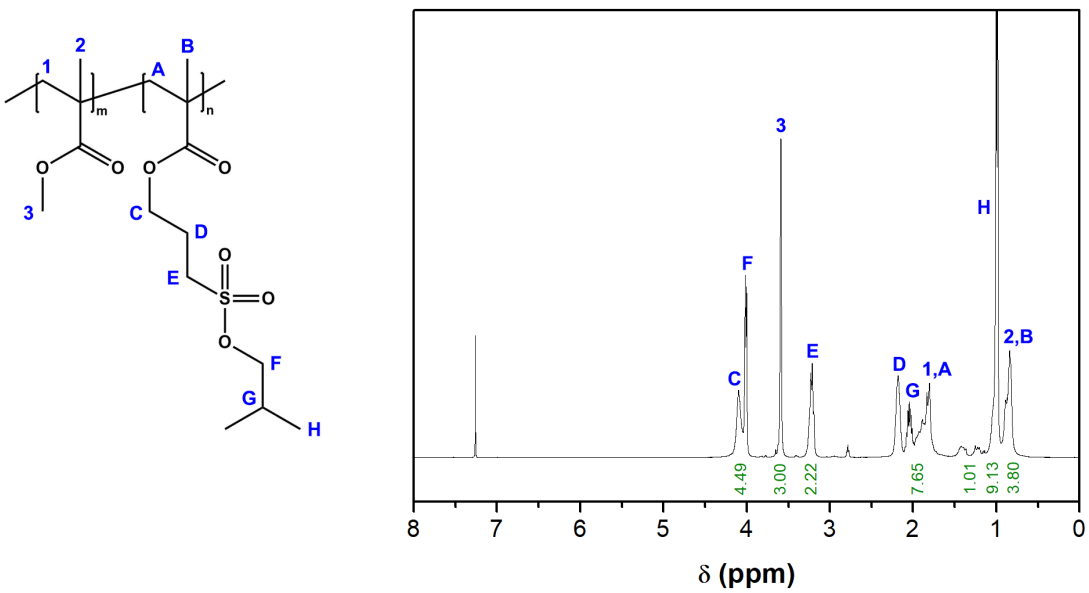


Figure S11: ^{1}H-NMR spectrum of PMMA-*b*-PBSPMA (BCP-3) recorded in $CDCl_3$. $x_{PMMA} = 0.47$; $f_{PMMA} = 0.25$.

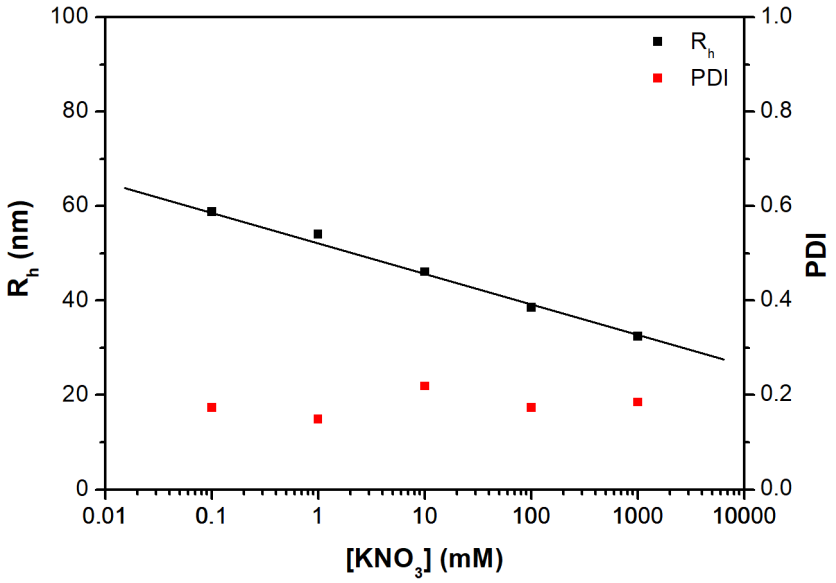


Figure S12: Hydrodynamic radii of BCP-4 aggregates as a function of the salt concentration. Tenfold dilutions of a stock solution (1.0 mg ml^{-1}, no salt) were prepared in the presence of different amounts of KNO_3. Since the PMMA cores are glassy at room temperature, the observed trend is a pure corona effect; salt screening induces contraction of the micelle corona.

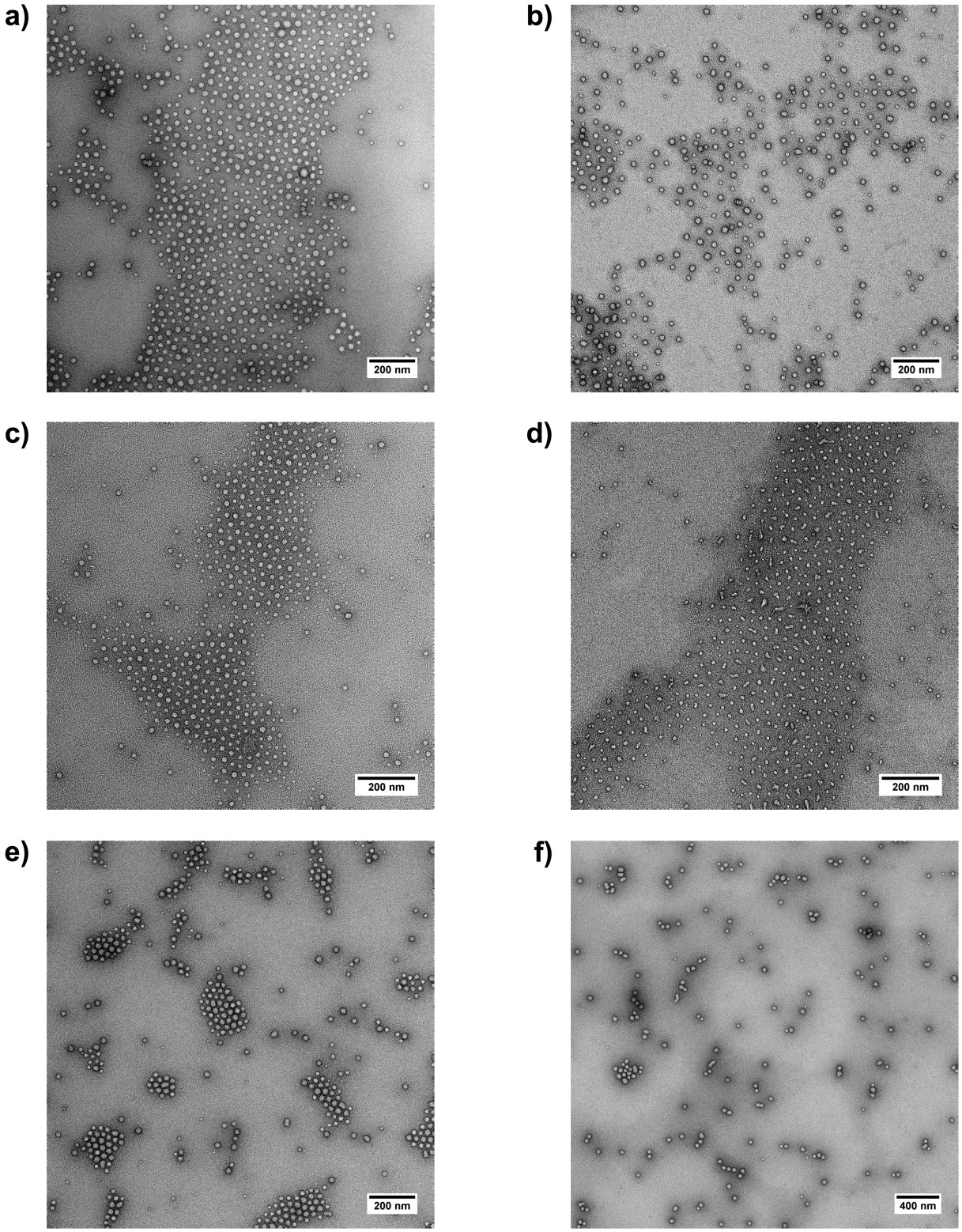


Figure S13: Transmission electron micrographs obtained at a lower magnification. Samples were negatively stained with 2 wt% uranyl acetate: BCP-1 (a), BCP-2 (b), BCP-3 (c), BCP-4 (d), BCP-5 (e), BCP-6 (f).

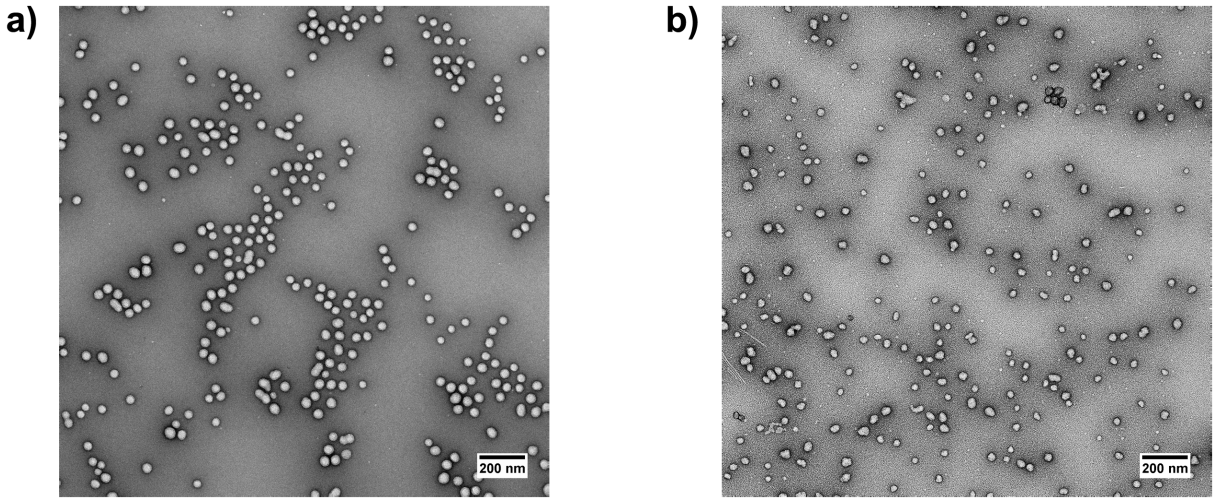


Figure S14: TEM images of (a) aggregates of BCP-6 prepared through direct dissolution (DD) after thermal annealing (80 °C, overnight), and (b) aggregates of BCP-6 prepared by the solution addition method (DMSO/H_2O).

BCP	R_h (DD)	PDI (DD)	ζ (DD)	R_h (SA)	PDI (SA)	ζ (SA)
BCP-1	52.1	0.265	−40.3	54.7	0.290	−36.0
BCP-2	70.0	0.330	−45.0	67.3	0.285	−37.0
BCP-3	28.6	0.163	−41.0	30.0	0.265	−36.1
BCP-4	44.8	0.245	−38.2	46.2	0.305	−35.9
BCP-5	21.9	0.062	−34.6	17.6	0.154	−32.0
BCP-6	37.4	0.142	−33.0	28.9	0.085	−30.7

Table S3: Comparison of solution self-assembled PMMA-*b*-PSPMA(Na) copolymers prepared by the direct dissolution (DD) and solvent addition (SA) method. R_h represents the hydrodynamic radius (nm), PDI the polydispersity index and ζ the zeta potential (mV). For SA 18 mg of the diblock copolymer was dissolved in 2 ml DMSO containing 0.1 M KNO_3. First 20 drops DMSO/H_2O (1/1) were added, then 10 ml water was added dropwise, and the clear solution was finally further diluted with another portion of water (6 ml). Final composition: 1.0 mg ml^{-1}, 11 mM KNO_3 and 13 wt% DMSO ($\eta = 1.12$ cP, $n = 1.35$).[4]

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