Strong Anionic/Charge-Neutral Block Copolymers from Cu(0)-Mediated Reversible Deactivation Radical Polymerization

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Supplementary Information

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Materials

Azobisisobutyronitrile (AIBN, 98 %), aluminium oxide (AlOx, basic, activated), benzoic acid (≥ 99.5 %) benzyl alcohol (BnOH, anhydrous 99.8 %), α-bromoisoobutyryl bromide (BiBB, 98 %), copper(0) wire (1.0 mm, ≥ 99.9 %), copper(II) bromide (CuBr₂, 99%), N,N-dimethylformamide (DMF, 99+ anhydrous), 1,4-dioxane (99.8 %), ethyl α-bromoisoobutyrate (EBiB. 98 %), iodomethane (MeI, ≥ 99.0 %), L-lactide (L-LA, 98 %), methyl acrylate (MA, 99 %), 3-sulfopropyl acrylate potassium salt (KSPA, %), triethylamine (TEA, ≥ 99.5 %), tris[2-(dimethylamino)ethyl]amine (Me₆-TREN, 97 %) and 4-vinylpyridine (4VP, 95 %) were purchased from Sigma-Aldrich. Dichloromethane (DCM, HPLC grade), diethyl ether (Et₂O, HPLC grade), ethyl acetate (EtOAc, HPLC grade), n-hexane (HPLC grade) and methanol (HPLC grade) were obtained from Macron Fine Chemicals. Hydrochloric acid solution (HCl, 37 %) and magnesium sulfate (MgSO₄, dried, extra pure) were sourced from Boom. Absolute ethanol (99.9 %) and dimethyl sulfoxide (DMSO, 99.9 %) were purchased from J.T. Baker. Diethylene glycol] ethyl ether acrylate (DEGA, > 98 %), poly(ethylene oxide) (PEO-OH, Mₙ = 4 000 Da) and oxalyl chloride ([COCl]₂, ≥ 98.0 %) were obtained from TCI. Silica gel for flash chromatography (40-63 μm) was sourced from Silicycle. Isobutanol ([iBuOH, 99+ %), lithium bromide (LiBr, 99+ %, anhydrous) and sodium iodide (NaI, ACS reagent grade) were purchased from Acros Organics. Dry DCM was obtained through a MB-SPS 800 purification machine from MBraun, equipped with HPLC grade DCM from Ossum Chemicals. 2-Cyanopropan-2-yl propyl trithiocarbonate (CPP-TTC) was produced as reported elsewhere.¹

AIBN was recrystallized twice from methanol. Commercially-available monomers were passed through a short AlOx column to remove inhibitors prior to polymerizations. All other chemicals were used as received.

Stirring bars used for SET-LRP were winded with copper wire (4 cm) and etched in HCl solution for 30 minutes followed by extensively washed with deionized water, ethanol and acetone prior to polymerizations.

Me₆-TREN/CuBr₂ stock solutions were prepared freshly prior polymerization by introducing 1 eq CuBr₂, 9 eq Me₆-TREN and DMSO into a glass vial and thorough mixing. A calculated volume of the stock solution was introduced into the reaction mixture so to obtain 0.01 eq CuBr₂ and 0.09 eq Me₆-TREN respective to the initiator or macroinitiator. An example of stock solution is as following: CuBr₂ (1 eq, 2.45 mg, 11.0 μmol), Me₆-TREN (9 eq, 22.5 mg, 97.8 μmol) and DMSO (10.14 mL).
Characterisation Techniques

Proton and carbon nuclear magnetic resonance (\(^{1}\text{H-NMR} \text{ and}^{13}\text{C-NMR}\)) spectra were recorded on an Agilent 400-MR 400 MHz spectrometer at 298 K. Deuterated chloroform (CDCl\(_3\), 99.8 %), deuterated dimethyl sulfoxide (DMSO-\(d_6\), 99.9 %), deuterated ethanol (ethanol-\(d_6\), 99.5 %), deuterated methanol (methanol-\(d_4\), 99.8 %) and deuterium oxide (D\(_2\)O, 99.9 %) were purchased from Sigma-Aldrich. Samples were dissolved in an appropriate solvent (= 5 g mL\(^{-1}\)) and analyzed with a pulse width of 45 \(\mu\)s, spectral width of 12/-2 ppm, recycle delay of 1 s and either 32 or 128 scans (conversion or purified samples respectively). Spectra were analyzed with MestreNova software version 14.1.

Size-exclusion chromatography (SEC) was performed on a GPCMax system from Viscotek equipped with 302 TDA detectors array and two columns in series (PolarGel L and M, both 8 \(\mu\)m 30 cm) from Agilent Technologies. The columns and detectors were maintained at a temperature of 50 °C. DMF (≥ 99.9 %, Sigma-Aldrich) containing 0.01 M LiBr was used as eluent at a flow rate of 1 mL min\(^{-1}\). Near monodisperse poly(methyl methacrylate) standards from Polymer Standard Services were used for the construction of a calibration curve. Samples were dissolved in the eluent at a concentration of \(\approx 3 \text{ g L}^{-1}\) and passed through a 0.45 \(\mu\)m PTFE filter prior to injection. Data acquisition and calculations were performed using Viscotek Omniseck software version 5.0.

Differential scanning calorimetry (DSC) measurements were recorded on a TA instruments DSCQ1000. The samples (~ 5 mg) were subjected to the following method: (i) equilibration at -80 °C, (ii) 5 min isotherm, (iii) ramp to 100 °C at 10 °C min\(^{-1}\), (iv) 5 min isotherm, (v) ramp to -80 °C at 10 °C min\(^{-1}\), (vi) 5 min isotherm and (vii) ramp to 100 °C at 10 °C min\(^{-1}\). Data analysis was performed on the second heating cycle using TA Instruments TRIOS software.

Thermogravimetric analysis (TGA) measurements were recorded on a TA instruments TGA5500 analyzer. The samples (~ 5 mg) were subjected to a 20 min isotherm at 130 °C to remove traces of solvent and moisture before returning to room temperature and zeroing the balance. Then, the samples were heated from 30 °C to 700 °C at a rate of 10 °C min\(^{-1}\) under a continuous nitrogen flow. The data acquisition and analysis was done using TA Instruments TRIOS software.

Dynamic light scattering (DLS) measurements were performed on a Malvern Panalytical Zetasizer Ultra system, equipped with a helium-neon laser (\(\lambda = 633 \text{ nm}\)) and an Avalanche Photodiode detector. Samples were prepared at a concentration of 1 g L\(^{-1}\) in triple-filtered (0.2
μm cellulose acetate) 10 mM KNO₃ solution. The nanoparticle solutions were measured at 25 °C in back scattering mode after 120 s equilibration time and using 30 cumulative recordings. The LCST of the homopolymer was determined by measurements at a controlled temperature between 5 and 25 °C in back scattering mode, after 120 s equilibration time, using 30 cumulative recordings and at a fixed attenuator value (determined from a preliminary scan at 25 °C). Samples were recorded in triplicates. Results were analyzed with ZS Xplorer software.

ζ-potential measurements were performed on a Malvern Panalytical Zetasizer ULtra system, equipped with a helium-neon laser (λ = 633 nm) and an Avalanche Photodiode detector. The measurements were taken at 25 °C while the acquisition times were determined automatically. Samples were recorded in triplicates.

UV-Vis spectroscopy measurements were performed on a Jasco V-650 spectrophotometer equipped with a PAC-743 Peltier cell. Polymer solutions were prepared at a concentration of 1 g L⁻¹ in triple-filtered (0.2 μm cellulose acetate) 10 mM KNO₃ solution and cooled or heated by the Peltier cell per 1.0 ± 0.1 °C increments while being stirred at 200 rpm. Short transmittance spectra were recorded between 600 and 605 nm with 0.5 nm intervals and the value in that range was averaged. Samples were recorded in triplicates.

Transmission electron microscopy (TEM) imaging was performed on a Philips CM120 transmission electron microscope equipped with a tungsten filament and operated at an accelerating voltage of 120 kV. Images were acquired using a Gatan slow-scan CCD camera. Negatively stained specimen were prepared by deposition of 5 μL of the nanoparticle dispersion (c ~ 1 g L⁻¹) onto a glow-discharged (15 s at 50 mA and 300 V) 400-mesh copper grid with carbon support film and adsorption for 1 min before blotting. Before the specimen was fully dried, 5 μL of 2 wt.% uranyl acetate staining solution was deposited onto the grid, immediately blotted and a new 5 μL drop of staining solution was deposited and left to adsorb for 1 min before blotting. TEM images were analyzed using Image J software, using the software brightness and contrast correction tools to enhance the general quality of the snapshots and the software-imbedded measurement tool was utilized to determine the dimensions of the nanoparticles. The particles’ diameter was measured center-to-center, i.e. from the center of one particle to the center of the neighboring one.

Atomic force microscopy (AFM) imaging was performed in standard tapping mode in air using a Bruker Dimension 3100 system, equipped with VTESPA-300 tapping mode cantilevers from Bruker. Freshly-prepared C3M samples (1 g L⁻¹ in 10 mM KNO₃) were spin-coated (4 000 rpm, 60 s) onto a freshly-cleaved mica disc (Ø = 9.5 mm, muscovite mica grade V-1,
Proscitech) and measured on the same day. Images were processed with Bruker NanoScope software.

The formation of complex coacervate core micelles (C3M) was done just before analysis. Each polymer was dissolved in triple-filtered (0.2 μm cellulose acetate) 10 mM KNO$_3$ buffer at a concentration of 1 g L$^{-1}$. The 4VPq units account for 100 wt.% of the quaternised homopolymer (neglecting end groups), while the SPA-Na units account for 85 or 93 wt.% of the PEO$_{90}$-b-PSPA-Na$_{110}$ or PEO$_{90}$-b-PSPA-Na$_{237}$ block copolymers respectively. The volumes of block copolymer solutions was calculated to provide a 1:1 ratio between the 4VPq and the SPA-Na units to achieve full charge compensation. Therefore, a volume of 300 μL of P4VPq solution (i.e. 1.22 μmol 4VPq, 300 μg 4VP) was introduced in a dust-free vial equipped with a stirring bar, before 309 μL of PEO$_{90}$-b-PSPA-Na$_{110}$ (i.e. 309 μg BCP, 263 μg SPA-Na, 1.22 μmol SPA-Na) or 282 μL of PEO$_{90}$-b-PSPA-Na$_{237}$ (i.e. 282 μg BCP, 263 μg SPA-Na, 1.22 μmol SPA-Na) was added upon stirring (250 rpm). The solutions were left to stir for 10 min before analysis.
Methods

Synthesis of 3-isobutoxysulfopropyl acrylate (BSPA)

The synthesis of the monomer was adapted from a previously reported procedure.\textsuperscript{1} KSPA (1 eq, 12.3 g, 52.9 mmol) and a stirring egg were charged in a 3-neck round bottom flask and subjected to several high vacuum / argon cycles to remove moisture before anhydrous DMF (40 mL) was added. The suspension was cooled over an ice bath before dropwise addition of (COCl)\textsubscript{2} (1.1 eq, 7.42 g, 58.5 mmol) in DCM (20 mL) under argon protection. In a separate round bottom flask, TEA (1.5 eq, 10.7 g, 106 mmol) and \textit{i}BuOH (1.2 eq, 4.73 g, 63.8 mmol) were dissolved in DCM (40 mL) and cooled over an ice bath. After an hour, the monomer/DMF/DCM solution was added to the second flask under argon protection using a dropping funnel, warmed-up to room temperature and left to stir overnight. Then, DI water (300 mL) was added and the reaction product was extracted with Et\textsubscript{2}O (3x 200 mL). The organic phases were combined, concentrated in vacuo and washed with DI water (200 mL) and dried over MgSO\textsubscript{4}. The monomer was further purified by flash column chromatography using \textit{n}-hexane:EtOAc 4:1 as eluent ($R_f \approx 0.44$) to yield a light yellow liquid. Yield\textsubscript{batch 1}: 10.1 g, 76 %. Yield\textsubscript{batch 2}: 10.4 g, 80 %. \textsuperscript{1}H-NMR (CDCl\textsubscript{3}): (ppm) = 0.97 (d, 2 CH\textsubscript{3}), 2.02 (m, CH), 2.23 (m, CH\textsubscript{2}), 3.20 (t, CH\textsubscript{2}), 3.99 (d, CH\textsubscript{2}), 4.28 (t, CH2), 5.86 (d, CH), 6.11 (q, CH), 6.42 (d, CH). \textsuperscript{13}C-NMR: (CDCl\textsubscript{3}): (ppm) = 18.8, 23.5, 28.4, 47.3, 62.0, 75.7, 128.0, 131.6, 165.9.
Cu(0)-RDRP of poly(3-isobutoxysulfopropyl acrylate) homopolymers (PBSPA$_x$, $x = 45, 81, 210, 370$ or $530$)

A typical Cu(0)-RDRP of 3-isobutoxysulfopropyl acrylate (polymerization of the protected monomer) is as following (here depicted for the synthesis of PBSPA$_{45}$): EB$_i$B (1 eq, 10.5 mg, 53.9 μmol, 100 μL of stock solution of 321 mg EB$_i$B in 3.07 mL DMSO), BSPA (48 eq, 648 mg, 2.59 mmol), Me$_6$-TREN (0.09 eq, 1.09 mg, 4.74 μmol, 262 μL of Me$_6$-TREN/CuBr$_2$ stock solution), CuBr$_2$ (0.01 eq, 0.117 mg, 0.525 μmol, 262 μL of Me$_6$-TREN/CuBr$_2$ stock solution), and DMSO (6 μL, total solvent volume: 200 eq, 363 μL) were charged in a Schlenk tube. A freshly-etched copper wire-winded stirring bar was introduced into the tube and kept above the liquid with a strong magnet before the tube was sealed with a rubber septum. The reaction mixture was deoxygenated with argon for 10 min before an aliquot was withdrawn under argon protection for $^1$H-NMR sampling. The tube was left under a slight positive pressure and the stirring bar was dropped into the solution to start the polymerization. After 4 hours at room temperature, the copper wire-winded stirring bar was lifted above the liquid and the tube opened to air. After withdrawal of an aliquot for $^1$H-NMR analysis, the reaction mixture was precipitated in cold 6:1 n-hexane:ethanol. The polymer was redissolved in excess THF, passed through a short AlOx column to remove excess copper, concentrated in vacuo and precipitated once more in cold 6:1 n-hexane:ethanol. The polymer was redissolved in minimal 1,4-dioxane and freeze-dried overnight to yield a transparent highly viscous liquid. Yield: 433 mg. $^1$H-NMR: conversion = 93 %, $D_{\text{NMR}} = 45$, $M_{\text{NMR}} = 11 400$ Da. SEC: $M_{\text{SEC}} = 15 900$ Da, $D = 1.12$.

All other Cu(0)-RDRP of BSPA were produced in a similar fashion, using the same amounts of BSPA and DMSO but lowering the amounts of EB$_i$B, Me$_6$-TREN and CuBr$_2$ accordingly. Detailed compositions of the reactions are summarized in Table S1.
Table S1: Compositions of the reaction mixtures used for the Cu(0)-RDRP of BSPA.

| Polymer | [EBiB]:[BSPA]:[Me6-TREN]:[CuBr2] | EBiB (μmol) | BSPA (mmol) | Me6-TREN (μmol) | CuBr2 (nmol) | DMSO (total, μL) | Yield (mg) |
|---------|----------------------------------|-------------|-------------|-----------------|--------------|------------------|------------|
| PBSPA_{45} | 1:48:0.09:0.01 | 53.9 | 2.59 | 4.74 | 525 | 363 | 547 |
| PBSPA_{81} | 1:91:0.09:0.01 | 27.5 | 2.56 | 2.35 | 264 | 363 | 433 |
| PBSPA_{210} | 1:250:0.09:0.01 | 10.4 | 2.60 | 0.974 | 108 | 363 | 468 |
| PBSPA_{370} | 1:500:0.09:0.01 | 5.23 | 2.62 | 0.509 | 56.1 | 363 | 394 |
| PBSPA_{530} | 1:980:0.09:0.01 | 2.72 | 2.66 | 0.255 | 28.0 | 363 | 309 |
Deprotection of PBSPA using NaI to produce poly(3-sulfopropyl acrylate) sodium salt (PSPA-Na, x = 45, 81, 210, 370 or 530)

The deprotection of poly(3-isobutoxysulfopropyl acrylate) was performed as reported before and a typical procedure is as following (here depicted for the synthesis of PSPA-Na_{45}):

PBSPA_{45} (1 eq, 108 mg, 432 μmol BSPA) and NaI (3 eq per BSPA unit, 212 mg, 1.42 mmol) were dissolved in DMSO (5 mL, 20 mg per mL) and charged into a glass vial equipped with a stirring bar. The reaction mixture was left to stir at 70 °C for 24 hours. The resulting dark brown solution was precipitated once in n-hexane:ethanol 1:2, redissolved in minimal DMSO and precipitated once more in n-hexane:ethanol 1:1 before a final wash with pure n-hexane. The polymer was redissolved in minimal DI water and freeze-dried overnight to yield an off-white brittle solid. Yield: 88 mg. \(^1\)H-NMR: deprotection ≈ 100 %, \(M_{\text{NMR}}\) = 9 900 Da.

Table S2: Compositions of the reaction mixtures used for the nucleophilic deprotection of PBSPA homopolymers using NaI.

| Polymer    | PBSPA (mg) | BSPA units (μmol) | NaI (mmol) | Yield (mg) | \(M_{\text{NMR}}\) (Da) |
|------------|------------|-------------------|------------|------------|--------------------------|
| PSPA-Na_{45} | 108        | 432               | 1.42       | 89         | 9 900                    |
| PSPA-Na_{81} | 103        | 412               | 1.24       | 88         | 17 700                   |
| PSPA-Na_{210} | 104       | 416               | 1.39       | 88         | 45 600                   |
| PSPA-Na_{370} | 74         | 296               | 1.15       | 62         | 80 100                   |
| PSPA-Na_{530} | 60         | 240               | 0.967      | 59         | 114 700                  |
Deprotection of PBSPA\textsubscript{x} with EMIMI to produce poly(3-sulfopropyl acrylate) 1-ethyl-3-methylimidazolium salt (PSPA-EMIM\textsubscript{x}, x = 45, 81, 210, 370 or 530)

The deprotection of PBSPA\textsubscript{x} using EMIMI as nucleophile was performed similarly to that of NaI and a typical procedure is as following (here depicted for the synthesis of PSPA-EMIM\textsubscript{45}): PBSPA\textsubscript{45} (1 eq, 108 mg, 432 μmol BSPA) and EMIMI (3 eq per BSPA unit, 301 mg, 1.26 mmol) were dissolved in DMSO (5 mL, 20 mg per mL) and charged into a glass vial equipped with a stirring bar. The reaction mixture was left to stir at 70 °C for 24 hours. The resulting dark brown solution was precipitated once in n-hexane:ethanol 6:1 and washed 4 times with n-hexane:ethanol 6:1 before a final wash with pure n-hexane. The polymer was redissolved in minimal DI water and freeze-dried overnight to yield a yellow and very gooey solid. Yield: 110 mg. \textsuperscript{1}H-NMR: deprotection ≈ 100 %, \( M_{n \text{NMR}} = 13\,900 \) Da.

**Table S3:** Compositions of the reaction mixtures used for the nucleophilic deprotection of PBSPA homopolymers using EMIMI.

| Polymer     | PBSPA (mg) | BSPA units (μmol) | EMIMI (mmol) | Yield (mg) | \( M_{n \text{NMR}} \) (Da) |
|-------------|------------|-------------------|--------------|------------|-----------------|
| PSPA-EMIM\textsubscript{45} | 108        | 432               | 1.27         | 110        | 13\,900         |
| PSPA-EMIM\textsubscript{81}  | 103        | 412               | 1.29         | 98         | 24\,800         |
| PSPA-EMIM\textsubscript{210} | 102        | 408               | 1.27         | 79         | 64\,000         |
| PSPA-EMIM\textsubscript{370} | 80.1       | 320               | 1.09         | 57         | 112\,700        |
| PSPA-EMIM\textsubscript{530} | 72.2       | 288               | 1.00         | 65         | 161\,300        |
Kinetic study on the Cu(0)-RDRP of 3-isobutoxysulfopropyl acrylate

EBIB (1 eq, 5.35 mg, 27.4 μmol, 49.6 μL of stock solution of 321 mg EBIB in 4.07 mL DMSO), BSAPA (94 eq, 640 mg, 2.56 mmol), Me₆-TREN (0.09 eq, 0.535 mg, 1.54 μmol, 41.5 μL of Me₆-TREN stock solution of 52.4 mg in 4.48 g DMSO), CuBr₂ (0.01 eq, 0.0572 mg, 0.257 μmol, 41.5 μL of CuBr₂ stock solution of 5.61 mg in 4.48 g DMSO), and DMSO (274 μL, total solvent volume: 200 eq, 363 μL) were charged in a Schlenk tube. A freshly-etched copper wire-winded stirring bar was introduced into the tube and kept above the liquid with a strong magnet before the tube was sealed with a rubber septum. The reaction mixture was deoxygenated with argon for 10 min before an aliquot was withdrawn under argon protection for ¹H-NMR sampling. The tube was left under slight positive pressure and the stirring bar was dropped to start the polymerization. Aliquots were withdrawn with a degassed syringe at preset time intervals under argon protection. ¹H-NMR samples (~ 2 drops) were directly diluted in CDCl₃ while SEC samples (~ 2 drops) were precipitated into cold 6:1 n-hexane:ethanol, dried in air and dissolved in eluent. After 4 hours at room temperature, the copper wire-winded stirring bar was lifted above the liquid and the tube was opened to air. The remainder of the reaction mixture was precipitated into cold 6:1 n-hexane:ethanol, redissolved in excess THF, passed through a short AlOx column to remove excess copper, concentrated in vacuo and precipitated once more in cold 6:1 n-hexane:ethanol. The polymer was redissolved in minimal 1,4-dioxane and freeze-dried overnight to yield a transparent highly viscous liquid. Yield: 323 mg. ¹H-NMR: conversion after 4 hours = 92 %, DP NMR = 86, Mₙ NMR = 21 700 Da. SEC: Mₙ SEC, purified = 45 200 Da, Đ SEC, purified = 1.10.
Synthesis of poly(methyl acrylate) macroinitiator (PMA\textsubscript{92})

EB\textsubscript{i}B (1 eq, 45.2 mg, 232 μmol), MA (100 eq, 1.99 g, 23.1 mmol), Me\textsubscript{6}-TREN (0.09 eq, 4.92 mg, 21.4 μmol, 420 μL of Me\textsubscript{6}-TREN stock solution of 59.6 mg Me\textsubscript{6}-TREN in 5.60 g DMSO), CuBr\textsubscript{2} (0.01 eq, 0.528 mg, 2.37 μmol, 420 μL of CuBr\textsubscript{2} stock solution of 6.4 mg CuBr\textsubscript{2} in 5.60 g DMSO), and DMSO (2.86 mL, total solvent volume: 200 eq, 3.27 mL) were charged in a Schlenk tube. A freshly-etched copper wire-winded stirring bar was introduced into the tube and kept above the liquid with a strong magnet before the tube was sealed with a rubber septum. The reaction mixture was deoxygenated via three freeze-pump-thaw cycles and backfilled with argon before an aliquot was withdrawn under argon protection for \textsuperscript{1}H-NMR sampling. The tube was left under a slightly positive pressure and the stirring bar was dropped to start the polymerization. After reacting for 4 hours at room temperature, the copper wire-winded stirring bar was lifted above the liquid and the tube was opened to air. After withdrawal of an aliquot for \textsuperscript{1}H-NMR sampling, the reaction mixture was precipitated into cold 6:1 \textit{n}-hexane:ethanol. The polymer was redissolved in excess THF, passed through a short AlO\textsubscript{x} column to remove excess copper, concentrated in vacuo and precipitated once more in cold 6:1 \textit{n}-hexane:ethanol. The polymer was redissolved in minimal 1,4-dioxane and freeze-dried overnight to yield a transparent highly viscous liquid. Yield: 1.75 g. \textsuperscript{1}H-NMR: conversion = 92 %, DP\textsubscript{NMR} = 92, M\textsubscript{n NMR} = 8 100 Da. SEC: M\textsubscript{w SEC} = 10 700 Da, D = 1.07.
Synthesis of poly(di[ethylene glycol] ethyl ether acrylate) macroinitiator (PDEGA$_{104}$)

EB$\beta$B (1 eq, 10.4 mg, 53.3 µmol, 100 µL of stock solution), DEGA (193 eq, 1.94 g, 10.3 mmol), Me$_6$-TREN (0.09 eq, 1.07 mg, 4.65 µmol, 136 µL of Me$_6$-TREN stock solution of 40.0 mg Me$_6$-TREN in 5.62 g DMSO), CuBr$_2$ (0.01 eq, 0.115 mg, 0.516 µmol, 420 µL of CuBr$_2$ stock solution of 4.27 mg CuBr$_2$ in 5.62 g DMSO), and DMSO (2.67 mL, total solvent volume: 800 eq, 2.90 mL) were charged in a Schlenk tube. A freshly-etched copper wire-winded stirring bar was introduced into the tube and kept above the liquid with a strong magnet before the tube was sealed with a rubber septum. The reaction mixture was deoxygenated via three freeze-pump-thaw cycles and backfilled with argon before an aliquot was withdrawn under argon protection for $^1$H-NMR sampling. The tube was left under a slightly positive pressure and the stirring bar was dropped to start the polymerization. After reacting for 30 min at room temperature, the copper wire-winded stirring bar was lifted above the liquid and the tube was opened to air. After withdrawal of an aliquot for $^1$H-NMR analysis, the reaction mixture was precipitated into cold 6:1 $n$-hexane:ethanol. The polymer was redissolved in excess THF, passed through a short AlOx column to remove excess copper, concentrated in vacuo and precipitated once more in cold 6:1 $n$-hexane:ethanol. The polymer was redissolved in minimal 1,4-dioxane and freeze-dried overnight to yield a transparent highly viscous liquid. Yield: 929 mg. $^1$H-NMR: conversion = 54 %, DP$_{^1}$H-NMR = 104, M$_{^1}$H-NMR = 19 700 Da. SEC: M$_r$SEC = 22 000 Da, Đ = 1.11.
Synthesis of poly(ethylene oxide) macroinitiator (PEO\textsubscript{96}-Br)

Poly(ethylene oxide) was modified via esterification of the hydroxy group by treating the polymer with an excess acid halide, a method adapted from an earlier reported procedure.\textsuperscript{2} PEO\textsubscript{96}-OH (1 eq, 25 g, 6.25 mmol) was charged into a three-neck 250 mL round bottom flask equipped with a stirring egg and subjected to several high-vacuum/argon cycles to remove residual moisture. Then, 100 mL dry DCM and TEA (1.5 eq, 947 mg, 1304 μL, 9.38 mmol) were added and the mixture was cooled over an ice bath before dropwise addition of BiBB (5 eq, 7188 mg, 3865 μL, 31.3 mmol) in 50 mL dry DCM over argon protection. The reaction mixture was allowed to warm up to room temperature and left to stir overnight before addition of 1 mL ethanol to quench unreacted BiBB. The solution was concentrated \textit{in vacuo} and precipitated once in cold \textit{n}-hexane. The polymer was recrystallised following a reported procedure,\textsuperscript{3} where the yellowish precipitate was redissolved in 200 mL hot ethanol (50 °C), cooled down in the fridge at 4 °C and centrifuged. The yellow supernatant was removed and the operation was repeated several times until the supernatant remained completely colourless. The polymer was finally dried in a vacuum oven to obtain a white powder. Yield: 22.5 g. \textsuperscript{1}H-NMR: $M_{n\text{NMR}} = 4100$ Da, functionalisation $\approx 100\%$. SEC: $M_{n\text{SEC}} = 7000$ Da, $\mathcal{D} = 1.06$. 
‘Deprotection’ of macroinitiators (i.e. negative control experiments)

PMA$_{92}$ (1 eq, 101 mg, 1.17 mmol MA) and NaI (3 eq per MA unit, 529 mg, 3.53 mmol) were dissolved in DMSO (5 mL, 20 mg per mL) and charged into a glass vial equipped with a stirring bar. The reaction mixture was left to stir at 70 °C for 24 hours. The resulting yellow solution was precipitated once in $n$-hexane:ethanol 6:1, redissolved in minimal THF and precipitated once more in $n$-hexane:ethanol 6:1. The polymer was redissolved in minimal 1,4-dioxane and freeze-dried overnight to yield a light yellow highly viscous liquid. Yield: 77 mg. SEC: $M_n^{SEC} = 10$ 500 Da, $D = 1.10$.

PEO$_{90}$-Br (1 eq, 102 mg, 2.32 mmol ethylene oxide) and NaI (3 eq per MA unit, 1.04 g, 6.93 mmol) were dissolved in DMSO (5 mL) and charged into a glass vial equipped with a stirring bar. The reaction mixture was left to stir at 70 °C for 24 hours. The resulting yellow solution was precipitated in $n$-hexane:ethanol 6:1 and washed three times with $n$-hexane:ethanol 6:1. The polymer was redissolved in minimal 1,4-dioxane and freeze-dried overnight to yield a light yellow powder. Yield: 20 mg. SEC: $M_n^{SEC} = 7$ 100 Da, $D = 1.07$.

PDEGA$_{104}$ (1 eq, 99.7 mg, 530 μmol di[ethylene glycol] ethyl ether acrylate) and NaI (3 eq per DEGA unit, 248 mg, 1.65 mmol) were dissolved in DMSO (5 mL) and charged into a glass vial equipped with a stirring bar. The reaction mixture was left to stir at 70 °C for 24 hours. The resulting yellow solution was dialysed against acetone and concentrated in vacuo. The polymer was then redissolved in minimal 1,4-dioxane and freeze-dried overnight to yield a light yellow viscous oil. Yield: 90.2 mg. SEC: $M_n^{SEC} = 22$ 100 Da, $D = 1.13$. 
Synthesis of poly(methyl acrylate)-block-poly(3-isobutoxysulfopropyl acrylate) (PMA<sub>92</sub>-b-PBS<sub>x</sub>, x = 103 or 231)

For PMA<sub>92</sub>-b-PBSPA<sub>103</sub>, PMA<sub>92</sub> (1 eq, 101.7 mg, 12.6 μmol), BSPA (99 eq, 311 mg, 1.24 mmol), Me<sub>6</sub>-TREN (0.09 eq, 0.264 mg, 1.15 μmol, 70.5 mg of a stock solution of 41.9 mg Me<sub>6</sub>-TREN in 11.2 g DMSO) and CuBr<sub>2</sub> (0.01 eq, 0.0281 mg, 0.126 μmol, 70.5 mg of a stock solution of 4.45 mg CuBr<sub>2</sub> in 11.2 g DMSO) and DMSO (438 μL, total solvent volume of 500 μL) were charged in a Schlenk tube. A freshly-etched copper wire-winded stirring bar was introduced into the tube and kept above the liquid with a strong magnet before the tube was sealed with a rubber septum. The reaction mixture was deoxygenated with argon for 5 min before an aliquot was withdrawn under argon protection for ¹H-NMR sampling. The tube was left under slight positive pressure and the stirring bar was dropped to start the polymerization. After 24 hours at room temperature, the copper wire-winded stirring bar was lifted above the liquid and the tube was opened to air. After withdrawal of an aliquot for ¹H-NMR analysis, the reaction mixture was precipitated into cold 6:1 n-hexane:ethanol. The polymer was redissolved in THF, passed through a short AIOx column to remove excess copper, concentrated in vacuo and precipitated once more in cold 6:1 n-hexane:ethanol. The polymer was redissolved in minimal 1,4-dioxane and freeze-dried overnight to yield a transparent highly viscous liquid. Yield: 325 mg. ¹H-NMR: conversion = 94 %, DP<sub>PBSPA,NMR</sub> = 103, M<sub>n NMR</sub> = 33 900 Da. SEC: M<sub>n SEC</sub> = 52 500 Da, Đ = 1.13.

PMA<sub>92</sub>-b-PBSPA<sub>231</sub> was prepared following the above-described procedure but using PMA<sub>92</sub> (1 eq, 101.6 mg, 12.5 μmol), BSPA (250 eq, 784 mg, 3.13 mmol), Me<sub>6</sub>-TREN (0.09 eq, 0.260 mg, 1.13 μmol, 69.3 mg of a stock solution of 41.9 mg Me<sub>6</sub>-TREN in 11.2 g DMSO) and CuBr<sub>2</sub> (0.01 eq, 0.0276 mg, 0.124 μmol, 69.3 mg of a stock solution of 4.45 mg CuBr<sub>2</sub> in 11.2 g DMSO) and DMSO (438 μL, total solvent volume of 500 μL). Yield: 639 mg. ¹H-NMR: conversion = 82 %, DP<sub>PBSPA,NMR</sub> = 231, M<sub>n NMR</sub> = 65 600 Da. SEC: M<sub>n SEC</sub> = 89 200 Da, Đ = 1.24.
Synthesis of poly(methyl acrylate)-block-poly(3-sulfopropyl acrylate) sodium salt block copolymers (PMA_{92-b}-PSPA-Na_{x}, x = 103 or 231)

For PMA_{92-b}-PSPA-Na_{103}, PMA_{92-b}-PBSPA_{103} (105 mg, 1 eq BSPA, 79.8 mg BSPA, 319 μmol BSPA), NaI (3 eq to BSPA, 144 mg, 958 μmol) and DMSO (2 mL) were charged into a glass vial equipped with a stirring bar. The polymer and the salt were dissolved at room temperature before the reaction mixture was heated at 70 °C for 24 hours. The polymer was isolated by precipitation into n-hexane:ethanol 1:1 once, washed 3 times with n-hexane:ethanol 1:1 before a final wash with pure n-hexane. The polymer was then dissolved in minimal mixture of 1,4-dioxane and DI water and freeze-dried to yield an off-white solid. Yield: 80 mg. ¹H-NMR: deprotection ≈ 100%, $M_n$ NMR = 30 300 Da, $x_{SPA-Na} = 53$ mol.%.

PMA_{92-b}-PSPA-Na_{231} was prepared following the above-described procedure but using PMA_{92-b}-PBSPA_{231} (111 mg, 1 eq BSPA, 97.7 mg BSPA, 391 μmol BSPA), NaI (3 eq to BSPA, 176 mg, 1.17 mmol) and DMSO (2 mL). Yield: 80 mg. ¹H-NMR: deprotection ≈ 100%, $M_n$ NMR = 58 000 Da, $x_{SPA-Na} = 72$ mol.%.
Synthesis of poly(methyl acrylate)-block-poly(3-sulfopropyl acrylate) 1-ethyl-3-methylimidazolium salt block copolymers (PMA_{92-b}-PSPA-EMIM_{x}, x = 103 or 231)

For PMA_{92-b}-PSPA-EMIM_{103}, PMA_{92-b}-PBSPA_{103} (94.0 mg, 1 eq BSPA, 71.4 mg BSPA, 286 μmol BSPA), EMIMI (3 eq to BSPA, 236 mg, 992 μmol) and DMSO (2 mL) were charged into a glass vial equipped with a stirring bar. The polymer and the salt were dissolved at room temperature before the reaction mixture was heated at 70 °C for 24 hours. The polymer was isolated by precipitation into n-hexane:ethanol 6:1 once, washed 3 times with n-hexane:ethanol 1:1 before a final wash with pure n-hexane. The polymer was then dissolved in minimal mixture of 1,4-dioxane and DI water and freeze-dried to yield a light yellow highly viscous liquid. Yield: 117 mg. \(^1\)H-NMR: deprotection ≈ 100 %, \(M_n\) \text{NMR} = 39 400 Da, \(x_{\text{SPA-EMIM}} = 53 \text{ mol.}%.

PMA_{92-b}-PSPA-EMIM_{231} was prepared following the above-described procedure but using PMA_{92-b}-PBSPA_{231} (99.4 mg, 1 eq BSPA, 87.5 mg BSPA, 350 μmol BSPA), EMIMI (3 eq to BSPA, 273 mg, 1.15 mmol) and DMSO (2 mL). Yield: 128 mg. \(^1\)H-NMR: deprotection ≈ 100 %, \(M_n\) \text{NMR} = 78 300 Da, \(x_{\text{SPA-EMIM}} = 72 \text{ mol.}%).
Synthesis of poly(di[ethylene glycol] ethyl ether acrylate)-block-poly(3-isobutoxysulfopropyl acrylate) (PDEGA\textsubscript{104-}b-PBSPA\textsubscript{y}, y = 94 or 228)

For PDEGA\textsubscript{104-}b-PBSPA\textsubscript{94}, PDEGA\textsubscript{104} (1 eq, 244 mg, 12.4 μmol), BSPA (99 eq, 306 mg, 1.22 mmol), Me\textsubscript{6}-TREN (0.09 eq, 0.272 mg, 1.18 μmol, 124 mg of a stock solution of 24.4 mg Me\textsubscript{6}-TREN in 11.2 g DMSO) and CuBr\textsubscript{2} (0.01 eq, 0.0293 mg, 0.131 μmol, 113 mg of a stock solution of 2.63 mg in 11.2 g DMSO) and DMSO (438 μL, total solvent volume of 500 μL) were charged in a Schlenk tube. A freshly-etched copper wire-winded stirring bar was introduced into the tube and kept above the liquid with a strong magnet before the tube was sealed with a rubber septum. The reaction mixture was deoxygenated with argon for 5 min before an aliquot was withdrawn under argon protection for \textsuperscript{1}H-NMR sampling. The tube was left under slight positive pressure and the stirring bar was dropped into the solution to start the polymerization. After 24 hours at room temperature, the copper wire-winded stirring bar was lifted above the liquid and the tube opened to air. After withdrawal of an aliquot for \textsuperscript{1}H-NMR sampling, the reaction mixture was precipitated in cold 6:1 n-hexane:ethanol. The polymer was redissolved in THF, passed through a short AlOx column to remove excess copper, concentrated in vacuo and precipitated once more in cold 6:1 n-hexane:ethanol. The polymer was redissolved in minimal 1,4-dioxane and freeze-dried overnight to yield a transparent highly viscous liquid. Yield: 422 mg. \textsuperscript{1}H-NMR: conversion = 85 %, DP\textsubscript{PBSPA\_NMR} = 94, M\textsubscript{N} \textsubscript{NMR} \textsubscript{NMR} = 43 200 Da. SEC: M\textsubscript{N} \textsubscript{SEC} = 48 100 Da, Đ = 1.25.

PDEGA\textsubscript{104-}b-PBSPA\textsubscript{228} was prepared following the above-detailed procedure but using PDEGA\textsubscript{104} (1 eq, 244 mg, 12.4 μmol), BSPA (249 eq, 774 mg, 3.10 mmol), Me\textsubscript{6}-TREN (0.09 eq, 0.260 mg, 1.13 μmol, 119 mg of a stock solution of 24.4 mg Me\textsubscript{6}-TREN in 11.2 g DMSO) and CuBr\textsubscript{2} (0.01 eq, 0.0280 mg, 0.126 μmol, 119 mg of a stock solution of 2.63 mg in 11.2 g DMSO) and DMSO (438 μL, total solvent volume of 500 μL). Yield: 766 mg. \textsuperscript{1}H-NMR: conversion = 84 %, DP\textsubscript{PBSPA\_NMR} = 228, M\textsubscript{N} \textsubscript{NMR} = 76 700 Da. SEC: M\textsubscript{N} \textsubscript{SEC} = 81 700 Da, Đ = 1.37.
Synthesis of poly(di[ethylene glycol] ethyl ether acrylate)-block-poly(3-sulfopropyl acrylate) sodium salt block copolymers (PDEGA\textsubscript{104-b-PSPA-Na\textsubscript{x}}, x = 94 or 228)

For PDEGA\textsubscript{104-b-PSPA-Na\textsubscript{94}}, PMA\textsubscript{104-b-PBSPA\textsubscript{94}} (105 mg, 1 eq BSPA, 56.7 mg BSPA, 227 μmol BSPA), NaI (3 eq to BSPA, 113 mg, 753 μmol) and DMSO (2 mL) were charged into a glass vial equipped with a stirring bar. The polymer and the salt were dissolved at room temperature before the reaction mixture was heated at 70 °C for 24 hours. The polymer was isolated by precipitation into n-hexane:ethanol 1:1 once, washed 3 times with n-hexane:ethanol 1:1 before a final wash with pure n-hexane. The polymer was then dissolved in a minimal amount of a mixture of 1,4-dioxane and DI water and freeze-dried to yield an off-white solid. Yield: 102 mg. \textsuperscript{1}H-NMR: deprotection ≈ 100 %, $M_n$ NMR = 40 000 Da, $x_{SPA-Na}$ = 48 mol.%.

PDEGA\textsubscript{104-b-PSPA-Na\textsubscript{228}} was prepared following the above-detailed procedure but using PDEGA\textsubscript{104-b-PBSPA\textsubscript{228}} (112 mg, 1 eq BSPA, 82.9 mg BSPA, 332 μmol BSPA), NaI (3 eq to BSPA, 164 mg, 1.09 mmol) and DMSO (2 mL). Yield: 101 mg. \textsuperscript{1}H-NMR: deprotection ≈ 100 %, $M_n$ NMR = 68 900 Da, $x_{SPA-Na}$ = 69 mol.%.
Synthesis of poly(di[ethylene glycol] ethyl ether acrylate)-block-poly(3-sulfopropyl acrylate) 1-ethyl-3-methylimidazolium salt block copolymers (PDEGA\textsubscript{104-}b-PSPA-EMIM\textsubscript{x}, x = 94 or 228)

For PDEGA\textsubscript{104-}b-PSPA-EMIM\textsubscript{94}, PMA\textsubscript{104-}b-PBSPA\textsubscript{94} (104 mg, 1 eq BSPA, 56.2 mg BSPA, 225 μmol BSPA), EMIMI (3 eq to BSPA, 201 mg, 704 μmol) and DMSO (2 mL) were charged into a glass vial equipped with a stirring bar. The polymer and the salt were dissolved at room temperature before the reaction mixture was heated at 70 °C for 24 hours. The polymer was isolated by precipitation into n-hexane:ethanol 1:1 once, washed 3 times with n-hexane:ethanol 1:1 before a final wash with pure n-hexane. The polymer was then dissolved in a minimal amount of a mixture of 1,4-dioxane and DI water and freeze-dried to yield a light yellow highly viscous liquid. Yield: 125 mg. \textsuperscript{1}H-NMR: deprotection ≈ 100 %, M\textsubscript{n NMR} = 48 300 Da, x\textsubscript{SPA-Na} = 48 mol.%.

PDEGA\textsubscript{104-}b-PSPA-EMIM\textsubscript{228} was prepared following the above-detailed procedure but using PDEGA\textsubscript{104-}b-PBSPA\textsubscript{228} (106 mg, 1 eq BSPA, 78.4 mg BSPA, 314 μmol BSPA), EMIMI (3 eq to BSPA, 244 mg, 853 μmol) and DMSO (2 mL). Yield: 146 mg. \textsuperscript{1}H-NMR: deprotection ≈ 100 %, M\textsubscript{n NMR} = 89 000 Da, x\textsubscript{SPA-Na} = 69 mol.%.
Synthesis of short poly(ethylene oxide)-block-poly(3-isobutoxysulfopropyl acrylate) (PEO<sub>90</sub>-b-PBSA<sub>y</sub>, y = 110 or 237)

For PEO<sub>90</sub>-b-PBSA<sub>110</sub>, PEO<sub>90</sub>-Br (1 eq, 50.4 mg, 12.3 μmol), BSPA (104 eq, 320 mg, 1.28 mmol), Me<sub>6</sub>-TREN (0.09 eq, 0.266 mg, 1.16 μmol, 89.6 mg of a stock solution 33.3 mg in 11.2 g DMSO) and CuBr<sub>2</sub> (0.01 eq, 0.0286 mg, 0.128 μmol, 89.6 mg of a stock solution 3.58 mg in 11.2 g DMSO) and DMSO (422 μL, total solvent volume of 500 μL) were charged in a Schlenk tube. A freshly-etched copper wire-winded stirring bar was introduced into the tube and kept above the liquid with a strong magnet before the tube was sealed with a rubber septum. The reaction mixture was deoxygenated with argon for 5 min before an aliquot was withdrawn under argon protection for <sup>1</sup>H-NMR sampling. The tube was left under slight positive pressure and the stirring bar was dropped to start the polymerization. After 24 hours at room temperature, the copper wire-winded stirring bar was lifted above the liquid and the tube opened to air. After withdrawal of an aliquot for <sup>1</sup>H-NMR sampling, the reaction mixture was precipitated in cold 6:1 n-hexane:ethanol. The polymer was redissolved in THF, passed through a short AlOx column to remove excess copper, concentrated in vacuo and precipitated once more in cold 6:1 n-hexane:ethanol. The polymer was redissolved in minimal 1,4-dioxane and freeze-dried overnight to yield a transparent highly viscous liquid. Yield: 289 mg. <sup>1</sup>H-NMR: conversion = 97 %, DP<sub>PBSA, NMR</sub> = 110, M<sub>n, NMR</sub> = 31 600 Da. SEC: M<sub>n, SEC</sub> = 44 400 Da, Đ = 113.

PEO<sub>90</sub>-b-PBSA<sub>237</sub> was prepared following the above-detailed procedure but using PEO<sub>90</sub>-Br (1 eq, 50.0 mg, 12.4 μmol), BSPA (102 eq, 316.7 mg, 1.27 mmol), Me<sub>6</sub>-TREN (0.09 eq, 0.256 mg, 1.11 μmol, 86.2 mg of a stock solution 33.3 mg in 11.2 g DMSO) and CuBr<sub>2</sub> (0.01 eq, 0.0276 mg, 0.124 μmol, 86.2 mg of a stock solution 3.58 mg in 11.2 g DMSO) and DMSO (922 μL, total solvent volume of 1000 μL). Yield: 626 mg. <sup>1</sup>H-NMR: conversion = 85 %, DP<sub>PBSA, NMR</sub> = 237, M<sub>n, NMR</sub> = 63 400 Da. SEC: M<sub>n, SEC</sub> = 76 700 Da, Đ = 1.21.
Synthesis of poly(ethylene oxide)-block-poly(3-sulfopropyl acrylate) sodium salt block copolymers (PEO\textsubscript{90}-b-PSPA-\textsubscript{Na\textsubscript{z}}, \(z = 110\) or 237)

For PEO\textsubscript{90}-b-PSPA-\textsubscript{Na\textsubscript{110}}, PEO\textsubscript{90}-b-PBSPA\textsubscript{110} (108 mg, 1 eq BSPA, 94.0 mg BSPA, 376 \(\mu\)mol BSPA), NaI (3 eq to BSPA, 169 mg, 1.13 mmol) and DMSO (2 mL) were charged into a glass vial equipped with a stirring bar. The polymer and the salt were dissolved at room temperature before the reaction mixture was heated at 70 °C for 24 hours. The polymer was isolated by precipitation into cold \(n\)-hexane:ethanol 1:1 once, washed 3 times with cold \(n\)-hexane:ethanol 1:1 before a final wash with pure \(n\)-hexane. The polymer was then redissolved in a minimal DI water and freeze-dried to yield an off-white solid. Yield: 99 mg. \(^1\)H-NMR: deprotection \(\approx 100\) %, \(M_n\)\textsubscript{NMR} = 27 900 Da, \(x_{SPA-\textsubscript{Na}} = 55\) mol.%.

PEO\textsubscript{90}-b-PSPA-\textsubscript{Na\textsubscript{237}} was prepared following the above-detailed procedure but using PEO\textsubscript{90}-b-PBSPA\textsubscript{237} (101 mg, 1 eq BSPA, 94.4 mg BSPA, 380 \(\mu\)mol BSPA), NaI (3 eq to BSPA, 171 mg, 1.14 mmol) and DMSO (2 mL). Yield: 90 mg. \(^1\)H-NMR: deprotection \(\approx 100\) %, \(M_n\)\textsubscript{NMR} = 55 300 Da, \(x_{SPA-\textsubscript{Na}} = 73\) mol.%.
Synthesis of poly(ethylene oxide)-block-poly(3-sulfopropyl acrylate) 1-ethyl-3-methylimidazolium salt block copolymers (PEO₉₀-b-PSPA-EMIMₓ, x = 110 or 237)

For PEO₉₀-b-PSPA-EMIM₁₁₀, PEO₉₀-b-PSPA₁₁₀ (97.0 mg, 1 eq BSPA, 84.4 mg BSPA, 338 μmol BSPA), EMIMI (3 eq to BSPA, 257 mg, 1.08 mmol) and DMSO (2 mL) were charged into a glass vial equipped with a stirring bar. The polymer and the salt were dissolved at room temperature before the reaction mixture was heated at 70 °C for 24 hours. The polymer was isolated by precipitation into n-hexane:ethanol 6:1 once, washed 3 times with n-hexane:ethanol 1:1 before a final wash with pure n-hexane. The polymer was then dissolved in a minimal amount of a mixture of 1,4-dioxane and DI water and freeze-dried to yield a light yellow highly viscous liquid. Yield: 125 mg. ¹H-NMR: deprotection ≈ 100 %, Mᵣ NMR = 37 500 Da, χSPA-EMIM = 53 mol.%.

PEO₉₀-b-PSPA-EMIM₂₃₇ was prepared following the above-detailed procedure but using PEO₉₀-b-PSPA₂₃₇ (99.7 mg, 1 eq BSPA, 93.7 mg BSPA, 3750 μmol BSPA), EMIMI (3 eq to BSPA, 273 mg, 1.15 mmol) and DMSO (2 mL). Yield: 121 mg. ¹H-NMR: deprotection ≈ 100 %, Mᵣ NMR = 76 100 Da, χSPA-EMIM = 53 mol.%.
Synthesis of quaternised poly(4-vinylpyridine) (P4VPq_{119})

P4VP was produced following a previously reported procedure. Here, CPP-TCC (1 eq, 108 mg, 493 μmol), 4VP (195 eq, 10.1 g, 96.2 mmol), AIBN (0.07 eq, 5.4 mg, 33 μmol) and DMF (13.8 mL) were charged into a round bottom flask equipped with a stirring egg. The reaction mixture was deoxygenated with argon for 45 min before being immersed in a pre-heated oil bath at 70 °C. After 21 hours, the vessel was removed from the oil bath and cooled down over ice and the rubber septum was opened to quench the reaction. The polymer was isolated by precipitation into toluene, redissolved in DMF and precipitated once more into toluene to yield a yellow solid. Yield: 5.51 g. $^1$H-NMR: conversion = 61 %, DP$_{P4VP,NMR}$ = 119, M$_{n,NMR}$ = 12 700 Da. SEC: M$_{n,SEC}$ = 10 400 Da, Đ = 1.17.

P4VP was quaternised according to an earlier-reported procedure. Here, P4VP (2.06 g, 1 eq 4VP, 19.6 mmol 4VP) and 20 mL DMSO were charged in a round bottom flask equipped with a stirring egg before MeI (2 eq to 4VP, 5.56 g, 39.2 mmol) was added and the flask was left to stir for 4 hours at room temperature. The quaternised polymer was isolated by precipitation into acetone and dried in vacuo to yield a light orange solid. Yield: 4.62 g. $^1$H-NMR: degree of quaternisation > 99 %, M$_{n,NMR}$ = 29 600 Da.
One-pot synthesis of poly(sulfopropyl acrylate) sodium salt (PSPA-Na$_{54}$)

EB_iB (1 eq, 5.81 mg, 29.8 $\mu$mol, 53.7 $\mu$L of stock solution at 321 mg EB_iB in 4.07 mL DMSO), BSPA (88 eq, 653 mg, 2.61 mmol), Me$_6$-TREN (0.09 eq, 0.556 mg, 2.42 $\mu$mol, 164 $\mu$L of Me$_6$-TREN stock solution of 33.3 mg Me$_6$-TREN in 11.2 g DMSO), CuBr$_2$ (0.01 eq, 0.0598 mg, 0.268 $\mu$mol, 164 $\mu$L of CuBr$_2$ stock solution of 3.58 mg CuBr$_2$ in 11.2 g DMSO), and DMSO (153 $\mu$L, total solvent volume: 200 eq, 363 $\mu$L) were charged in a Schlenk tube. A freshly-etched copper wire-winded stirring bar was introduced into the tube and kept above the liquid with a strong magnet before the tube was sealed with a rubber septum. The reaction mixture was deoxygenated with argon for 10 min before an aliquot was withdrawn under argon protection for $^1$H-NMR sampling. The tube was left under slight positive pressure and the stirring bar was dropped into the reaction mixture to start the polymerization. After 4 hours at room temperature, the copper wire-winded stirring bar was lifted above the liquid and the tube was opened to air. One drop of the mixture was withdrawn for $^1$H-NMR sampling and two more drops were precipitated in cold 6:1 n-hexane:ethanol to isolate a PBSPA sample. Then, NaI (3 eq per BSPA unit, 1.17 g, 7.80 mmol) were dissolved in DMSO (10 mL) and charged into the Schlenk tube along with a new copper-free stirring bar. The vessel was immersed in a pre-heated oil bath and the reaction mixture was left to stir at 70 °C for 24 hours. The resulting dark brown solution was precipitated once in n-hexane:ethanol 1:2, redissolved in minimal DMSO and precipitated once more in n-hexane:ethanol 1:1 before a final wash with n-hexane. The polymer was redissolved in minimal DI water and freeze-dried overnight to yield an off-white brittle solid. Yield: 247 mg. $^1$H-NMR: conversion = 61 %, $\text{DP}_{\text{NMR}}$ = 54, $M_n$ NMR PSPA = 13 700 Da, deprotection $\approx$ 100 %, $M_n$ NMR PSPA = 11 900 Da. SEC: $M_n$ PBSPA = 27 000 Da, $\text{DP}_{\text{PBSPA}}$ = 1.16.
Table S4: Characteristics of the PSPA-Na based block copolymers and their respective precursors synthesized for this study.

|                | $x_{\text{SPA}}^\dagger$ (mol. %) | $M_n \text{ NMR}^{\dagger}$ (Da) | $M_n \text{ SEC}^\neq$ (Da) | $D^\neq$ |
|----------------|-----------------------------------|----------------------------------|----------------------------|----------|
| PMA$_{92}$     | 8 100                             | 10 700                           | 1.07                       |
| PMA$_{92}$-b-PBSPA$_{103}$ | 33 900                           | 52 500                           | 1.13                       |
| PMA$_{92}$-b-PSPA-Na$_{103}$ | 53                               | 30 300                           | n.a.                      | n.a.     |
| PMA$_{92}$-b-PBSPA$_{231}$ | 65 600                           | 89 200                           | 1.24                       |
| PMA$_{92}$-b-PSPA-Na$_{231}$ | 72                               | 58 000                           | n.a.                      | n.a.     |
| PEO$_{90}$-Br  | 4 100                             | 7 000                            | 1.06                       |
| PEO$_{90}$-b-PBSPA$_{110}$ | 31 600                           | 44 400                           | 1.13                       |
| PEO$_{90}$-b-PSPA-Na$_{110}$ | 55                               | 27 900                           | n.a.                      | n.a.     |
| PEO$_{90}$-b-PBSPA$_{237}$ | 63 400                           | 76 700                           | 1.21                       |
| PEO$_{90}$-b-PSPA-Na$_{237}$ | 73                               | 55 300                           | n.a.                      | n.a.     |
| PDEGA$_{104}$  | 19 700                            | 22 000                           | 1.11                       |
| PDEGA$_{104}$-b-PBSPA$_{94}$ | 43 200                           | 48 100                           | 1.25                       |
| PDEGA$_{104}$-b-PSPA-Na$_{94}$ | 48                               | 40 000                           | n.a.                      | n.a.     |
| PDEGA$_{104}$-b-PBSPA$_{228}$ | 76 700                           | 81 700                           | 1.37                       |
| PDEGA$_{104}$-b-PSPA-Na$_{228}$ | 69                               | 68 900                           | n.a.                      | n.a.     |

$\dagger$ determined from a combination of $^1$H-NMR conversion samples and end-group analysis; $^\neq$ determined from SEC data in DMF with 0.01 M LiBr and calibrated against near-monodisperse PMMA standards.
Supplementary Figures

S1: NMR spectroscopy of the BSPA monomer

Figure S1: Heteronuclear single quantum coherence (HSQC) spectrum of 3-isobutoxysulfopropyl acrylate, recorded in CDCl₃.
S2: Kinetic analysis of the PBSPA homopolymerization

**Figure S2**: Polymerization kinetics of 3-isobutoxysulfopropyl acrylate by Cu(0)-RDRP. (A) Conversion and (B) ln([M]₀/[[M]] kinetic plots extracted from 'H-NMR analysis. (C) Elugrams and (D) dispersity plot obtained by SEC. Time points are 15 min (black), 30 min (red), 60 min (dark blue), 120 min (green) and 240 min (light blue). [EB:B]:[BSPA]:[DMSO]:[Me₆-TREN]:[CuBr₂] ratios used for the kinetic study were 1:94:200:0.09:0.01.
S3: $^1$H-NMR analysis on deprotected homopolymers

**Figure S3-1**: Comparative $^1$H-NMR spectra of the PBSPA$_{45}$ (red, * = residual 1,4-dioxane) and corresponding PSPA$_{45}$ (green) in DMSO-$d_6$.

**Figure S3-2**: $^1$H-NMR spectra (D$_2$O) of (A) PSPA-Na$_{45}$ and (B) PSPA-EMIM$_{45}$ obtained after nucleophilic deprotection of PBSPA$_{45}$ using NaI or EMIMI respectively.
Figure S3-3: Comparative $^1$H-NMR spectra of PSPA-Na$_{45}$ in (A) D$_2$O and (B) DMSO-$d_6$.

Figure S3-4: Comparative $^1$H-NMR spectra of PSPA-EMIM$_{45}$ in (A) D$_2$O, (B) DMSO-$d_6$, (C) methanol-$d_4$ and (D) ethanol-$d_6$. 
S4: Thermal analyses on the homopolymers

Figure S4-1: Comparitive thermogravimetric analyses (TGA) on various protected homopolymers: PBSPA\textsubscript{45} (black), PBSPA\textsubscript{81} (red), PBSPA\textsubscript{210} (green), PBSPA\textsubscript{370} (blue) and PBSPA\textsubscript{530} (magenta).

Table S5: Degradation temperatures and associated weight losses obtained through thermogravimetric analyses on the various PBSPA homopolymers.

| Sample     | \( T_{\text{deg 1}} \) \( ^\circ \text{C} \) | Weight loss at \( T_{\text{deg 1}} \) (%) | \( T_{\text{deg 2}} \) \( ^\circ \text{C} \) | Weight loss at \( T_{\text{deg 2}} \) (%) |
|------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| PBSPA\textsubscript{45} | 195 | 75.5 | 420 | 16.8 |
| PBSPA\textsubscript{81} | 191 | 73.2 | 418 | 15.7 |
| PBSPA\textsubscript{210} | 195 | 71.0 | 420 | 17.8 |
| PBSPA\textsubscript{370} | 194 | 69.3 | 406 | 18.6 |
| PBSPA\textsubscript{530} | 194 | 72.9 | 432 | 16.3 |

\( ^\dagger \) temperature corresponding to the maximal rate at \( T_{\text{deg}} \) (\( i.e. \) decomposition temperature)
Figure S4-2: Comparative differential scanning calorimetry (DSC) analyses on various protected homopolymers: PBSPA45 (black), PBSPA81 (red), PBSPA210 (green), PBSPA370 (blue) and PBSPA530 (magenta).

Figure S4-3: Differential scanning calorimetry analyses of various PSPA-EMIM homopolymers: PSPA-EMIM45 (black, $T_g = -23.5$ °C), PSPA-EMIM81 (red, $T_g = -23.3$ °C), PSPA-EMIM210 (green, $T_g = -20.4$ °C), PSPA-EMIM370 (blue, $T_g = -24.5$ °C) and PSPA-EMIM530 (magenta, $T_g = -16.8$ °C).
Figure S4-4: Comparative (A) thermogravimetric and (B) differential scanning calorimetry analyses on PBSPA$_{45}$ (red), PSPA-$\text{Na}_{45}$ (green) and PSPA-$\text{EMIM}_{45}$ (dark cyan).

Table S6: Glass transition temperatures, degradation temperatures and associated weight losses observed through thermal analyses on a protected PBSPA homopolymer and various deprotected analogues.

| Sample         | $T_g$ (°C) | $T_{\text{deg}^1}$ (°C) | Weight loss at $T_{\text{deg}^1}$ (%) | $T_{\text{deg}^2}$ (°C) | Weight loss at $T_{\text{deg}^2}$ (%) |
|----------------|------------|--------------------------|---------------------------------------|--------------------------|---------------------------------------|
| PBSPA$_{45}$   | -27.9      | 195                      | 75.5                                  | 420                      | 16.8                                  |
| PSPA-$\text{Na}_{45}$ | n.a.    | 186                      | 5.28                                  | 355                      | 42.3                                  |
| PSPA-$\text{EMIM}_{45}$ | -23.3  | 174/238*                 | 2.67/4.01*                            | 361                      | 77.9                                  |

$^\dagger$ temperature corresponding to the maximal rate at $T_{\text{deg}}$ (i.e. decomposition temperature)

* two small degradation steps were observed in-lieu of the single one for other polymers, both of them are reported individually here.
S5: Evaporation tests on MA and BSPA monomers

Figure S5: (A) $^1$H-NMR spectra (CDCl$_3$) of methyl acrylate reaction mixtures before and after deoxygenation via 10 min bubbling with argon. Ratios between acrylic (CH 5.82, CH 6.11 and CH 6.38 ppm) and DMF (CH 8.00 ppm) signals significantly dropped after bubbling (~ 40 % loss). (B) $^1$H-NMR spectra (CDCl$_3$) of 3-[isobutoxysulfonyl]propyl acrylate before and after deoxygenation via 10 min bubbling with argon. Ratios between acrylic (CH 5.87, CH 6.12 and CH 6.41 ppm) and DMF (CH 8.00 ppm) signals remained unaffected by bubbling.
S6: $^1$H-NMR and SEC analyses of block copolymers

Figure S6-1: (A) $^1$H-NMR spectra of the PMA$_{92}$ macroinitiator (black, CDCl$_3$), PMA$_{92}$-b-PBSPA$_{231}$ protected BCP obtained by Cu(0)-RDRP (red, CDCl$_3$) and resulting amphiphilic PMA$_{92}$-b-PSPA-Na$_{231}$ block copolymer (green, 40:60 vol.% DMSO-$d_6$:D$_2$O) obtained after nucleophilic deprotection. (B) SEC elugrams of PMA$_{92}$ macroinitiator (black) and PMA$_{92}$-b-PBSPA$_{231}$ protected block copolymer (red).

Figure S6-2: (A) $^1$H-NMR spectra of the PDEGA$_{104}$ macroinitiator (grey, CDCl$_3$), PDEGA$_{104}$-b-PBSPA$_{228}$ protected BCP obtained by Cu(0)-RDRP (red, CDCl$_3$) and resulting PDEGA$_{104}$-b-PSPA-Na$_{228}$ block copolymer (green, DMSO-$d_6$) obtained after nucleophilic deprotection. (B) SEC elugrams of PDEGA$_{104}$ macroinitiator (grey) and PDEGA$_{104}$-b-PBSPA$_{228}$ protected block copolymer (red).
Figure S6-3: (A) $^1$H-NMR spectra of the pristine PEO$_{90}$-OH (grey, CDCl$_3$) and PEO$_{90}$-Br macroinitiator (blue, CDCl$_3$) obtained after end-group modification. (B) SEC elugrams of the pristine PEO$_{90}$-OH (grey) and PEO$_{90}$-Br macroinitiator (blue).

Figure S6-4: (A) $^1$H-NMR spectra of the PEO$_{90}$-Br macroinitiator (blue, CDCl$_3$), PEO$_{90}$-b-PBS$\text{PA}_{237}$ protected BCP obtained by Cu(0)-RDRP (red, CDCl$_3$) and resulting amphiphilic PEO$_{90}$-b-PSPA-Na$_{237}$ block copolymer (green, D$_2$O) obtained after nucleophilic deprotection. (B) SEC elugrams of PEO$_{90}$-Br macroinitiator (black) and PEO$_{90}$-b-PBS$\text{PA}_{237}$ protected block copolymer (red).
S7: Determination of the LCST of PDEGA homopolymer

**Figure S7-1:** Plot of the mean count rate of a PDEGA_{104} solution at 1 g L\(^{-1}\) in 10 mM KNO\(_3\) as a function of temperature. All data points were measured in triplicate. The LCST can be approximated by the drop of the mean count rate when the temperature is decreased, here LCST\(_{DLS}\) \(\approx\) 14 °C.

**Figure S7-2:** (A) Plot of the transmittance at 600 nm of a PDEGA\(_{104}\) solution at 1 g L\(^{-1}\) in 10 mM KNO\(_3\) as a function of the temperature and (B) cycles between low and high temperature and resulting transmittance values. The LCST can be more accurately measured in UV-Vis and the value was determined as the maximum of the inflection point, here LCST\(_{UV\text{-vis}}\) = 14 °C. All data points were measured in triplicate.
Figure S8-1: (A) $^1$H-NMR spectra (CDCl$_3$) and (B) SEC elugrams of the PMA$_{92}$ macroinitiator before (solid line) and after (dashed line) treatment with NaI.

Figure S8-2: (A) $^1$H-NMR spectra (CDCl$_3$) and (B) SEC elugrams of the PDEGA$_{104}$ macroinitiator before (solid line) and after (dashed line) treatment with NaI.
Figure S8-3: (A) $^1$H-NMR spectra (CDCl$_3$) and (B) SEC elugrams of the PEO$_{92}$-Br macroinitiator before (solid line) and after (dashed line) treatment with NaI.
S9: \textsuperscript{1}H-NMR analysis on EMIMI-deprotected block copolymers

Figure S9-1: \textsuperscript{1}H-NMR spectra of EMIMI-deprotected PMA-based block copolymers. (A) PMA\textsubscript{92} (black, CDCl\textsubscript{3}), PMA\textsubscript{92}-b-PBSPA\textsubscript{103} (red, CDCl\textsubscript{3}), PMA\textsubscript{92}-b-PSPA-EMIM\textsubscript{103} (dark cyan, DMSO-\textit{d}6). (B) PMA\textsubscript{92} (grey, CDCl\textsubscript{3}), PMA\textsubscript{92}-b-PBSPA\textsubscript{231} (red, CDCl\textsubscript{3}), PMA\textsubscript{92}-b-PSPA-EMIM\textsubscript{231} (dark cyan, DMSO-\textit{d}6).

Figure S9-2: \textsuperscript{1}H-NMR spectra of EMIMI-deprotected PDEGA-based block copolymers. (A) PDEGA\textsubscript{104} (grey, CDCl\textsubscript{3}), PDEGA\textsubscript{104}-b-PBSPA\textsubscript{94} (red, CDCl\textsubscript{3}), PDEGA\textsubscript{104}-b-PSPA-EMIM\textsubscript{94} (dark cyan, DMSO-\textit{d}6). (B) PDEGA\textsubscript{104} (grey, CDCl\textsubscript{3}), PDEGA\textsubscript{104}-b-PBSPA\textsubscript{228} (red, CDCl\textsubscript{3}), PDEGA\textsubscript{104}-b-PSPA-EMIM\textsubscript{228} (dark cyan, DMSO-\textit{d}6).
Figure S9-3: $^1$H-NMR spectra of EMIMI-deprotected PEO-based block copolymers. (A) PEO$_{90}$-Br (blue, CDCl$_3$), PEO$_{90}$-b-PBSPA$_{110}$ (red, CDCl$_3$) and PEO$_{90}$-b-PSPA-EMIM$_{110}$ (dark cyan, D$_2$O). (B) PEO$_{90}$-Br (blue, CDCl$_3$), PEO$_{90}$-b-PBSPA$_{237}$ (red, CDCl$_3$) and PEO$_{90}$-b-PSPA-EMIM$_{237}$ (dark cyan, D$_2$O).
S10: Thermal analyses on the EMIMI-deprotected block copolymers

Figure S10-1: (A) TGA and (B) DSC thermograms of one EMIMI-deprotected PMA-based block copolymer: PMA$_{92}$ (black), PMA$_{92}$-b-PBSPA$_{103}$ (red) and PMA$_{92}$-b-PSPA-EMIM$_{103}$ (dark cyan).

Table S7: Glass transition temperatures, degradation temperatures and associated weight losses obtained through thermal analyses on the PMA macrorinitiator and PMA-based block copolymers.

| Sample                        | $T_g$ ($^\circ$C) |
|-------------------------------|-------------------|
| PMA$_{92}$                    | 8.3               |
| PMA$_{92}$-b-PBSPA$_{103}$    | -20.3             |
| PMA$_{92}$-b-PSPA-Na$_{103}$  | n.a.              |
| PMA$_{92}$-b-PSPA-EMIM$_{103}$| 3.4               |
| PMA$_{92}$-b-PBSPA$_{231}$    | -17.4             |
| PMA$_{92}$-b-PSPA-Na$_{231}$  | n.a.              |
| PMA$_{92}$-b-PSPA-EMIM$_{231}$| -2.2              |

determined using a 10 °C min$^{-1}$ heating rate
Figure S10-2: (A) TGA and (B) DSC thermograms of one EMIMI-deprotected PDEGA-based block copolymer: PDEGA\textsubscript{104} (grey), PDEGA\textsubscript{104}-b-PBSPA\textsubscript{94} (red), PDEGA\textsubscript{104}-b-PSPA-EMIM\textsubscript{94} (dark cyan).

Table S8: Glass transition temperatures, degradation temperatures and associated weight losses obtained through thermal analyses on the PMA macroinitiator and PMA-based block copolymers.

| Sample | \( T_g \) (°C) |
|--------|----------------|
| PDEGA\textsubscript{104} | n.a. |
| PDEGA\textsubscript{104}-b-PBSPA\textsubscript{94} | -11.3 |
| PDEGA\textsubscript{104}-b-PSPA-Na\textsubscript{94} | n.a. |
| PDEGA\textsubscript{104}-b-PSPA-EMIM\textsubscript{94} | -0.4 |
| PDEGA\textsubscript{104}-b-PBSPA\textsubscript{228} | -9.6 |
| PDEGA\textsubscript{104}-b-PSPA-Na\textsubscript{228} | n.a. |
| PDEGA\textsubscript{104}-b-PSPA-EMIM\textsubscript{228} | 2.1 |

determined using a 10 °C min\textsuperscript{-1} heating rate
**Figure S10-3:** (A) TGA and (B) DSC thermograms of one EMIMI-deprotected PEO-based block copolymer: PEO$_{90}$-Br (blue), PEO$_{90}$-b-PBSA$_{237}$ (red) and PEO$_{90}$-b-PSPA-EMIM$_{237}$ (dark cyan).

**Table S9:** Glass transition temperatures, degradation temperatures and associated weight losses obtained through thermal analyses on the PMA macroinitiator and PMA-based block copolymers.

| Sample            | $T_g$ (°C) | $T_m$ (°C) | Enthalpy $T_m$ (J g$^{-1}$) | $T_c$ (°C) | Enthalpy $T_c$ (J g$^{-1}$) |
|-------------------|------------|------------|------------------------------|------------|------------------------------|
| PEO$_{90}$        | n.a.       | 57.3       | 152                          | 34.7       | 37.1                         |
| PEO$_{90}$-b-PBSA$_{110}$ | -24.1      | 48.8       | 1.00                         | n.a.       | n.a.                         |
| PEO$_{90}$-b-PSPA-Na$_{110}$ | n.a.       | 33.8       | 9.50                         | -40.1      | 4.50                         |
| PEO$_{90}$-b-PSPA-EMIM$_{110}$ | 5.4        | n.a.       | n.a.                         | n.a.       | n.a.                         |
| PEO$_{90}$-b-PBSA$_{237}$ | -18.4      | n.a.       | n.a.                         | n.a.       | n.a.                         |
| PEO$_{90}$-b-PSPA-Na$_{237}$ | n.a.       | 35.6       | 4.90                         | -36.4      | 3.34                         |
| PEO$_{90}$-b-PSPA-EMIM$_{237}$ | 6.4        | 35.8       | 5.65                         | -35.4      | 1.85                         |

determined using a 10 °C min$^{-1}$ heating rate
S1: Electron microscopy on the self-assembled PMA-based nanoparticles

**Figure S11-1:** TEM images of uranyl acetate-stained nanoparticles self-assembled from a solution of PMA$_{92}$-b-PSPA-Na$_{103}$ amphiphilic block copolymer at 1 g L$^{-1}$ in 10 mM KNO$_3$.

**Figure S11-2:** TEM images of uranyl acetate-stained nanoparticles self-assembled from a solution of PMA$_{92}$-b-PSPA-Na$_{231}$ amphiphilic block copolymer at 1 g L$^{-1}$ in 10 mM KNO$_3$. 
S12: Dynamic light scattering analysis on the PDEGA-based nanoparticles

**Figure S12-1:** DLS intensity plot of the nanoparticles achieved from direct dissolution of PDEGA\(_{104}\)-b-PSPA-Na\(_{228}\) at 1 g L\(^{-1}\) in 10 mM KNO\(_3\).

**Figure S12-2:** Plot of the mean count rate vs. the temperature enabled the determination of the LCST of the PDEGA\(_{104}\) segment (i.e. hydrophobic domain) of the PDEGA-based nanoparticles, here PDEGA\(_{104}\)-b-PSPA-Na\(_{94}\) was studied at a concentration of 1 g L\(^{-1}\) (10 mM KNO\(_3\)).
**S13: Characterisation of the pristine and quaternised poly(4-vinylpyridine)**

**Figure S13-1:** $^1$H-NMR spectra of the P4VP$_{119}$ (wine red, CDCl$_3$) and P4VP$_{q119}$ (orange, D$_2$O). *: residual toluene, *: residual water.

**Figure S13-2:** SEC elugram of P4VP homopolymer measured at 50 °C in DMF with 0.01 M LiBr.
Figure S14: DLS intensity plot of the C3Ms obtained through electrostatic complexation between PEO$_{90}$-b-PSPA-Na$_{237}$ (1 g L$^{-1}$ in 10 mM KNO$_3$ solution) and P4VP$_{116}$ (1 g L$^{-1}$ in 10 mM KNO$_3$ solution).
Figure S15-1: AFM height images of the C3Ms obtained through electrostatic complexation between PEO$_{90}$-b-PSPA-\textit{Na}_{110} (1 g L$^{-1}$ in 10 mM KNO$_3$ solution) and P4VPq$_{116}$ (1 g L$^{-1}$ in 10 mM KNO$_3$ solution) deposited on mica discs (A-C and D-E). z-scale is ± 2.5 nm.

Figure S15-2: (A,B and D-F) AFM height images of the C3Ms obtained through electrostatic complexation between PEO$_{90}$-b-PSPA- \textit{Na}_{237} (1 g L$^{-1}$ in 10 mM KNO$_3$ solution) and P4VPq$_{116}$ (1 g L$^{-1}$ in 10 mM KNO$_3$ solution) deposited on mica discs. (D) cross-sectional analysis across a nanoparticle (dashed line in image B). z-scale is ± 5 nm.
S16: Electron microscopy on the PEO-based C3Ms

**Figure S16-1:** TEM images of uranyl acetate-stained C3M obtained through electrostatic complexation between PEO$_{90}$-b-PSPA-Na$_{110}$ (1 g L$^{-1}$ in 10 mM KNO$_3$ solution) and P4VP$_{116}$ (1 g L$^{-1}$ in 10 mM KNO$_3$ solution).

**Figure S16-2:** TEM images of uranyl acetate-stained C3Ms obtained through electrostatic complexation between PEO$_{90}$-b-PSPA- Na$_{237}$ (1 g L$^{-1}$ in 10 mM KNO$_3$ solution) and P4VP$_{116}$ (1 g L$^{-1}$ in 10 mM KNO$_3$ solution).
Figure S16-3: Statistical analyses on the core and overall diameters of the C3M particles obtained through electrostatic complexation between (A) PEO$_{90}$-$b$-PSPA-$Na_{110}$ or (B) PEO$_{90}$-$b$-PSPA-$Na_{237}$ (both at 1 g L$^{-1}$ in 10 mM KNO$_3$ solution) and P4VP$_{116}$ (1 g L$^{-1}$ in 10 mM KNO$_3$ solution). Data extracted from 250 specimen across multiple TEM images.
Figure S17: Strong polyanions can be produced in one-pot fashion through polymerization and in-situ nucleophilic deprotection. (A) Schematic depiction of the procedure and characterisation of the resulting polymer by (B) $^1$H-NMR and (C) SEC.
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