

# **Influence of Counterions on the Thermal and Solution Properties of Strong Polyelectrolytes**

Théophile Pelras<sup>a\*</sup>, Julien Es Sayed<sup>b</sup>, Jin Pierick<sup>b</sup>, Andrea Giuntoli<sup>c</sup>, Anton H. Hofman<sup>b</sup>, Katja Loos<sup>a</sup> and Marleen Kamperman<sup>b\*</sup>

<sup>a</sup> Macromolecular Chemistry and New Polymeric Materials, Zernike Institute for Advanced Materials, University of Groningen, The Netherlands

<sup>b</sup> Polymer Science, Zernike Institute for Advanced Materials, University of Groningen, The Netherlands

<sup>c</sup> Micromechanics, Zernike Institute for Advanced Materials, University of Groningen, The Netherlands

## **Supporting Information**

# Table of Contents

Materials .....	3
Characterisation Techniques .....	4
Synthesis of homopolymers .....	7
Synthesis of polyelectrolytes .....	9
Synthesis of block copolymers .....	15
Supporting Figures.....	21
S1: Characterisation of hydrophobic homopolymers.....	21
S2: <sup>1</sup> H NMR spectroscopy of the polyelectrolyte homopolymers.....	23
S3: <sup>19</sup> F-NMR spectroscopy of the polyelectrolyte homopolymers.....	29
S4: FTIR spectroscopy of deprotected polymers .....	30
S5: Aqueous SEC on polyelectrolytes .....	32
S6: Thermal characterisation of hydrophobic homopolymers.....	34
S7: Thermal characterisation of polyelectrolytes.....	35
S8: Solubility tests on polyelectrolytes.....	36
S9: <sup>1</sup> H NMR spectra of the block copolymers .....	38
S10: Thermal characterisation of block copolymers.....	43
S11: DLS and ζ-potential on block copolymers in aqueous media .....	45
S12: TEM on block copolymers in aqueous media .....	47
S13: DLS on block copolymers in methanol .....	52
S14: DLS on block copolymers in ethanol .....	53
S15: TEM on block copolymers in methanol.....	55
S16: TEM on block copolymers in ethanol.....	57
Supporting References .....	61

## Materials

The monomer 3-isobutoxysulphopropyl methacrylate (BSPMA) was synthesised as reported before.<sup>[1]</sup> 2,2'-Azobis(2-methylpropionitrile) (AIBN, 98 %), 4-cyano-4-(thiobenzoylthio)pentanoic acid (CTBPA), *N,N*-dimethylformamide (DMF, 99+% anhydrous) and phenyltriethylammonium iodide (PTEAI, 97 %) were obtained from Sigma-Aldrich.

Diethyl ether (Et<sub>2</sub>O, AR grade), *n*-hexane (AR grade) and methanol (absolute, AR grade) were obtained from Macron Fine Chemicals. Absolute ethanol (99.9 %) and dimethylsulphoxide (DMSO, 99.9 %) were purchased from J.T. Baker. Butyrylthiocholine iodide (BTCl, > 99.0 %), caesium iodide (CsI, > 99.0 %), 1-ethyl-3-methylimidazolium iodide (EMIMI, > 98.0 %), lithium iodide (LiI, > 97.0 %), tetramethylammonium iodide (TMA, > 98.0 %), 3-(trifluoromethyl)phenyltrimethylammonium iodide (FPTMAI, > 98.0 %) were purchased from TCI Chemicals. Sodium iodide (NaI, ACS reagent grade) was sourced from Acros Organics. Acetone (AR grade) and tetrahydrofuran (THF, AR grade, BHT stabilised) were obtained from Biosolve. Acetonitrile (ACN, > 99.9 %) was sourced from Honeywell.

AIBN was recrystallised twice from methanol. All other chemicals were used as received.

## Characterisation Techniques

**Proton nuclear magnetic resonance ( $^1\text{H NMR}$ )** spectra were acquired on an Agilent 400-MR 400 MHz spectrometer at 298 K. Deuterated acetone (acetone- $d_6$ , 99.8 %), deuterated chloroform ( $\text{CDCl}_3$ , 99.8 %), deuterated dimethylsulphoxide (DMSO- $d_6$ , 99.9 %), deuterium oxide ( $\text{D}_2\text{O}$ , 99.9 %) deuterated ethanol (ethanol- $d_6$ , 99.8 %) and deuterated methanol (methanol- $d_4$ , 99.8 %) were purchased from Sigma-Aldrich. Samples were dissolved in an appropriate solvent or solvent mixture ( $\approx 5 \text{ g L}^{-1}$ ) and measured with a pulse width of 45  $\mu\text{s}$ , spectral width of 12/-2 ppm, recycle delay of 1 s and either 32 or 128 scans (conversion or purified samples, respectively). Spectra were analysed with MestReNova software version 14.1.

**Fluorine nuclear magnetic resonance ( $^{19}\text{F-NMR}$ )** spectra were acquired on a Bruker Avance 600 MHz spectrometer at 298 K and measured with a pulse width of 45  $\mu\text{s}$ , spectral width of -20/-120 ppm, recycle delay of 1 s and either 128 scans. Spectra were analysed with MestReNova software version 14.1.

**DMF-based size-exclusion chromatography (DMF-SEC)** was conducted on a GPCMax system from Viscotek equipped with a 302 TDA detector array and two columns in series (PolarGel L and M, both 8  $\mu\text{m}$  30 cm) from Agilent Technologies. The columns and detector were kept at a temperature of 50  $^\circ\text{C}$ . *N,N'*-dimethylformamide (DMF) containing 0.01 M lithium bromide (LiBr) was used as eluent at a flow rate of 1  $\text{mL min}^{-1}$ . Near monodisperse poly(methyl methacrylate) (PMMA) standards from Polymer Standard Services were used as calibrants. Samples were dissolved in the eluent at a concentration of  $\approx 3 \text{ g L}^{-1}$  and passed through a 0.45 or 0.22  $\mu\text{m}$  PTFE filter prior to injection. Data acquisition and calculations were performed using Viscotek Omnisec software version 5.0.

**Aqueous size-exclusion chromatography (Aq-SEC)** measurements were performed on a Vanquish system from ThermoScientific equipped with an ERC refractoMax520 RI detector and two columns in series (novemaMAx Linear M) from PSS. The columns and detector were kept at a temperature of 40  $^\circ\text{C}$ . Milli-Q water containing 0.1 M NaCl and 0.1 wt.% acetic acid was used at a flow rate of 1  $\text{mL min}^{-1}$ . Near monodisperse pullulan (3 500 – 500 000 Da) standards from PSS were used as calibrants. Samples were dissolved in the eluent at a concentration of  $\approx 3 \text{ g L}^{-1}$  and passed through a 0.45  $\mu\text{m}$  cellulose acetate filter prior to injection. Data analysis was conducted on PSS WinGPC UniChrom software version 8.40.

**Attenuated total reflection–Fourier transform infrared (ATR-FTIR)** spectra were acquired on a Bruker VERTEX 70 spectrometer mounted with an ATR diamond single reflection module. The spectra were recorded in transmittance within the range of 4000–400  $\text{cm}^{-1}$  with a spectral resolution of 2  $\text{cm}^{-1}$  and using 64 scans for each sample. Atmospheric compensation and baseline correction

(concave rubberband correction) were applied to the collected spectra using Bruker's OPUS spectroscopy software version 7.0.

**Differential scanning calorimetry (DSC)** measurements were recorded on a TA instruments DSCQ 1000 analyzer. The samples (~ 5 mg) were subjected to the following method: (i) equilibration at -80 °C, (ii) 5 min isotherm, (iii) ramp to 120 °C at 20 °C min<sup>-1</sup>, (iv) 5 min isotherm, (v) ramp to -80 °C at 5 °C min<sup>-1</sup>, (vi) 5 min isotherm and (vii) ramp to 120 °C at 20 °C min<sup>-1</sup>. 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 (~ 3 mg) were heated from 40 °C to 700 °C at a rate of 10 °C min<sup>-1</sup> under a flow of nitrogen. When moisture content was high, a 20 minute isotherm at 120 °C was conducted prior to the measurements. The data acquisition and analysis were done using TA Instruments TRIOS software.

**Dynamic light scattering (DLS)** measurements were conducted on a Malvern Panalytical Zetasizer Ultra system, featuring a helium-neon laser ( $\lambda = 633$  nm) and an Avalanche photodiode detector. The polymer micelles solutions were measured at 25 °C after a 120 s equilibration time and using 30 cumulative recordings. Back scattering mode was used for samples in water and ethanol, while side scattering mode was used for samples in ethanol. Measurements were done in triplicate. The results were analyzed with ZS Xplorer software.

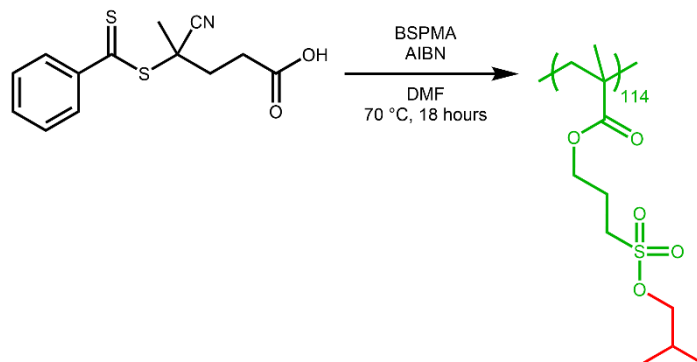
**$\zeta$ -potential** measurements were performed on the same Malvern Panalytical Zetasizer Ultra system at 25 °C, while the acquisition times were determined automatically. Samples were recorded in triplicate and the results were analyzed with ZS Xplorer software.

**Transmission electron microscopy (TEM)** images were recorded on a Philips CM120 transmission electron microscope equipped with a LaB<sub>6</sub> cathode operated at an accelerating voltage of 120 kV and using a Gatan 4k CCD camera. TEM grids (carbon, 400 mesh with carbon support film) were glow-discharged (for aqueous samples only, 15 s at 50 mA and 300 V) prior to sample preparation. Specimens were prepared by deposition of 5  $\mu$ L of the polymer micelles dispersion (c ~ 1 g L<sup>-1</sup>) onto the grid and adsorption for 1 min before blotting. Before the specimen was fully dried, 5  $\mu$ L of saturated 2 wt.% uranyl acetate staining solution was deposited onto the grid and immediately blotted, before a new 5  $\mu$ L drop of staining solution was deposited and left to adsorb for 1 min before blotting. TEM images were analysed using ImageJ software, employing brightness and contrast correction tools to enhance the general quality of the snapshots.

**Solubility tests** of polyelectrolytes were conducted by charging 5.0 mg of freeze-dried polymer into a 1.5 mL glass vial and adding 1 mL of solvent. The flasks were shaken and vortexed several times before visual assessment. All solvents were either deuterated ones or of AR/HPLC grade, as given above. THF ( $\geq 99.8\%$ , unstabilised, Ossum Chemicals) was passed through an MBraun MB SPS 800 system prior use.

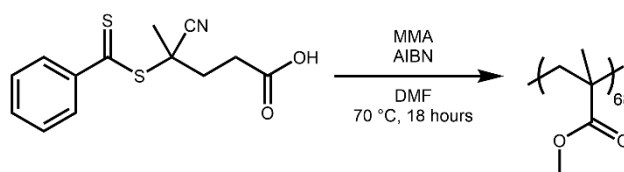
# Synthesis of homopolymers

## Synthesis of poly(3-isobutoxysulphopropyl methacrylate) (PBSPMA<sub>114</sub>)



CTBPA (1 eq, 30.2 mg, 108  $\mu\text{mol}$ ), BSPMA (119 eq, 3.41 g, 12.9 mmol), AIBN (0.1 eq, 2.00 mg, 12.2  $\mu\text{mol}$ ; 194  $\mu\text{L}$  of a 20.6 mg AIBN in 2.00 mL DMF) and DMF (4.50 mL) were charged into a round bottom flask equipped with a stirring egg. An aliquot was withdrawn for  $^1\text{H}$  NMR conversion analysis before the reaction mixture was deoxygenated via argon bubbling for 10 min and the flask immersed into a pre-heated oil bath at 70 °C. After 18 hours, the vessel was cooled down to room temperature and opened to air before withdrawal of an aliquot for  $^1\text{H}$  NMR conversion analysis. The polymer was precipitated into cold 6:1 *n*-hexane:ethanol, redissolved in minimal THF and further precipitated into pure *n*-hexane twice. The polymer was later redissolved in minimal 1,4-dioxane and freeze-dried. Yield: 3.14 g.  $^1\text{H}$  NMR: conversion = 96 %, DP = 114,  $M_{n\text{NMR}} = 30\,400$  Da. SEC:  $M_{n\text{SEC}} = 43\,000$  Da,  $\bar{D} = 1.10$ .

## Synthesis of poly(methyl methacrylate) (PMMA<sub>68</sub>)



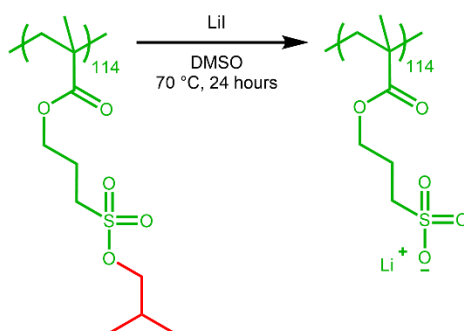
CTBPA (1 eq, 60.1 mg, 215  $\mu\text{mol}$ ), MMA (120 eq, 2.59 g, 25.9 mmol), AIBN (0.1 eq, 3.72 mg, 22.7  $\mu\text{mol}$ ; 361  $\mu\text{L}$  of a 20.6 mg AIBN in 2.00 mL DMF) and DMF (9.00 mL) were charged into a round bottom flask equipped with a stirring egg. An aliquot was withdrawn for  $^1\text{H}$  NMR conversion analysis before the reaction mixture was deoxygenated via argon bubbling for 10 min and the flask immersed into a pre-heated oil bath at 70 °C. After 18 hours, the vessel was cooled down to room temperature and opened to air before withdrawal of an aliquot for  $^1\text{H}$  NMR conversion analysis. The polymer was precipitated into cold 6:1 *n*-hexane:ethanol, redissolved in minimal THF and further precipitated into

pure *n*-hexane twice. The polymer was later redissolved in minimal 1,4-dioxane and freeze-dried. Yield: 1.49 g.  $^1\text{H NMR}$ : conversion = 60 %,  $\text{DP}_{\text{NMR}} = 72$ ,  $M_{n\text{NMR}} = 7\,500$  Da. SEC:  $M_{n\text{SEC}} = 7\,100$  Da,  $\text{DP}_{\text{SEC}} = 68$ ,  $\bar{D} = 1.20$ .



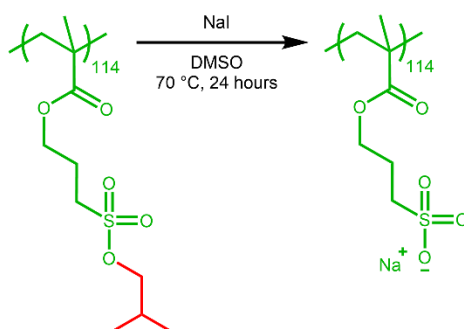
# Synthesis of polyelectrolytes

## Synthesis of poly(3-sulphopropyl methacrylate) lithium salt (PSPMA-Li<sub>114</sub>)



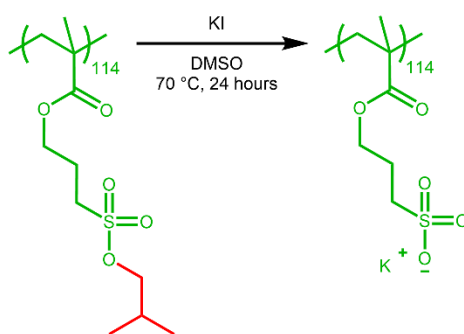
PBSPMA<sub>114</sub> (1 eq, 200 mg polymer, 0.758 mmol BSPMA), Lil (3 eq, 382 mg, 2.85 mmol) and 3 mL DMSO were charged into a glass vial equipped with a stirring bar before being immersed in a pre-heated oil bath at 70 °C. After 24 hours, the vial was removed and the polymer isolated via precipitation in 2:1 ethanol:*n*-hexane. After decanting the supernatant, the polymer was further washed with 2:1 ethanol:*n*-hexane several times and once more with pure *n*-hexane, before being redissolved in minimal DI water and freeze-dried to produce a brittle white solid. Yield: 143 mg. <sup>1</sup>H NMR: deprotection ≈ 100 %,  $M_{n,NMR} = 24\ 700$  Da.

## Synthesis of poly(3-sulphopropyl methacrylate) sodium salt (PSPMA-Na<sub>114</sub>)



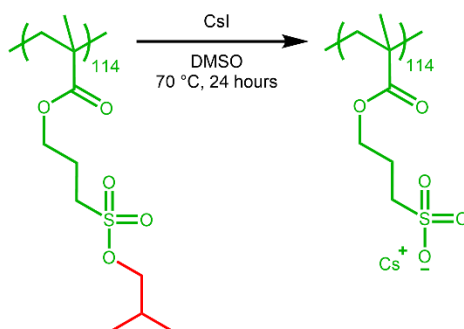
PBSPMA<sub>114</sub> (1 eq, 201 mg polymer, 0.758 mmol BSPMA), NaI (3 eq, 390 mg, 2.60 mmol) and 3 mL DMSO were charged into a glass vial equipped with a stirring bar before being immersed in a pre-heated oil bath at 70 °C. After 24 hours, the vial was removed and the polymer isolated via precipitation in 2:1 ethanol:*n*-hexane. After decanting the supernatant, the polymer was further washed with 2:1 ethanol:*n*-hexane several times and once more with pure *n*-hexane, before being redissolved in minimal DI water and freeze-dried to produce a brittle white solid. Yield: 166 mg. <sup>1</sup>H NMR: deprotection ≈ 100 %,  $M_{n,NMR} = 26\ 500$  Da.

## Synthesis of poly(3-sulphopropyl methacrylate) potassium salt (PSPMA-K<sub>114</sub>)



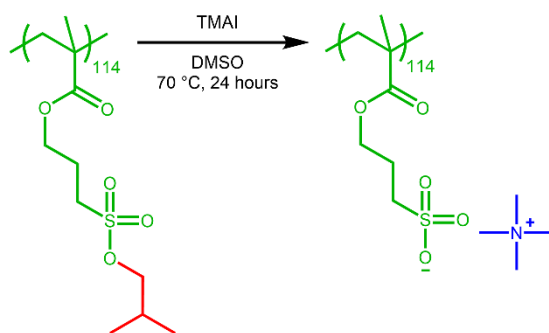
PBSPMA<sub>114</sub> (1 eq, 200 mg polymer, 0.758 mmol BSPMA), KI (3 eq, 416 mg, 2.51 mmol) and 3 mL DMSO were charged into a glass vial equipped with a stirring bar before being immersed in a pre-heated oil bath at 70 °C. After 24 hours, the vial was removed and the polymer isolated via precipitation in 1:6 ethanol:*n*-hexane. After decanting the supernatant, the polymer was further washed with 1:6 ethanol:*n*-hexane several times and once more with pure *n*-hexane, before being redissolved in minimal DI water and freeze-dried to produce a brittle yellow solid. Yield: 200 mg. <sup>1</sup>H NMR: deprotection ≈ 100 %,  $M_{n,NMR} = 28\,300$  Da.

## Synthesis of poly(3-sulphopropyl methacrylate) caesium salt (PSPMA-Cs<sub>114</sub>)



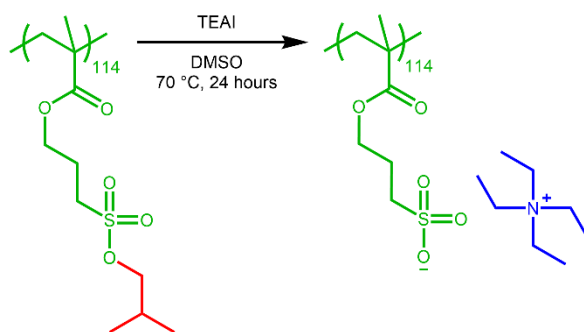
PBSPMA<sub>114</sub> (1 eq, 202 mg polymer, 0.765 mmol BSPMA), CsI (3 eq, 725 mg, 2.79 mmol) and 3 mL DMSO were charged into a glass vial equipped with a stirring bar before being immersed in a pre-heated oil bath at 70 °C. After 24 hours, the vial was removed and the polymer isolated via precipitation in 2:1 ethanol:*n*-hexane. After decanting the supernatant, the polymer was further washed with 2:1 ethanol:*n*-hexane several times and once more with pure *n*-hexane, before being redissolved in minimal DI water and freeze-dried to produce a brittle yellow solid. Yield: 455 mg. <sup>1</sup>H NMR: deprotection ≈ 100 %,  $M_{n,NMR} = 39\,000$  Da.

## Synthesis of poly(3-sulphopropyl methacrylate) trimethylammonium salt (PSPMA-TMA<sub>114</sub>)



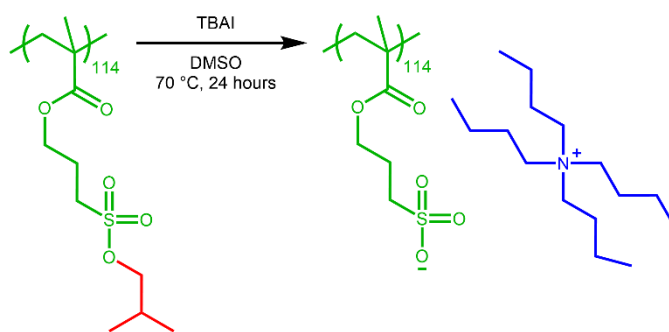
PBSPMA<sub>114</sub> (1 eq, 201 mg polymer, 0.761 mmol BSPMA), TMAI (3 eq, 511 mg, 2.54 mmol) and 3 mL DMSO were charged into a glass vial equipped with a stirring bar before being immersed in a pre-heated oil bath at 70 °C. After 24 hours, the vial was removed and the polymer isolated via precipitation in 2:1 ethanol:*n*-hexane. After decanting the supernatant, the polymer was dried, dissolved in 2 mL DI water and precipitated twice in acetone. The solid was washed with pure *n*-hexane, before being redissolved in minimal DI water and freeze-dried to produce a brittle white solid. Yield: 425 mg. <sup>1</sup>H NMR: deprotection ≈ 100 %,  $M_{n,NMR} = 32\,300$  Da.

## Synthesis of poly(3-sulphopropyl methacrylate) triethylammonium salt (PSPMA-TEA<sub>114</sub>)



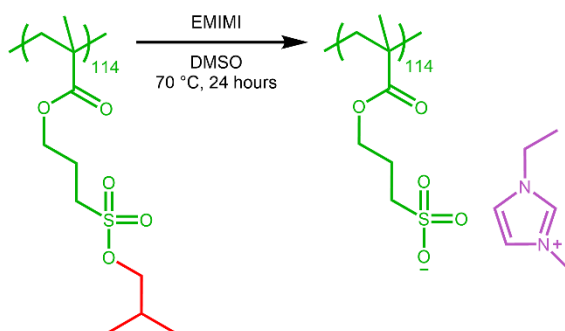
PBSPMA<sub>114</sub> (1 eq, 202 mg polymer, 0.765 mmol BSPMA), TEAI (3 eq, 605 mg, 2.35 mmol) and 3 mL DMSO were charged into a glass vial equipped with a stirring bar before being immersed in a pre-heated oil bath at 70 °C. After 24 hours, the vial was removed and the polymer isolated via precipitation in 2:1 ethanol:*n*-hexane. After decanting the supernatant, the polymer was dried, dissolved in 2 mL DI water and precipitated twice in acetone. The solid was washed with pure *n*-hexane, before being redissolved in minimal DI water and freeze-dried to produce an off-white slightly sticky solid. Yield: 425 mg. <sup>1</sup>H NMR: deprotection ≈ 100 %,  $M_{n,NMR} = 38\,700$  Da.

## Synthesis of poly(3-sulphopropyl methacrylate) tributylammonium salt (PSPMA-TBA<sub>114</sub>)



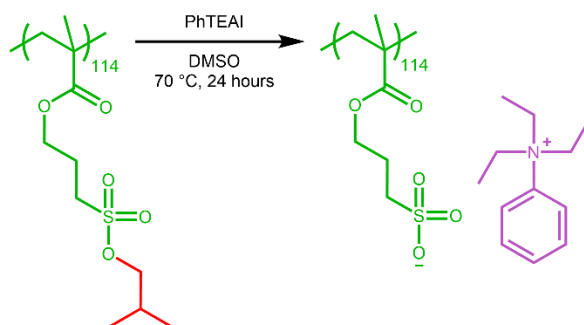
PBSPMA<sub>114</sub> (1 eq, 200 mg polymer, 0.758 mmol BSPMA), TBAI (3 eq, 908 mg, 2.82 mmol) and 3 mL DMSO were charged into a glass vial equipped with a stirring bar before being immersed in a pre-heated oil bath at 70 °C. After 24 hours, the vial was removed and the polymer isolated via precipitation in 6:1 Et<sub>2</sub>O:ethanol and subsequently washed with 6:1 Et<sub>2</sub>O:ethanol. After decanting the supernatant, the polymer was dried, dissolved in 2 mL acetone and precipitated twice in Et<sub>2</sub>O. The solid was washed with pure Et<sub>2</sub>O, before being redissolved in minimal DI water and freeze-dried to produce an off-white brittle solid. Yield: 395 mg. <sup>1</sup>H NMR: deprotection ≈ 100 %,  $M_{n,NMR}$  = 51 800 Da.

## Synthesis of poly(3-sulphopropyl methacrylate) 1-ethyl-3-methylimidazolium salt (PSPMA-EMIM<sub>114</sub>)



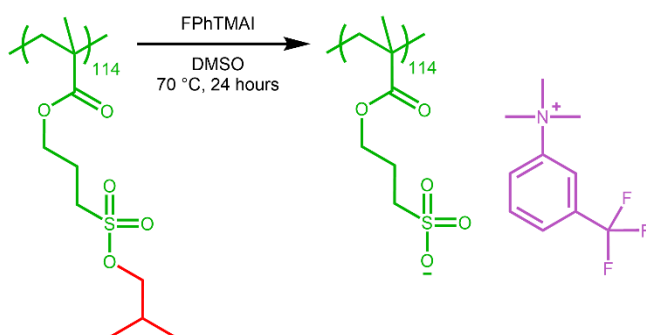
PBSPMA<sub>114</sub> (1 eq, 201 mg polymer, 0.761 mmol BSPMA), EMIMI (3 eq, 654 mg, 2.75 mmol) and 3 mL DMSO were charged into a glass vial equipped with a stirring bar before being immersed in a pre-heated oil bath at 70 °C. After 24 hours, the vial was removed and the polymer isolated via precipitation in 1:6 ethanol:*n*-hexane and further washed with 1:6 ethanol:*n*-hexane several times. After decanting the supernatant, the polymer was dried, dissolved in 2 mL ethanol and precipitated into pure *n*-hexane, before being redissolved in minimal DI water and freeze-dried to produce a dark brown sticky solid. Yield: 257 mg. <sup>1</sup>H NMR: deprotection ≈ 100 %,  $M_{n,NMR}$  = 36 500 Da.

## Synthesis of poly(3-sulphopropyl methacrylate) phenyltriethylammonium salt (PSPMA-PhTEA<sub>114</sub>)



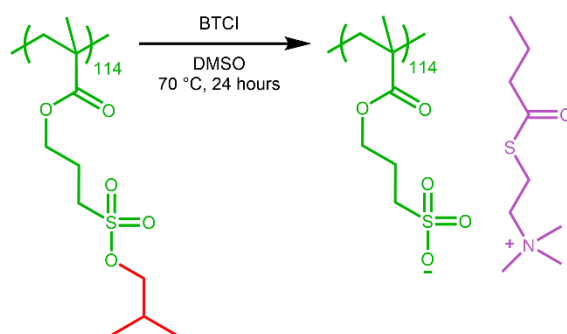
PBSPMA<sub>114</sub> (1 eq, 201 mg polymer, 0.761 mmol BSPMA), PhTEAI (3 eq, 755 mg, 2.48 mmol) and 3 mL DMSO were charged into a glass vial equipped with a stirring bar before being immersed in a pre-heated oil bath at 70 °C. After 24 hours, the vial was removed and the polymer isolated via precipitation in 1:6 ethanol:*n*-hexane and further washed with 1:6 ethanol:*n*-hexane several times. After decanting the supernatant, the polymer was dried, dissolved in 2 mL ethanol and precipitated into pure *n*-hexane, before being redissolved in minimal DI water and freeze-dried to produce a dark brown sticky solid. Yield: 320 mg. <sup>1</sup>H NMR: deprotection ≈ 100 %,  $M_{n,NMR} = 44\ 200$  Da.

## Synthesis of poly(3-sulphopropyl methacrylate) 3-(trifluoromethyl)phenyltrimethyl ammonium salt (PSPMA-FPhTMA<sub>114</sub>)



PBSPMA<sub>114</sub> (1 eq, 200 mg polymer, 0.758 mmol BSPMA), FPhTMAI (3 eq, 813 mg, 2.46 mmol) and 3 mL DMSO were charged into a glass vial equipped with a stirring bar before being immersed in a pre-heated oil bath at 70 °C. After 24 hours, the vial was removed and the polymer isolated via precipitation in 1:6 ethanol:*n*-hexane and further washed with 1:6 ethanol:*n*-hexane several times. After decanting the supernatant, the polymer was dried, dissolved in 2 mL DI water and precipitated into pure acetone, before being redissolved in minimal DI water and freeze-dried to produce a white slightly sticky solid. Yield: 301 mg. <sup>1</sup>H NMR: deprotection ≈ 100 %,  $M_{n,NMR} = 47\ 100$  Da.

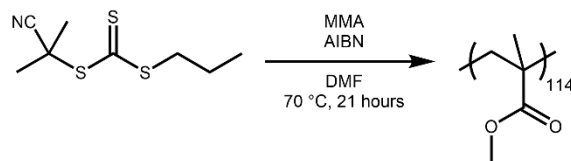
## Synthesis of poly(3-sulphopropyl methacrylate) butyrylthiocholine salt (PSPMA-BTC<sub>114</sub>)



PBSPMA<sub>114</sub> (1 eq, 200 mg polymer, 0.758 mmol BSPMA), BTCI (3 eq, 803 mg, 2.53 mmol) and 3 mL DMSO were charged into a glass vial equipped with a stirring bar before being immersed in a pre-heated oil bath at 70 °C. After 24 hours, the vial was removed and the polymer isolated via precipitation in 1:6 ethanol:*n*-hexane and further washed with 1:6 ethanol:*n*-hexane several times. After decanting the supernatant, the polymer was dried, dissolved in 2 mL ethanol and precipitated into pure *n*-hexane, before being redissolved in minimal DI water and freeze-dried to produce a yellow brittle solid. Yield: 560 mg. <sup>1</sup>H NMR: deprotection ≈ 100 %,  $M_{n,NMR} = 45\,300$  Da.

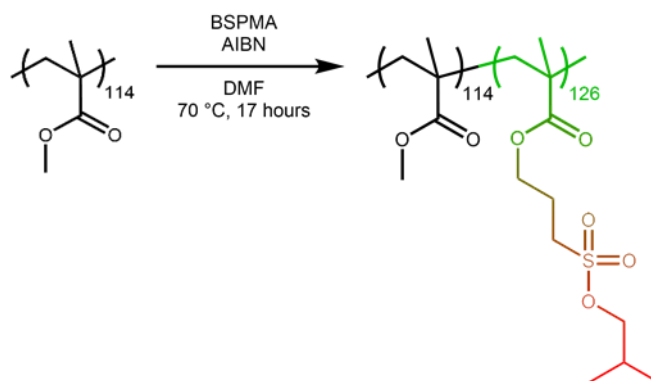
# Synthesis of block copolymers

## Synthesis of poly(methyl methacrylate) (PMMA<sub>114</sub>)



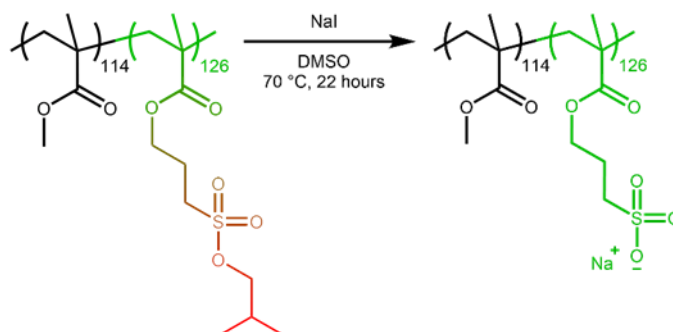
The synthesis of PMMA<sub>114</sub> was performed as described elsewhere.[1] In a nutshell, CPP-TTC, MMA, AIBN and DMF were charged into a round bottom flask equipped with a stirring egg and deoxygenated via nitrogen bubbling. After 21 hours at 70 °C, the reaction was stopped and the polymer was precipitated into 2:1 *n*-hexane:ethanol and washed with pure *n*-hexane, before drying *in vacuo*. <sup>1</sup>H NMR: conversion = 77 %. SEC:  $M_{n\text{SEC}} = 11\,400$  Da,  $DP_{\text{SEC}} = 114$ ,  $\mathcal{D} = 1.27$ . Note that the DP of 114 was kept for further use, as determined by SEC through calibration against PMMA standards.

## Synthesis of poly(methyl methacrylate)-*block*-poly(3-isobutoxysulphopropyl methacrylate) (PMMA<sub>114</sub>-*b*-PBSPMA<sub>126</sub>)



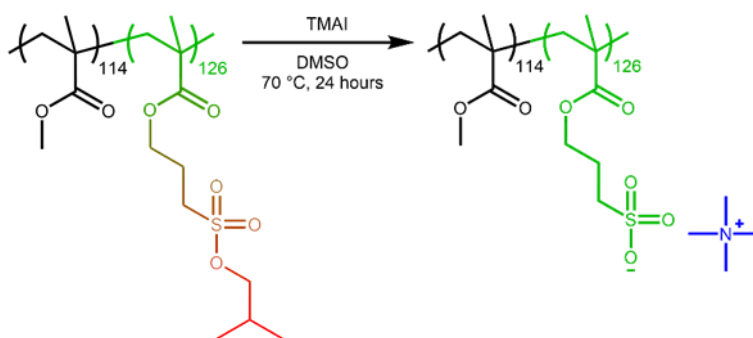
The synthesis of PMMA<sub>114</sub>-*b*-PBSPMA<sub>126</sub> was performed as described elsewhere.[1] In a nutshell, PMMA<sub>114</sub>, BSPMA, AIBN and DMF were charged into a round bottom flask equipped with a stirring egg and deoxygenated via nitrogen bubbling. After 17 hours at 70 °C, the reaction was stopped, diluted with acetone and the polymer was precipitated into 5:1 *n*-hexane:ethanol, washed with 5:1 *n*-hexane:ethanol and then with pure *n*-hexane, before drying *in vacuo*. <sup>1</sup>H NMR: conversion = 98 %,  $DP_{\text{NMR}} = 114\text{-}b\text{-}126$ . SEC:  $M_{n\text{SEC+NMR}} = 44\,800$  Da,  $\mathcal{D} = 1.18$ .

## Synthesis of poly(methyl methacrylate)-*block*-poly(3-sulphopropyl methacrylate) sodium salt (PMMA<sub>114</sub>-*b*-PSPMA-Na<sub>126</sub>)



The synthesis of PMMA<sub>114</sub>-*b*-PSPMA-Na<sub>126</sub> was performed for a previous study.<sup>[1]</sup> In a nutshell, PMMA<sub>114</sub>-*b*-PBSPMA<sub>126</sub>, NaI and DMSO were charged into a round bottom flask equipped with a stirring egg. After 22 hours at 70 °C, the reaction was stopped and the polymer was precipitated into 1:1 *n*-hexane:ethanol, washed with 1:1 *n*-hexane:ethanol and once more with pure *n*-hexane, before drying *in vacuo* to produce a brittle white solid. <sup>1</sup>H NMR: deprotection ≈ 100 %;  $M_n$  SEC+NMR = 40 400 Da.

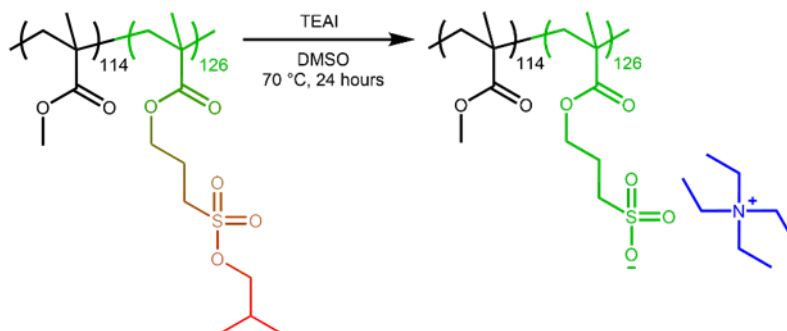
## Synthesis of poly(methyl methacrylate)-*block*-poly(3-sulphopropyl methacrylate) tetramethylammonium salt (PMMA<sub>114</sub>-*b*-PSPMA-TMA<sub>126</sub>)



PMMA<sub>114</sub>-*b*-PBSPMA<sub>126</sub>, (1 eq, 105 mg BCP, 78 mg BSPMA, 0.294 mmol BSPMA), TMAI (3 eq, 192 mg, 0.955 mmol) and 2 mL DMSO were charged into a round bottom flask equipped with a stirring egg before being immersed in a pre-heated oil bath at 70 °C. After 24 hours, the reaction was stopped and the polymer was precipitated into 6:1 ethanol:*n*-hexane. The solid was redissolved in 1 mL DMSO and precipitated once more with 6:1 ethanol:*n*-hexane, before one wash with 6:1 ethanol:*n*-hexane. A final wash with pure *n*-hexane was done, followed by drying *in vacuo* to produce a soft yellow solid. Yield: 276 mg. <sup>1</sup>H NMR: deprotection ≈ 100 %;  $M_n$  SEC+NMR = 46 800 Da.

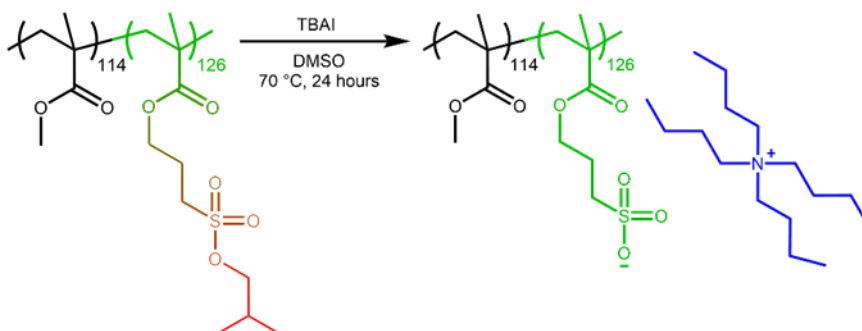


### Synthesis of poly(methyl methacrylate)-*block*-poly(3-sulphopropyl methacrylate) tetraethylammonium salt (PMMA<sub>114</sub>-*b*-PSPMA-TEA<sub>126</sub>)



PMMA<sub>114</sub>-*b*-PBSPMA<sub>126</sub>, (1 eq, 105 mg BCP, 78 mg BSPMA, 0.294 mmol BSPMA), TEAI (3 eq, 234 mg, 0.911 mmol) and 2 mL DMSO were charged into a round bottom flask equipped with a stirring egg before being immersed in a pre-heated oil bath at 70 °C. After 24 hours, the reaction was stopped and the polymer was precipitated into 6:1 ethanol:*n*-hexane. The solid was redissolved in 1 mL DMSO and precipitated once more in 6:1 ethanol:*n*-hexane, before one wash with 6:1 ethanol:*n*-hexane. A final wash with pure *n*-hexane was done, followed by drying *in vacuo* to produce a sticky brown solid. Yield: 264 mg. <sup>1</sup>H NMR: deprotection ≈ 100 %;  $M_n$  SEC+NMR = 45 300 Da.

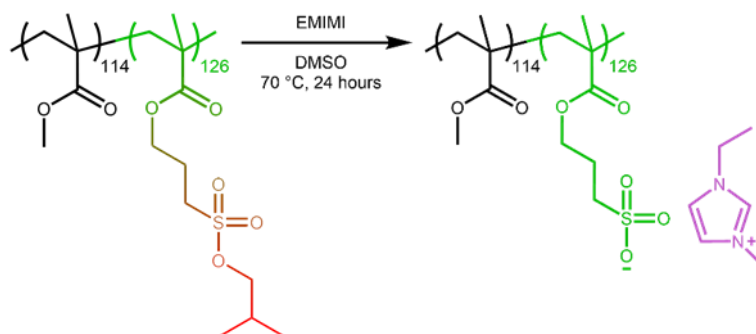
### Synthesis of poly(methyl methacrylate)-*block*-poly(3-sulphopropyl methacrylate) tetrabutylammonium salt (PMMA<sub>114</sub>-*b*-PSPMA-TBA<sub>126</sub>)



PMMA<sub>114</sub>-*b*-PBSPMA<sub>126</sub>, (1 eq, 101 mg BCP, 75 mg BSPMA, 0.283 mmol BSPMA), TBAI (3 eq, 342 mg, 0.927 mmol) and 2 mL DMSO were charged into a round bottom flask equipped with a stirring egg before being immersed in a pre-heated oil bath at 70 °C. After 24 hours, the reaction was stopped and the polymer was precipitated into 6:1 ethanol:*n*-hexane. The solid was redissolved in 1 mL DMSO and precipitated once more into 6:1 ethanol:*n*-hexane, before one wash with 6:1

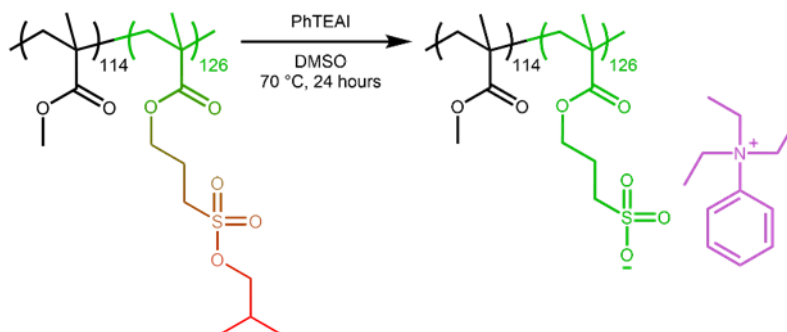
ethanol:*n*-hexane. A final wash with pure Et<sub>2</sub>O was done, followed by drying *in vacuo* to produce a sticky yellowish solid. Yield: 166 mg. <sup>1</sup>H NMR: deprotection ≈ 100 %:  $M_{n,SEC+NMR} = 54\,800$  Da.

### Synthesis of poly(methyl methacrylate)-*block*-poly(3-sulphopropyl methacrylate) 1-ethyl-3-methylimidazolium salt (PMMA<sub>114</sub>-*b*-PSPMA-EMIM<sub>126</sub>)



PMMA<sub>114</sub>-*b*-PSPMA<sub>126</sub>, (1 eq, 102 mg BCP, 76 mg BSPMA, 0.286 mmol BSPMA), EMIMI (4 eq, 270 mg, 1.13 mmol) and 2 mL DMSO were charged into a round bottom flask equipped with a stirring egg before being immersed in a pre-heated oil bath at 70 °C. After 24 hours, the reaction was stopped and the polymer was precipitated into 6:1 ethanol:*n*-hexane. The solid was redissolved in 1 mL DMSO and precipitated once more into 6:1 ethanol:*n*-hexane, washed once with 6:1 ethanol:*n*-hexane and once with pure *n*-hexane, followed by drying *in vacuo* to produce a sticky brown solid. Yield: 148 mg. <sup>1</sup>H NMR: deprotection ≈ 100 %:  $M_{n,SEC+NMR} = 51\,500$  Da.

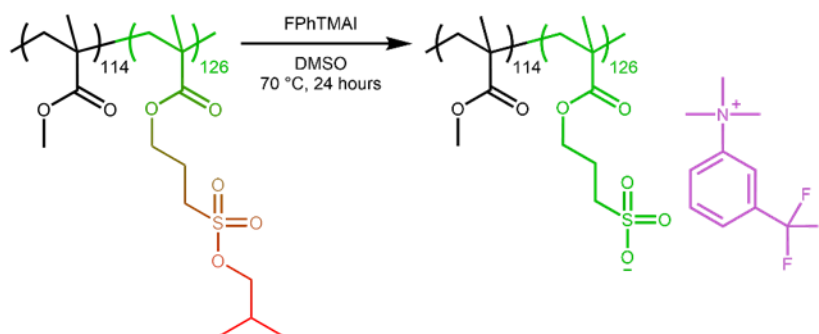
### Synthesis of poly(methyl methacrylate)-*block*-poly(3-sulphopropyl methacrylate) phenyltriethylammonium salt (PMMA<sub>114</sub>-*b*-PSPMA-PhTEA<sub>126</sub>)



PMMA<sub>114</sub>-*b*-PSPMA<sub>126</sub>, (1 eq, 103 mg BCP, 76 mg BSPMA, 0.289 mmol BSPMA), PhTEAI (4 eq, 289 mg, 0.948 mmol) and 2 mL DMSO were charged into a round bottom flask equipped with a stirring egg before being immersed in a pre-heated oil bath at 70 °C. After 24 hours, the reaction

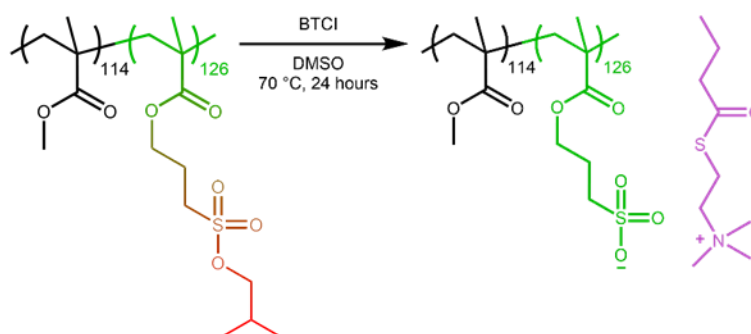
was stopped and the polymer was precipitated into 6:1 ethanol:*n*-hexane. The solid was redissolved in 1 mL DMSO and precipitated once more in 6:1 ethanol:*n*-hexane, washed once with 6:1 ethanol:*n*-hexane and once with pure *n*-hexane, followed by drying *in vacuo* to produce a sticky yellow solid. Yield: 168 mg.  $^1\text{H NMR}$ : deprotection  $\approx 100\%$ :  $M_{n\text{SEC+NMR}} = 59\,900$  Da.

### Synthesis of poly(methyl methacrylate)-*block*-poly(3-sulphopropyl methacrylate) 3-(trifluoromethyl)phenyltrimethyl ammonium salt (PMMA<sub>114</sub>-*b*-PSPMA-FPhTMA<sub>126</sub>)



PMMA<sub>114</sub>-*b*-PSPMA<sub>126</sub>, (1 eq, 102 mg BCP, 76 mg BSPMA, 0.286 mmol BSPMA), FPhTMAI (4 eq, 332 mg, 1.00 mmol) and 2 mL DMSO were charged into a round bottom flask equipped with a stirring egg before being immersed in a pre-heated oil bath at 70 °C. After 24 hours, the reaction was stopped and the polymer was precipitated into 6:1 ethanol:*n*-hexane. The solid was redissolved in 1 mL DMSO and precipitated once more in 6:1 ethanol:*n*-hexane, before one wash with 6:1 ethanol:*n*-hexane. A final wash with pure *n*-hexane was done, followed by drying *in vacuo* to produce a soft off-white solid. Yield: 320 mg.  $^1\text{H NMR}$ : deprotection  $\approx 100\%$ :  $M_{n\text{SEC+NMR}} = 63\,200$  Da.

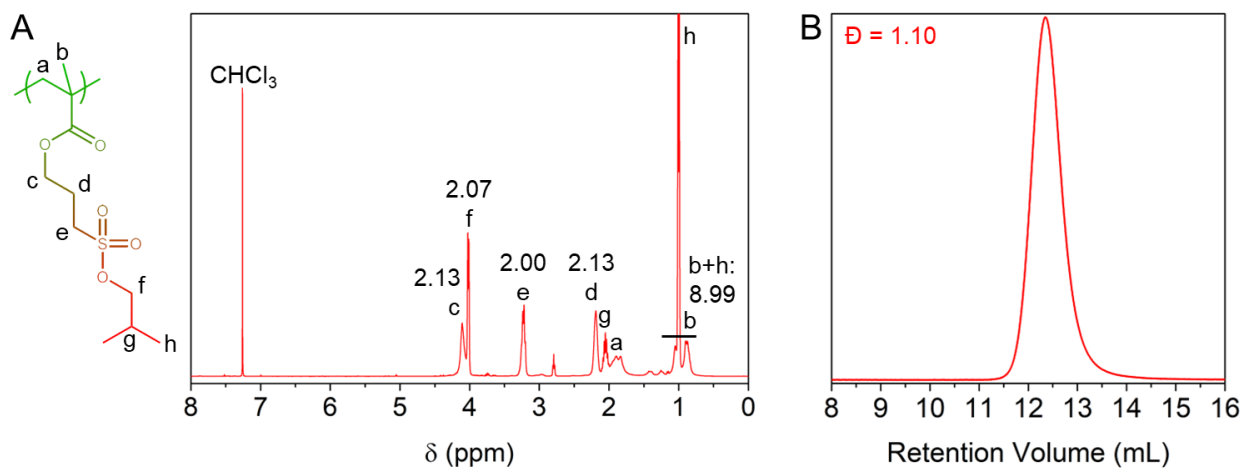
### Synthesis of poly(methyl methacrylate)-*block*-poly(sulphopropyl methacrylate) butyrylthiocholine salt (PMMA<sub>114</sub>-*b*-PSPMA-BTC<sub>126</sub>)



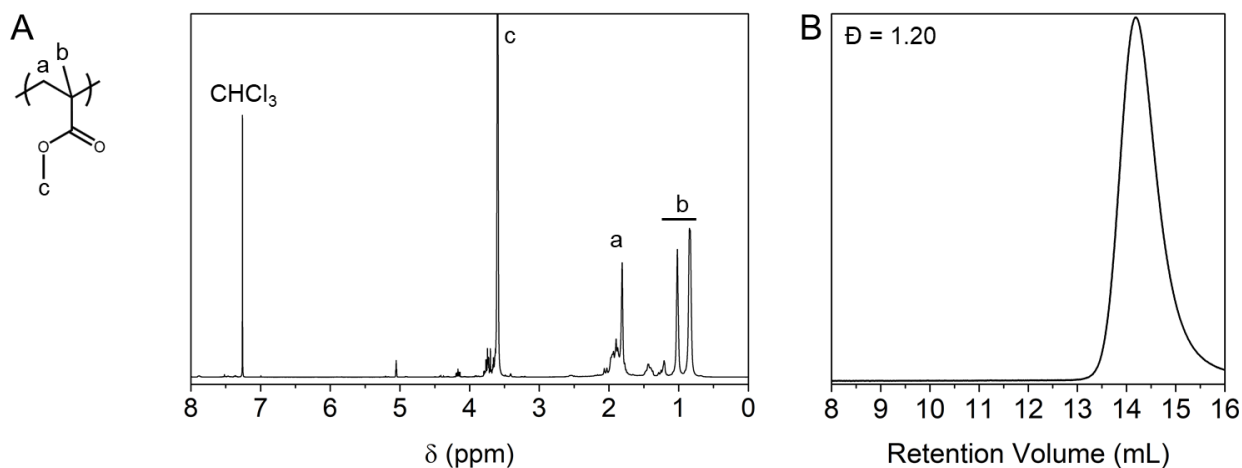
PMMA<sub>114</sub>-*b*-PBSPMA<sub>126</sub>, (1 eq, 101 mg BCP, 75 mg BSPMA, 0.283 mmol BSPMA), BTCl (4 eq, 281 mg, 0.886 mmol) and 2 mL DMSO were charged into a round bottom flask equipped with a stirring egg before being immersed in a pre-heated oil bath at 70 °C. After 24 hours, the reaction was stopped and the polymer was precipitated into 6:1 ethanol:*n*-hexane. The solid was redissolved in 1 mL DMSO and precipitated once more in 6:1 ethanol:*n*-hexane, washed once with 6:1 ethanol:*n*-hexane and once with pure *n*-hexane, followed by drying *in vacuo* to produce a sticky yellow solid. Yield: 167 mg. <sup>1</sup>H NMR: deprotection ≈ 100 %:  $M_{n\text{SEC+NMR}} = 61\,400$  Da.

# Supporting Figures

## S1: Characterisation of hydrophobic homopolymers



**Figure S1-1:** (A) <sup>1</sup>H NMR spectrum recorded in CDCl<sub>3</sub> and (B) SEC elugram of a PBSPMA<sub>114</sub> homopolymer measured in DMF with 0.01 M LiBr. Integration of the NMR signals (numbers in A, reference set as 2H for e) evidences the absence of unwanted deprotection during the polymerisation.



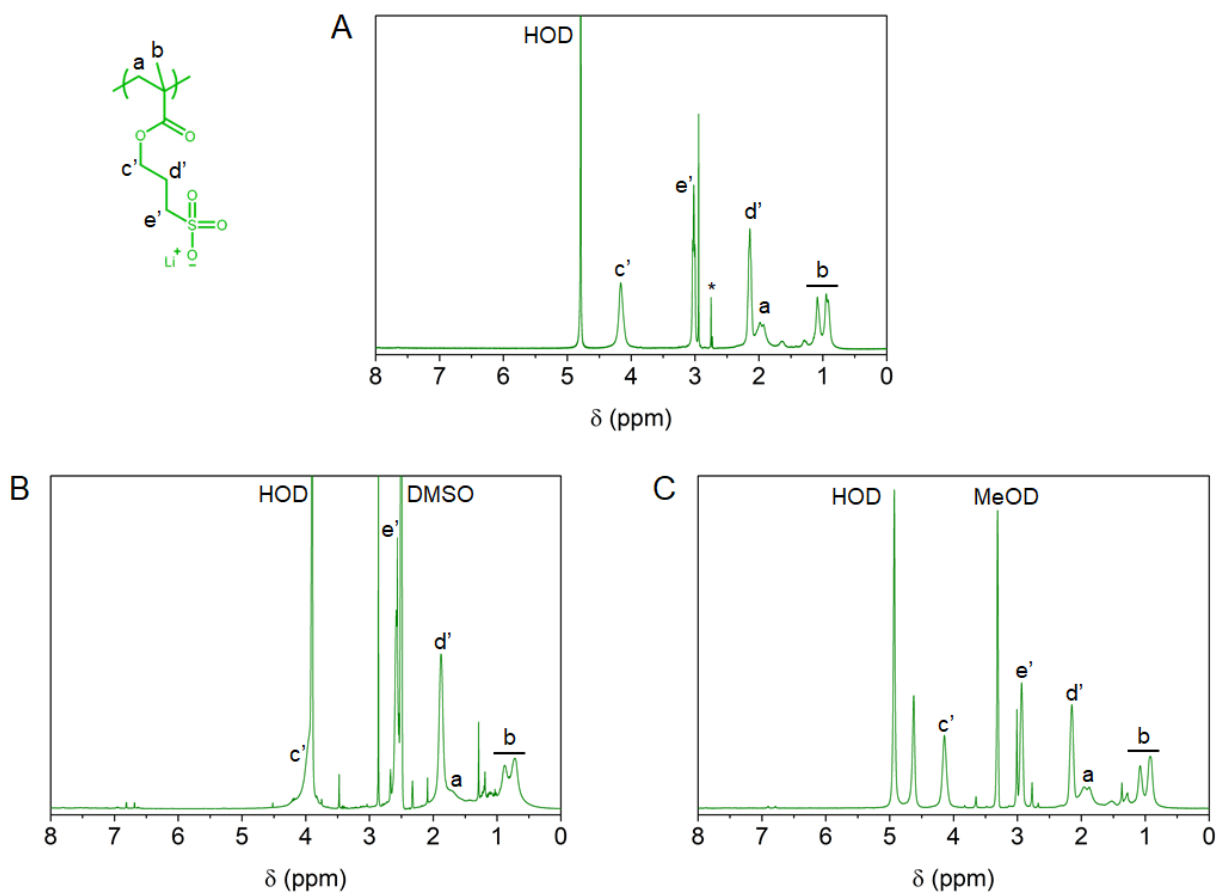
**Figure S1-2:** (A) <sup>1</sup>H NMR spectrum recorded in CDCl<sub>3</sub> and (B) SEC elugram measured in DMF with 0.01 M LiBr of a PMMA<sub>68</sub> homopolymer.

**Table S1:** Characteristics of the poly(3-isobutoxysulphopropyl methacrylate) homopolymer and its poly(methyl methacrylate) analogue.

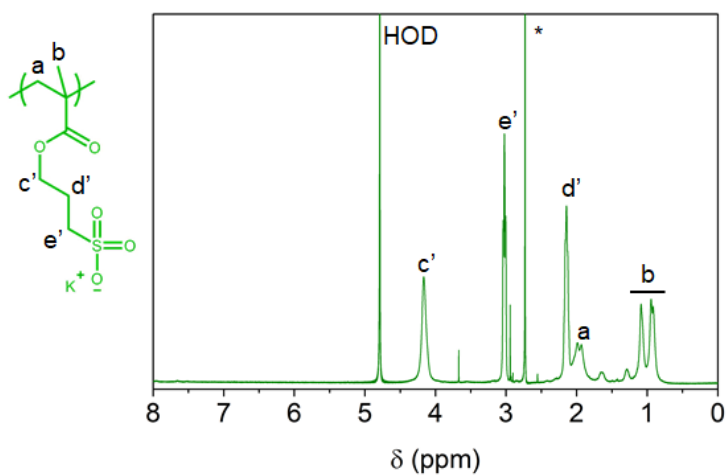
Polymer	[CTA]:[M]	<i>t</i> (h)	conv. ‡ (%)	DP‡	<i>M<sub>n</sub></i> <sup>NMR</sup> ‡ (Da)	<i>M<sub>n</sub></i> <sup>SEC</sup> ‡ (Da)
PBSPMA <sub>114</sub>	119	18	96	114	30 400	43 000
PMMA <sub>68</sub>	120	18	60	72	7 500	7 100

[CTA]:[M]: chain transfer agent-to-monomer ratio. *t*: reaction time. ‡ Determined by <sup>1</sup>H NMR using conversion samples. † Determined from SEC data in DMF with 0.01 M LiBr and calibrated against near-monodisperse PMMA standards.

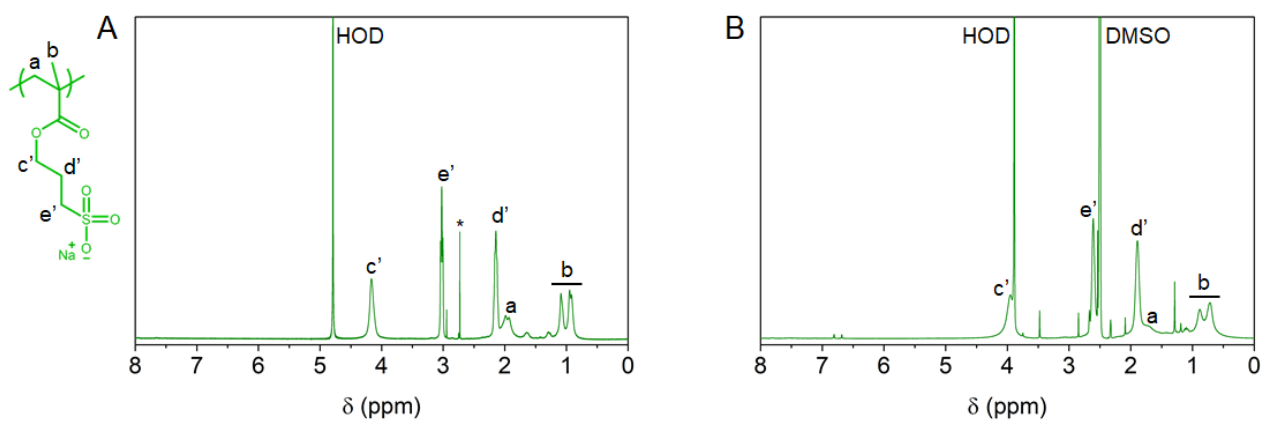
## S2: $^1\text{H}$ NMR spectroscopy of the polyelectrolyte homopolymers



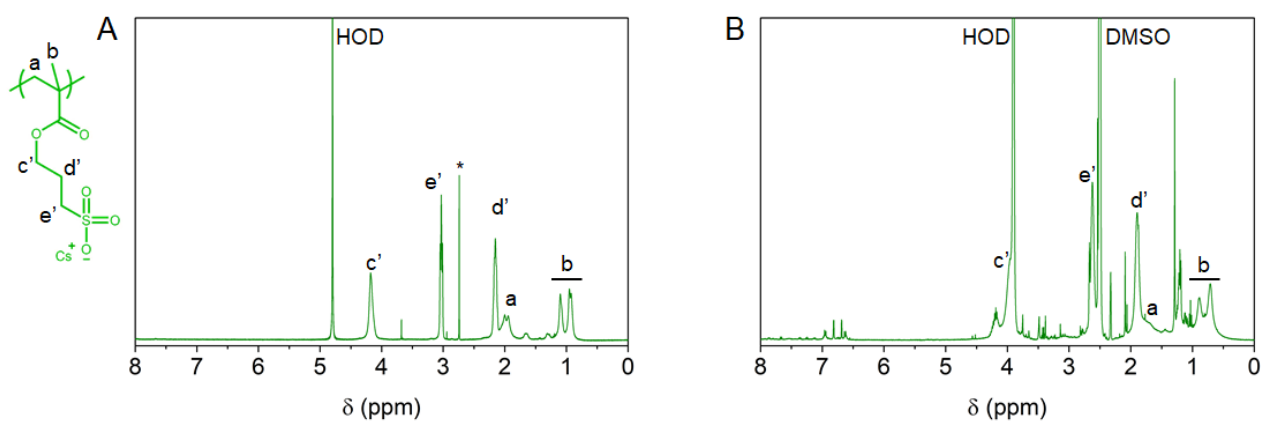
**Figure S2-1:** Comparative  $^1\text{H}$  NMR spectra (400 MHz) of PSPMA-Li<sub>14</sub> in (A) D<sub>2</sub>O, (B) 91:9 vol.% DMSO-*d*<sub>6</sub>:D<sub>2</sub>O and (C) 91:9 vol.% methanol-*d*<sub>4</sub>:D<sub>2</sub>O.



**Figure S2-2:**  $^1\text{H}$  NMR spectrum (400 MHz, D<sub>2</sub>O) of PSPMA-K<sub>14</sub>. \*: residual DMSO.

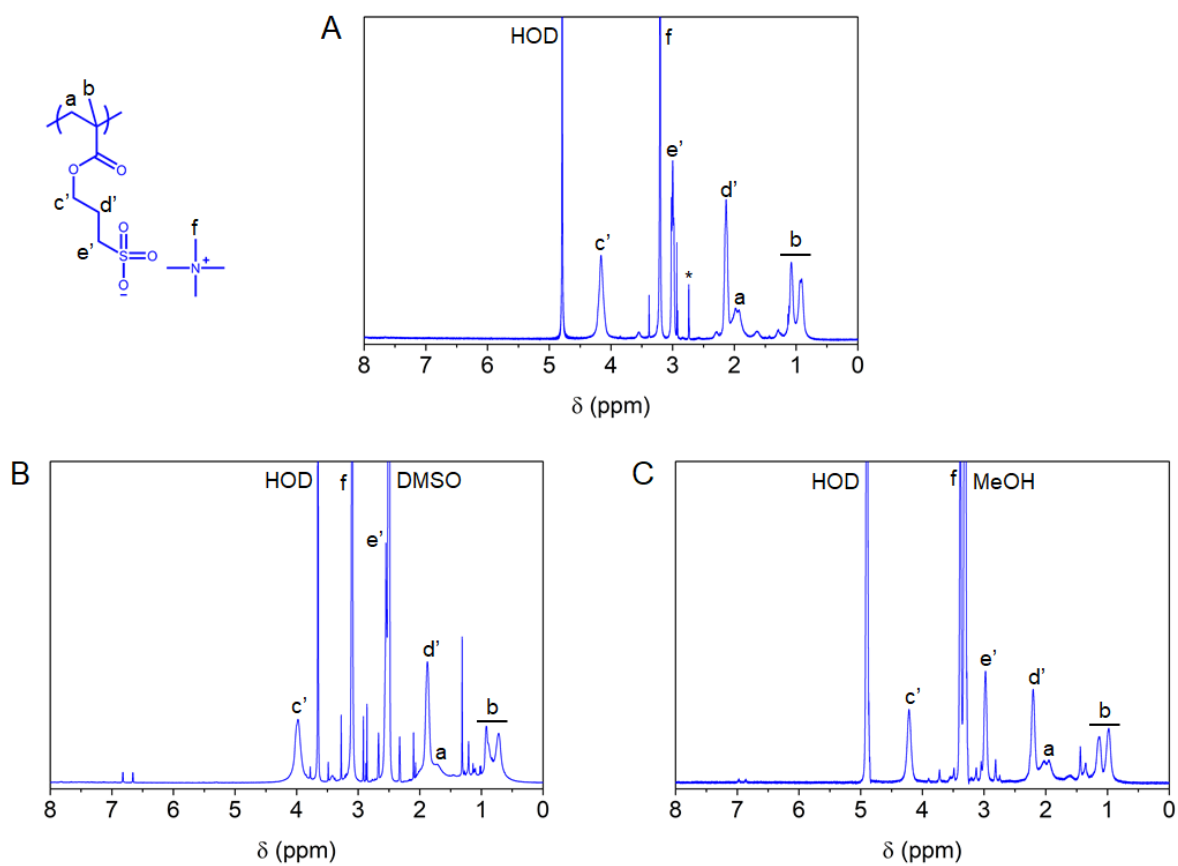


**Figure S2-3:** Comparative  $^1\text{H}$  NMR spectra (400 MHz) of PSPMA- $\text{Na}_{114}$  in (A)  $\text{D}_2\text{O}$  and (B) 91:9 vol.%  $\text{DMSO-}d_6$ : $\text{D}_2\text{O}$ .

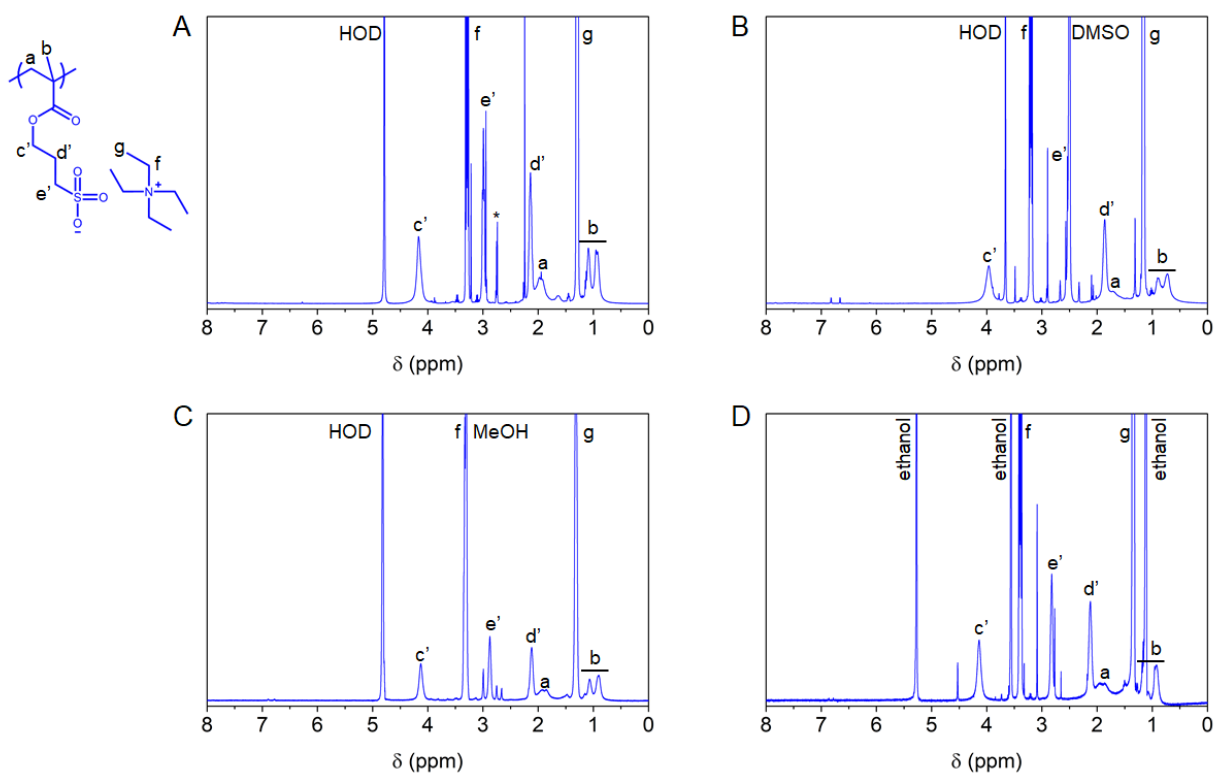


**Figure S2-4:** Comparative  $^1\text{H}$  NMR spectra (400 MHz) of PSPMA- $\text{Cs}_{114}$  in (A)  $\text{D}_2\text{O}$  and (B) 91:9 vol.%  $\text{DMSO-}d_6$ : $\text{D}_2\text{O}$ .

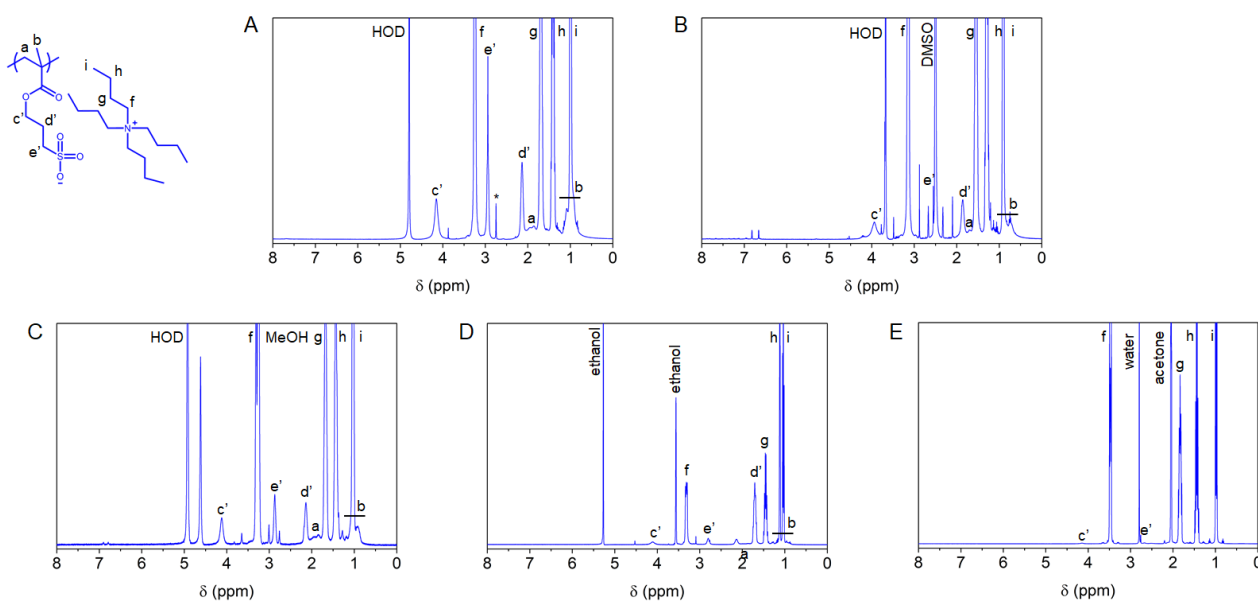




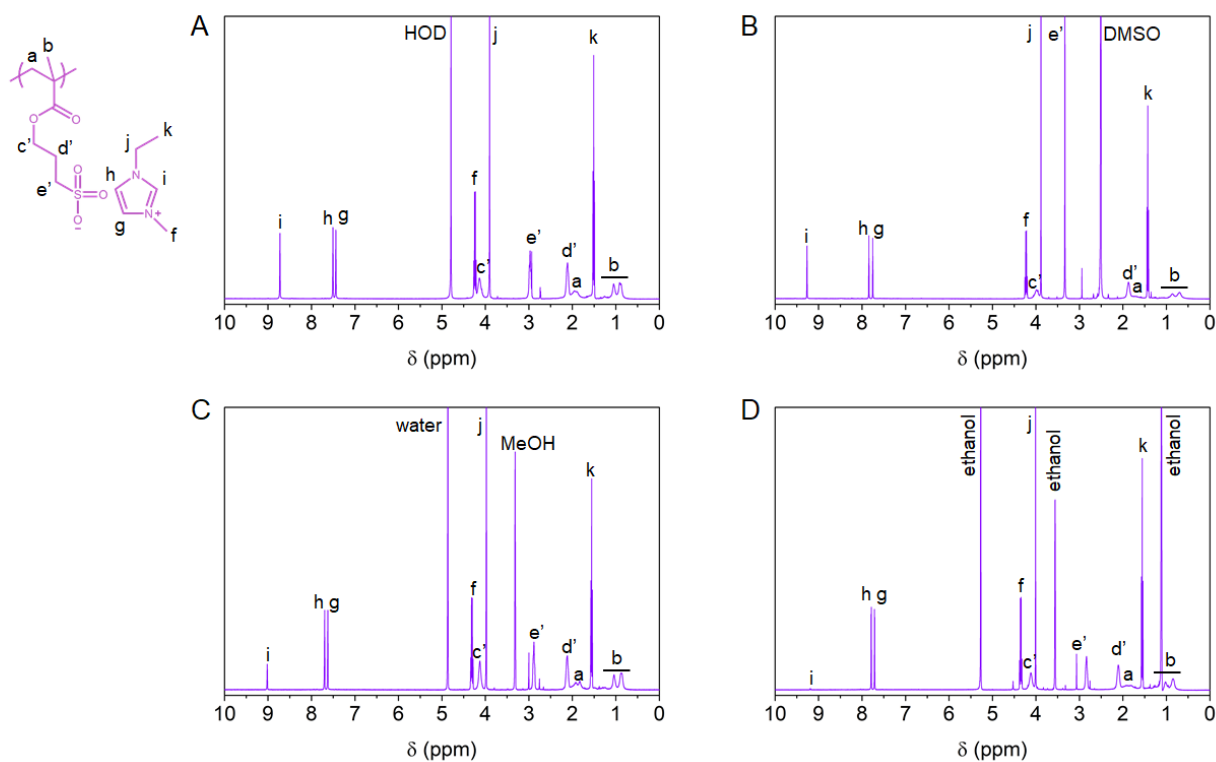
**Figure S2-5:** Comparative  $^1\text{H}$  NMR spectra (400 MHz) of PSPMA-TMA<sub>114</sub> in (A)  $\text{D}_2\text{O}$ , (B) 91:9 vol.%  $\text{DMSO-}d_6\text{:D}_2\text{O}$  and (C) 91:9 vol.%  $\text{methanol-}d_4\text{:D}_2\text{O}$ .



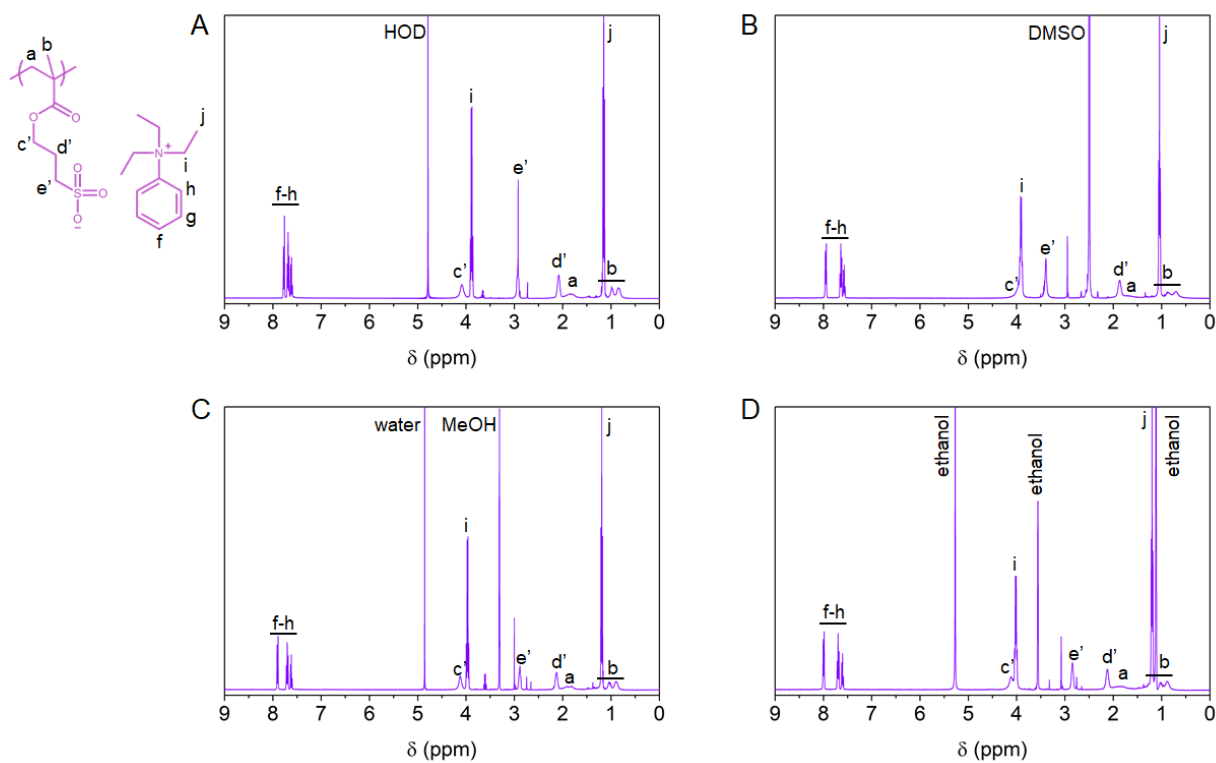
**Figure S2-6:** Comparative  $^1\text{H}$  NMR spectra (400 MHz) of PSPMA-TEA<sub>114</sub> in (A) D<sub>2</sub>O, (B) 91:9 vol.% DMSO-*d*<sub>6</sub>:D<sub>2</sub>O, (C) 91:9 vol.% methanol-*d*<sub>4</sub>:D<sub>2</sub>O 91:9 and (D) neat ethanol-*d*<sub>6</sub>.



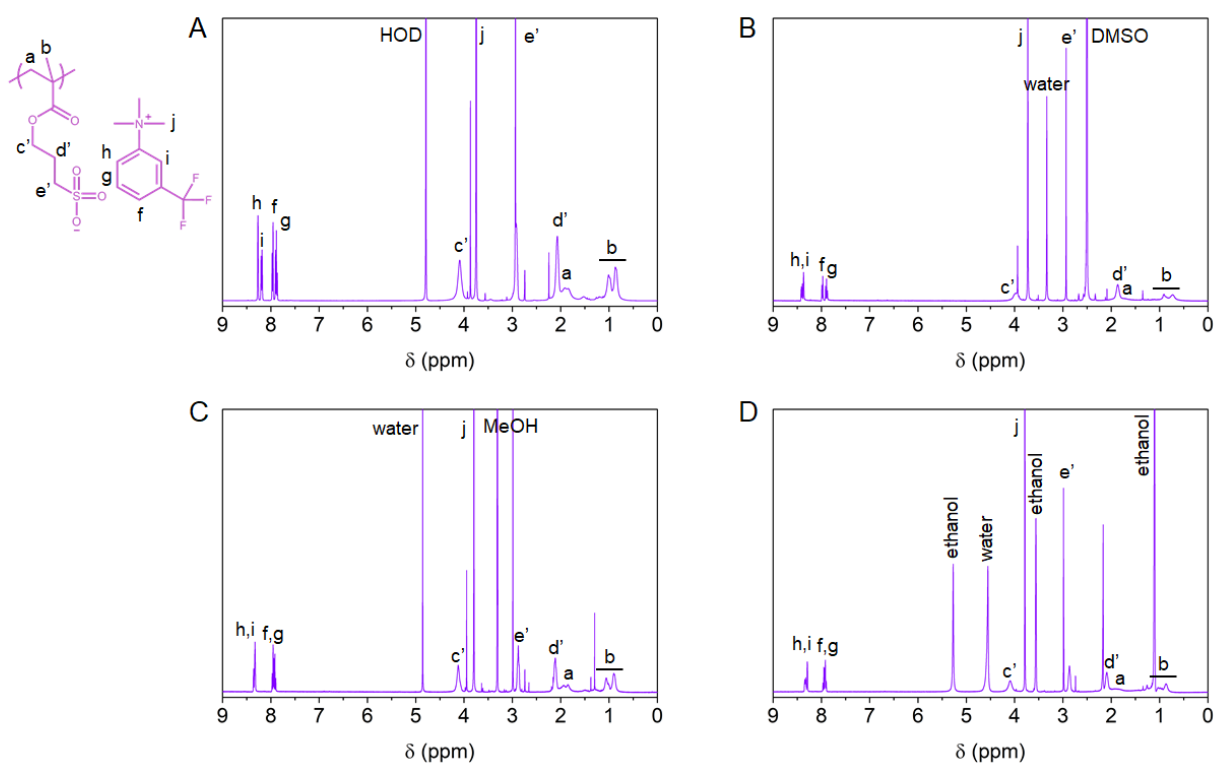
**Figure S2-7:** Comparative  $^1\text{H}$  NMR spectra (400 MHz) of PSPMA-TBA<sub>114</sub> in (A) D<sub>2</sub>O, (B) 91:9 vol.% DMSO-*d*<sub>6</sub>:D<sub>2</sub>O, (C) 91:9 vol.% methanol-*d*<sub>4</sub>:D<sub>2</sub>O, (D) neat ethanol-*d*<sub>6</sub> and (E) neat acetone-*d*<sub>6</sub>. Note that only signals of TBA<sup>+</sup> are visible in acetone-*d*<sub>6</sub>, albeit the solution being fully transparent, suggesting an aggregation of the PSPMA<sup>-</sup> chains surrounded by TBA<sup>+</sup> counterions acting as stabilisers.



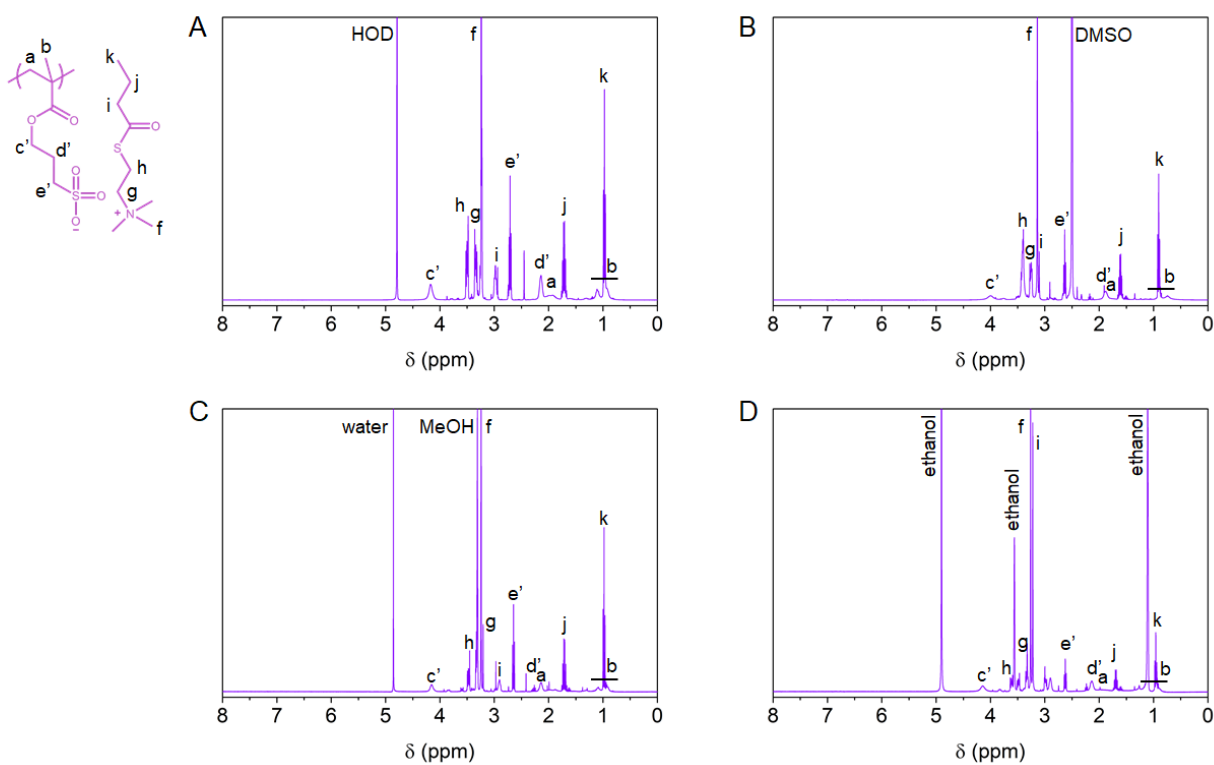
**Figure S2-8:** Comparative  $^1\text{H}$  NMR spectra (400 MHz) of PSPMA-EMIM<sub>114</sub> in (A)  $\text{D}_2\text{O}$ , (B) neat  $\text{DMSO-}d_6$ , (C) neat  $\text{methanol-}d_4$  and (D) neat  $\text{ethanol-}d_4$ .



**Figure S2-9:** Comparative  $^1\text{H}$  NMR spectra (400 MHz) of PSPMA-PhTEA<sub>114</sub> in (A)  $\text{D}_2\text{O}$ , (B) neat  $\text{DMSO-}d_6$ , (C) neat  $\text{methanol-}d_4$  and (D) neat  $\text{ethanol-}d_4$ .

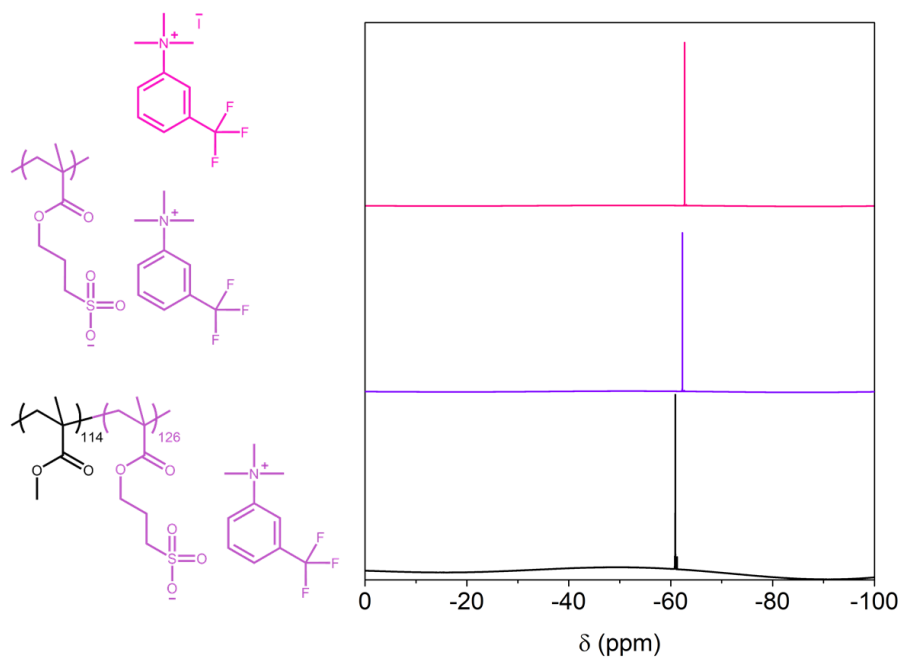


**Figure S2-10:** Comparative  $^1\text{H}$  NMR spectra (400 MHz) of PSPMA-FPhTMA<sub>114</sub> in (A)  $\text{D}_2\text{O}$ , (B) neat  $\text{DMSO-}d_6$ , (C) neat methanol- $d_4$  and (D) 88:12 vol.% ethanol- $d_4$ : $\text{D}_2\text{O}$ .



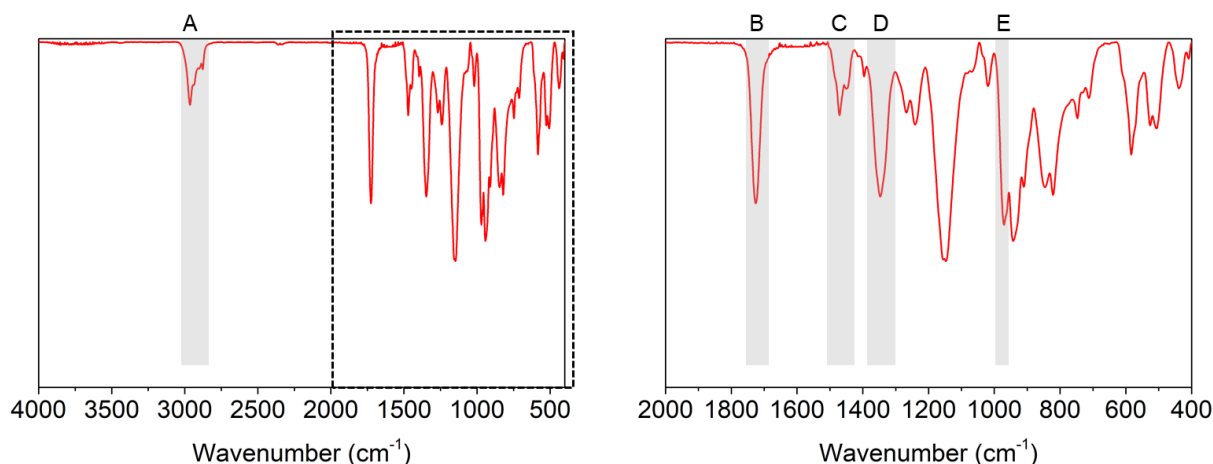
**Figure S2-11:** Comparative  $^1\text{H}$  NMR spectra (400 MHz) of PSPMA-BTC<sub>114</sub> in (A)  $\text{D}_2\text{O}$ , (B) neat  $\text{DMSO-}d_6$ , (C) neat methanol- $d_4$  and (D) 88:12 vol.% ethanol- $d_4$ : $\text{D}_2\text{O}$ .

### S3: $^{19}\text{F}$ -NMR spectroscopy of the polyelectrolyte homopolymers

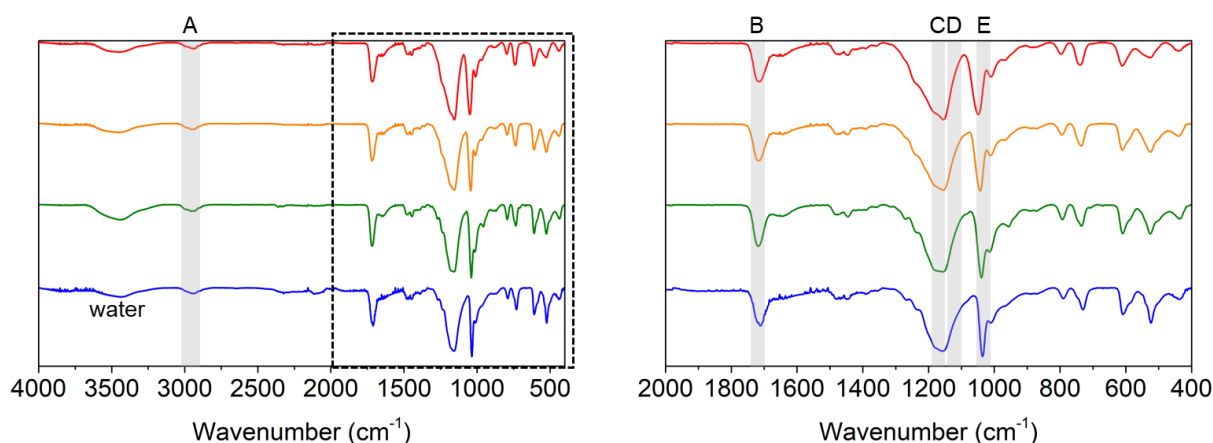


**Figure S3:** Comparative  $^{19}\text{F}$ -NMR spectra (600 MHz) of 3-(trifluoromethyl)phenyltrimethylammonium iodide salt (pink,  $\text{D}_2\text{O}$ ), PSPMA-FPhTMA<sub>114</sub> homopolymer (purple,  $\text{D}_2\text{O}$ ) and PMMA<sub>114</sub>-*b*-PSPMA-FPhTMA<sub>126</sub> block copolymer (black,  $\text{DMSO}-d_6$ ).

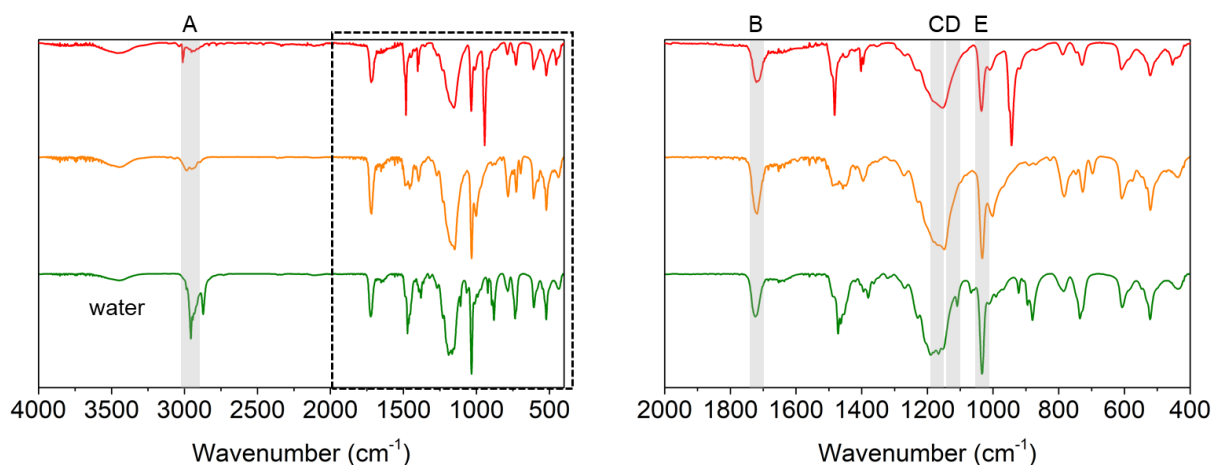
#### S4: FTIR spectroscopy of deprotected polymers



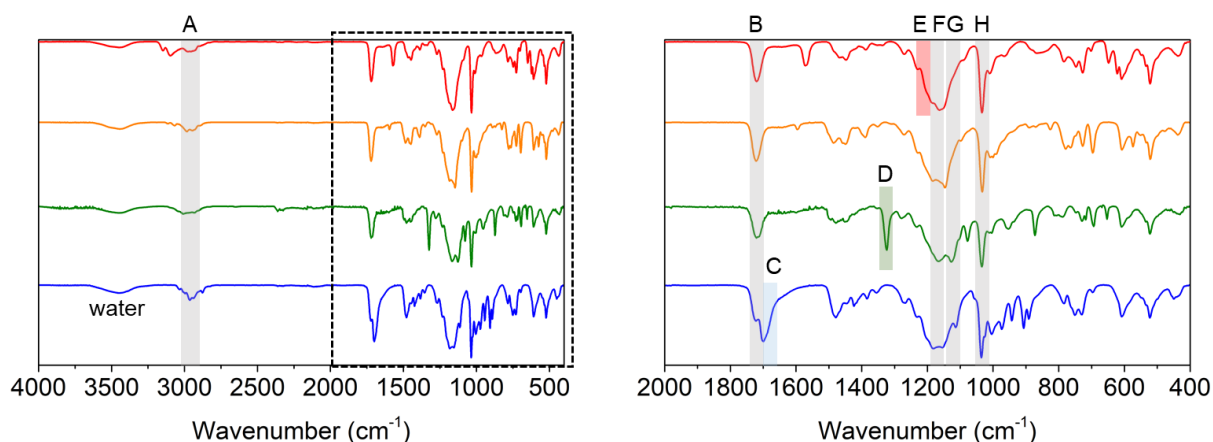
**Figure S4-1:** Reference FTIR spectra of PBSPMA<sub>114</sub>. Assigned signals are: (A) C-H stretching of backbone ( $\approx 2960 \text{ cm}^{-1}$ ), (B) C=O stretching of acrylate ( $1726 \text{ cm}^{-1}$ ), (C) C-H bending of backbone ( $1436 \text{ cm}^{-1}$ ), (D) S=O bending of sulphonate ( $1347 \text{ cm}^{-1}$ ) and (E) S-O-R sulfonic ester ( $941 \text{ cm}^{-1}$ ).



**Figure S4-2:** Comparative FTIR spectra of polyelectrolyte homopolymers featuring inorganic counterions: PSPMA-Li<sub>114</sub> (red), PSPMA-Na<sub>114</sub> (orange), PSPMA-K<sub>114</sub> (green) and PSPMA-Cs<sub>114</sub> (blue). Assigned signals are: (A) C-H stretching of backbone ( $\approx 2960 \text{ cm}^{-1}$ ), (B) C=O stretching of acrylate ( $1726 \text{ cm}^{-1}$ ), (C) S=O stretching ( $1192 \text{ cm}^{-1}$ ), (D) C-O stretching of acrylate ( $1156 \text{ cm}^{-1}$ ) and (E) S=O stretching ( $1045 \text{ cm}^{-1}$ ).

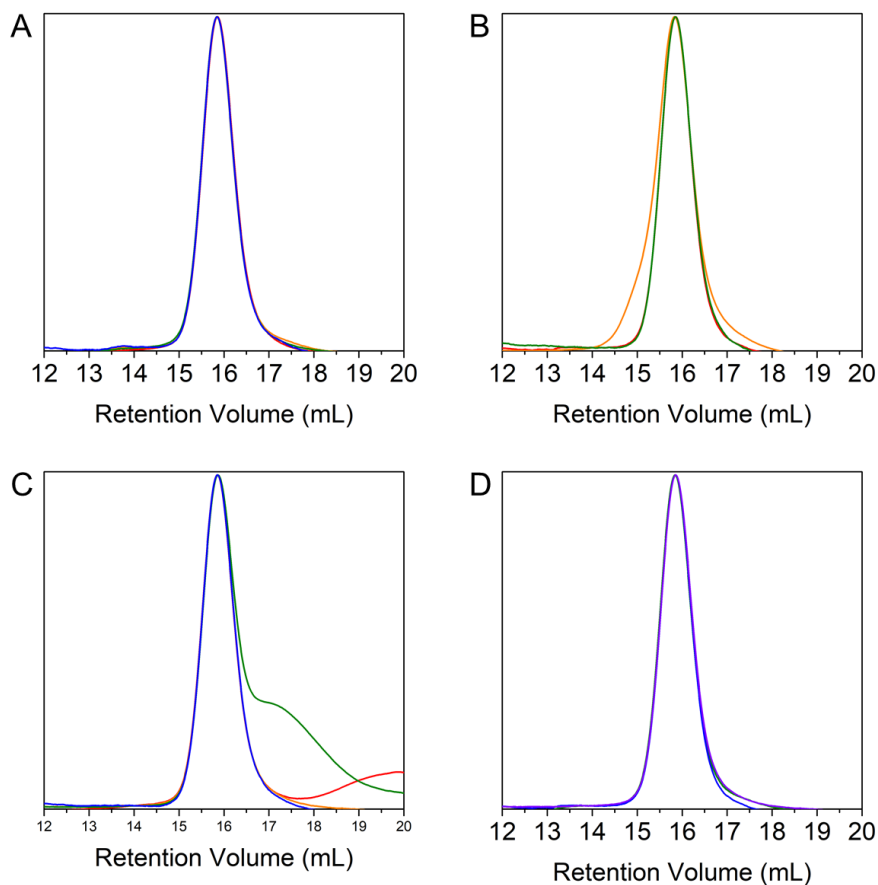


**Figure S4-3:** Comparative FTIR spectra of polyelectrolyte homopolymers featuring quaternary ammonium counterions: PSPMA-TMA<sub>114</sub> (red), PSPMA-TEA<sub>114</sub> (orange) and PSPMA-TBA<sub>114</sub> (green). Assigned signals are: (A) C-H stretching of backbone ( $\approx 2960\text{ cm}^{-1}$ ), (B) C=O stretching of acrylate ( $1726\text{ cm}^{-1}$ ), (C) S=O stretching ( $1192\text{ cm}^{-1}$ ), (D) -C-O stretching of acrylate ( $1156\text{ cm}^{-1}$ ) and (E) S=O stretching ( $1045\text{ cm}^{-1}$ ).



**Figure S4-4:** Comparative FTIR spectra of polyelectrolyte homopolymers featuring organic counterions: PSPMA-EMIM<sub>114</sub> (red), PSPMA-PhTEA<sub>114</sub> (orange), PSPMA-FPhTMA<sub>114</sub> (green) and PSPMA-BTC<sub>114</sub> (blue). Grey boxes apply to all, colour-specific boxes apply to individual samples. Assigned signals are: (A) C-H stretching of backbone and N-H stretching of amine salt ( $\approx 2960\text{ cm}^{-1}$ ), (B) C=O stretching of acrylate ( $1726\text{ cm}^{-1}$ ), (C) C=O stretching of BTC ketone ( $1699\text{ cm}^{-1}$ ), (D) C-F stretching of FPhTMA ( $1324\text{ cm}^{-1}$ ), (E) C-N stretching of EMIM aromatic amine ( $\approx 1200\text{ cm}^{-1}$ ), (F) S=O stretching ( $1192\text{ cm}^{-1}$ ), (G) -C-O stretching of acrylate ( $1156\text{ cm}^{-1}$ ) and (H) S=O stretching ( $1045\text{ cm}^{-1}$ ).

## S5: Aqueous SEC on polyelectrolytes



**Figure S5:** Aqueous SEC elugrams of polyelectrolyte homopolymers with varying counterions. (A) Elugrams of PSPMA-Li<sub>114</sub> (red), PSPMA-Na<sub>114</sub> (orange), PSPMA-K<sub>114</sub> (green) and PSPMA-Cs<sub>114</sub> (blue). (B) Elugrams of PSPMA-TMA<sub>114</sub> (red), PSPMA-TEA<sub>114</sub> (orange) and PSPMA-TBA<sub>114</sub> (green). (C) Elugrams of PSPMA-EMIM (red), PSPMA-PhTEA<sub>114</sub> (orange), PSPMA-FPhTMA<sub>114</sub> (green) and PSPMA-BTC<sub>114</sub> (blue). (D) Comparative elugrams of inorganic and organic systems: PSPMA-Na<sub>114</sub> (green), PSPMA-TMA<sub>114</sub> (blue) and PSPMA-PhTEA<sub>114</sub> (purple). The should of PSPMA-FPhTMA<sub>114</sub> suggests an interaction between the polymer coils and the column material.

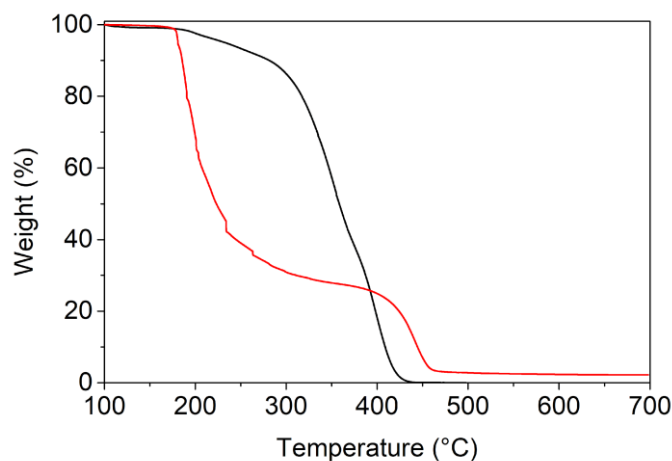


**Table S2:** Characteristics of the polyelectrolytes as measured by aqueous SEC.

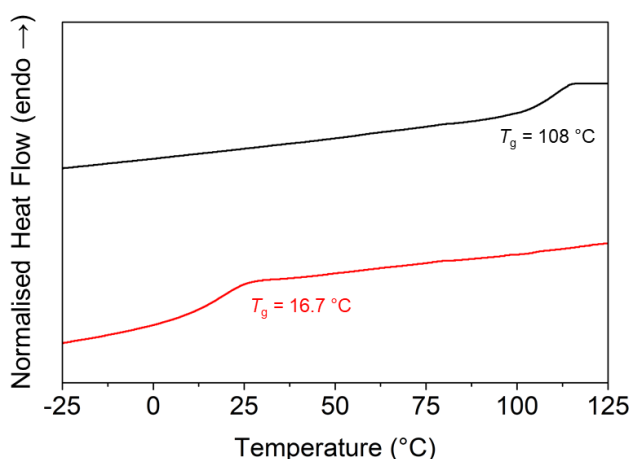
Polyelectrolyte	$M_n$ (Da)	$M_p$ (Da)	$\bar{D}$
PSPMA-Li	77 600	88 700	1.13
PSPMA-Na	73 300	89 600	1.20
PSPMA-K	76 400	88 700	1.19
PSPMA-Cs	74 200	88 700	1.16
PSPMA-TMA	79 700	88 500	1.10
PSPMA-TEA	75 100	90 700	1.27
PSPMA-TBA	77 400	89 100	1.12
PSPMA-EMIM	81 200	88 700	1.08
PSPMA-PhTEA	76 300	88 200	1.13

Determined from SEC data in Milli-Q water containing 0.1 M NaCl and 0.1 wt.% acetic acid was used at a flow rate of 1 mL min<sup>-1</sup> and calibrated against near-monodisperse pullulan standards.

## S6: Thermal characterisation of hydrophobic homopolymers



**Figure S6-1:** Comparative thermogravimetric analyses of PMMA<sub>68</sub> (black) and PBSPMA<sub>114</sub> (red) homopolymers.



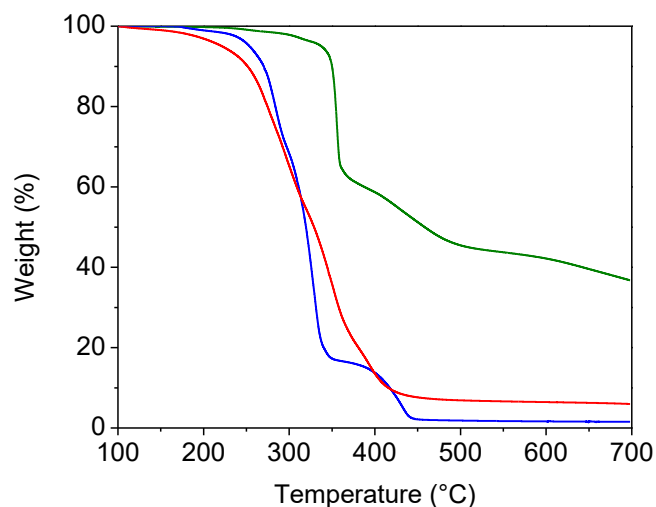
**Figure S6-2:** Comparative differential scanning calorimetry analyses of PMMA<sub>68</sub> (black) and PBSPMA<sub>114</sub> (red) homopolymers.

**Table S3:** Comparative differential scanning calorimetry and thermogravimetric analyses of PMMA<sub>68</sub> and PBSPMA<sub>114</sub> homopolymers.

Polymer	$T_g^*$ (°C)	$T_{deg\ 1}^\ddagger$ (°C)	$W_{deg\ 1}^\ddagger$ (%)	$T_{deg\ 2}^\ddagger$ (°C)	$W_{deg\ 2}^\ddagger$ (%)
PBSPMA <sub>114</sub>	16.7	195	72.3	439	25.4
PMMA <sub>68</sub>	108	352+397	96.2	n.a.	n.a.

\* Determined from DSC using a 20 °C min<sup>-1</sup> heating rate. ‡ Temperature corresponding to a maximal rate of degradation (*i.e.* decomposition temperature) and <sup>±</sup> corresponding weight loss at  $T_{deg}$ , both determined from TGA using a 10 °C min<sup>-1</sup> heating rate under nitrogen flow.

## S7: Thermal characterisation of polyelectrolytes



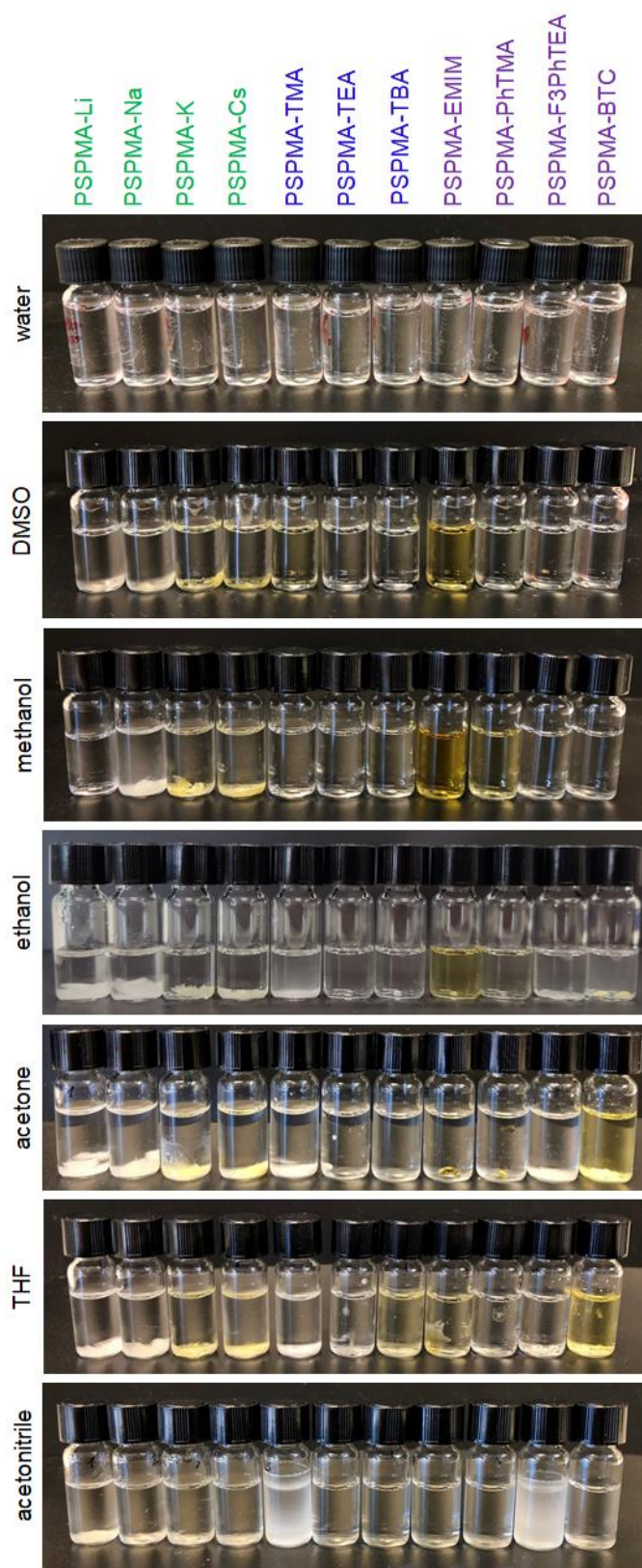
**Figure S7:** Comparative thermogravimetric analyses of various polyelectrolyte homopolymers: PSPMA-Na114 (green), PSPMA-TMA114 (blue) and PSPMA-EMIM114 (red).

**Table S4:** Comparative differential scanning calorimetry and thermogravimetric analyses of polyelectrolyte homopolymers

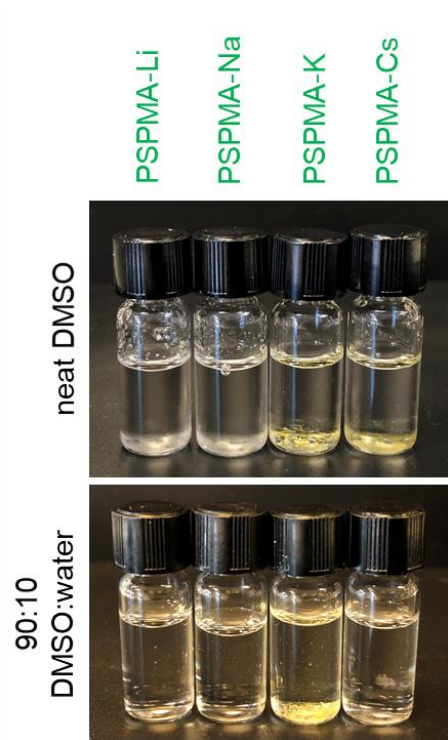
Polyelectrolyte	$T_g^*$ (°C)	$T_{deg\ 1}^\ddagger$ (°C)	$W_{deg\ 1}^\ddagger$ (%)	$T_{deg\ 2}^\ddagger$ (°C)	$W_{deg\ 2}^\ddagger$ (%)
PSPMA-Li	n.a.	295	17.0	391	49.6
PSPMA-Na	n.a.	354	39.0	432	21.8
PSPMA-K	n.a.	242	4.2	368	53.0
PSPMA-Cs	n.a.	361	18.6	>700	24.5
PSPMA-TMA	n.a.	321	82.8	425	14.7
PSPMA-TEA	-12.6	301	70.4	399	22.0
PSPMA-TBA	2.7	230	88.0	409	9.0
PSPMA-EMIM	~50	345	91.6	n.a.	n.a.
PSPMA-PhTEA	11.7	174	40.3	258+421	41.3+14.0
PSPMA-FPhTMA	55.1	268	77.7	490	18.2
PSPMA-BTC	53.9	251	84.4	425	11.2

\* Determined from DSC using a 20 °C min<sup>-1</sup> heating rate. ‡ Temperature corresponding to the maximal rate of degradation (*i.e.* decomposition temperature) and ± corresponding weight loss at  $T_{deg}$ , both determined from TGA using a 10 °C min<sup>-1</sup> heating rate under nitrogen flow.

## S8: Solubility tests on polyelectrolytes

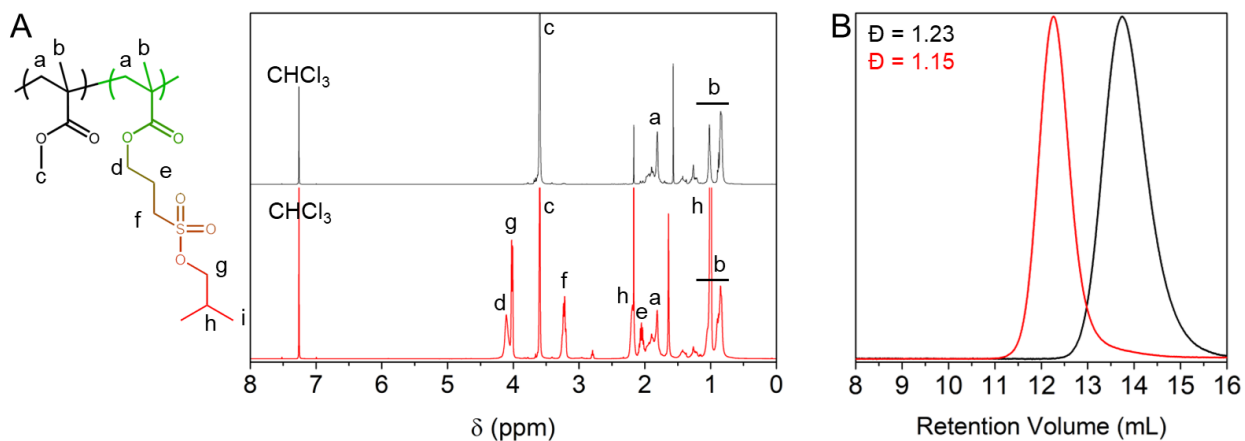


**Figure S8-1:** Photographs of polyelectrolyte homopolymer solutions in various neat solvents.

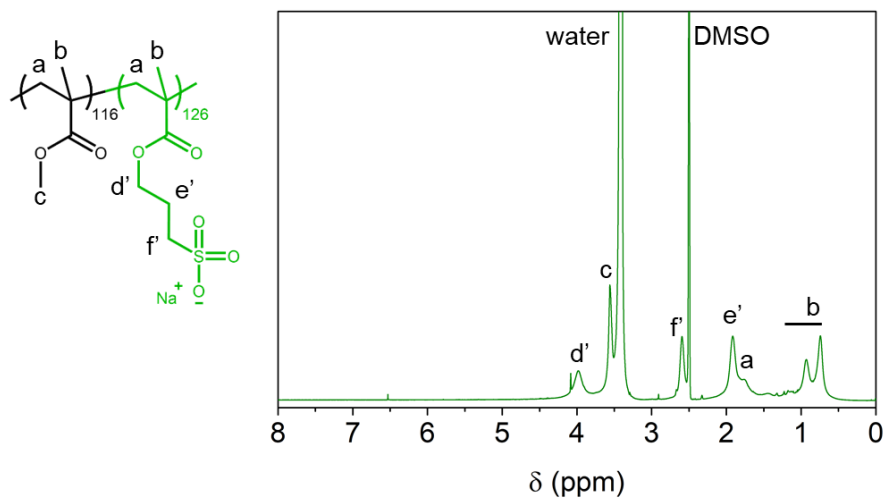


**Figure S8-2:** Photographs of polyelectrolyte homopolymer solutions in neat and 'wet' DMSO.

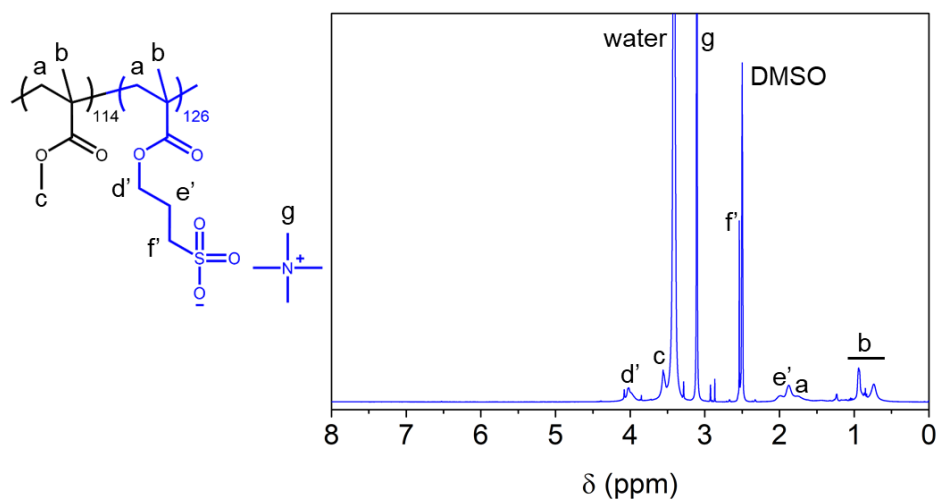
### S9: $^1\text{H}$ NMR spectra of the block copolymers



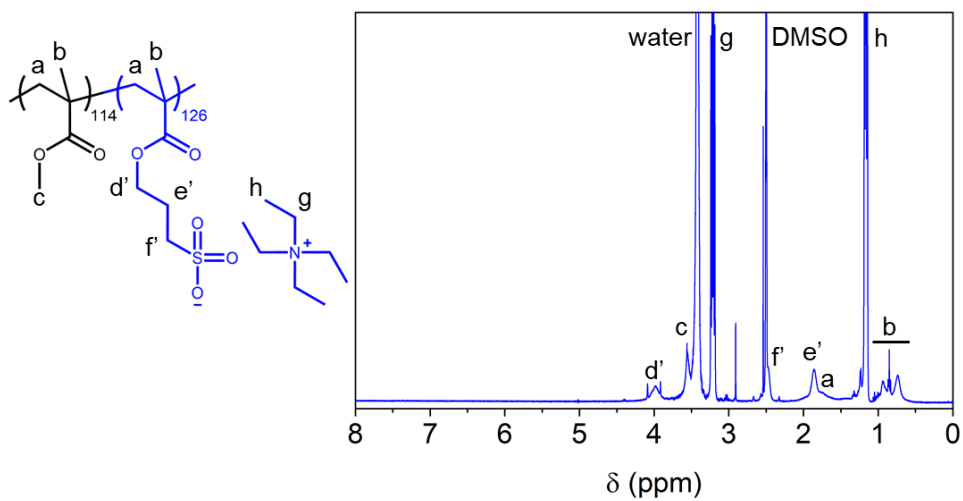
**Figure S9-1:** (A)  $^1\text{H}$  NMR spectra of PMMA<sub>114</sub> macro-CTA (black, CDCl<sub>3</sub>) and PMMA<sub>114</sub>-b-PBSPMA<sub>126</sub> (red, CDCl<sub>3</sub>) protected block copolymer and (B) corresponding SEC elugrams measured in DMF with/containing 0.01 M LiBr.



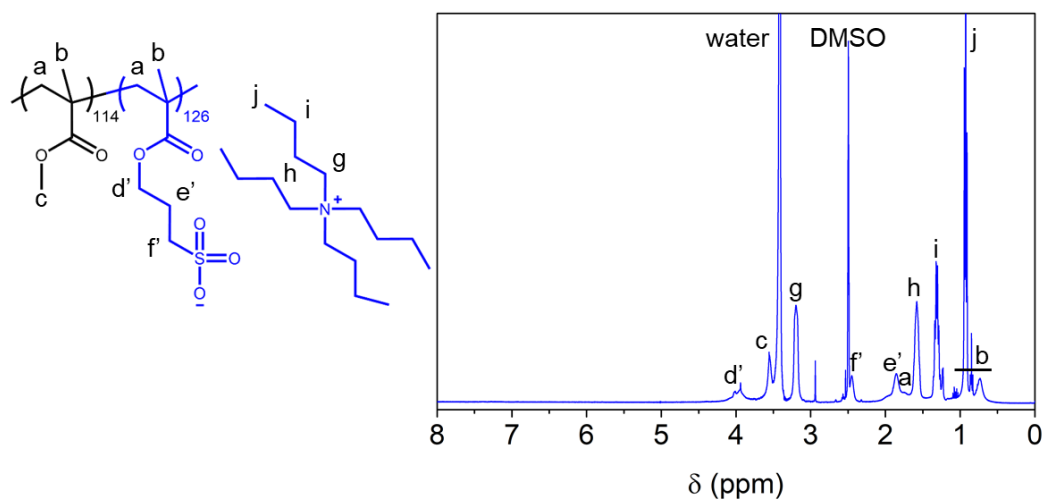
**Figure S9-2:**  $^1\text{H}$  NMR spectrum (400 MHz, DMSO-*d*<sub>6</sub>) of PMMA<sub>114</sub>-b-PSPMA-Na<sub>126</sub>.



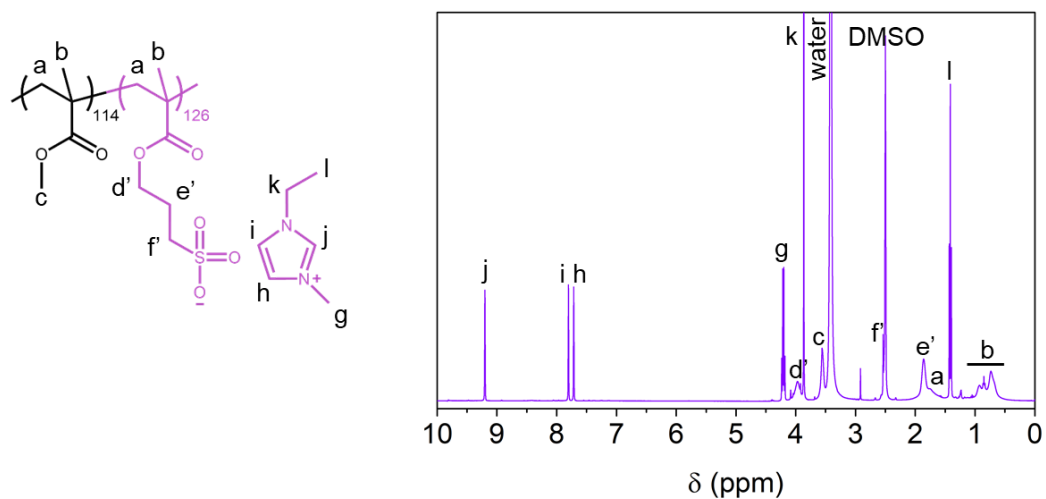
**Figure S9-3:**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{DMSO-}d_6$ ) of  $\text{PMMA}_{114}\text{-}b\text{-PSPMA-TMA}_{126}$ .



**Figure S9-4:**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{DMSO-}d_6$ ) of  $\text{PMMA}_{114}\text{-}b\text{-PSPMA-TBA}_{126}$ .

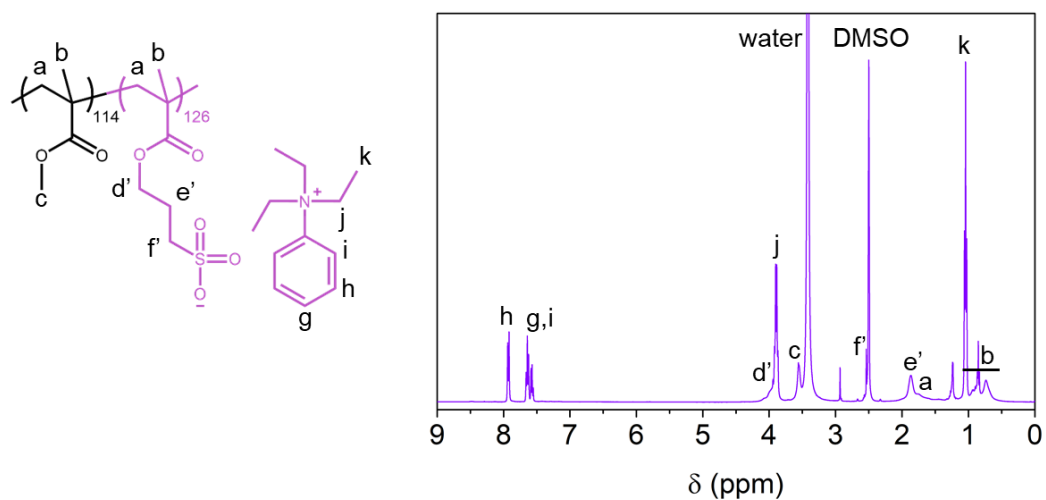


**Figure S9-5:**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{DMSO-}d_6$ ) of  $\text{PMMA}_{114}\text{-}b\text{-PSPMA-TBA}_{126}$ .

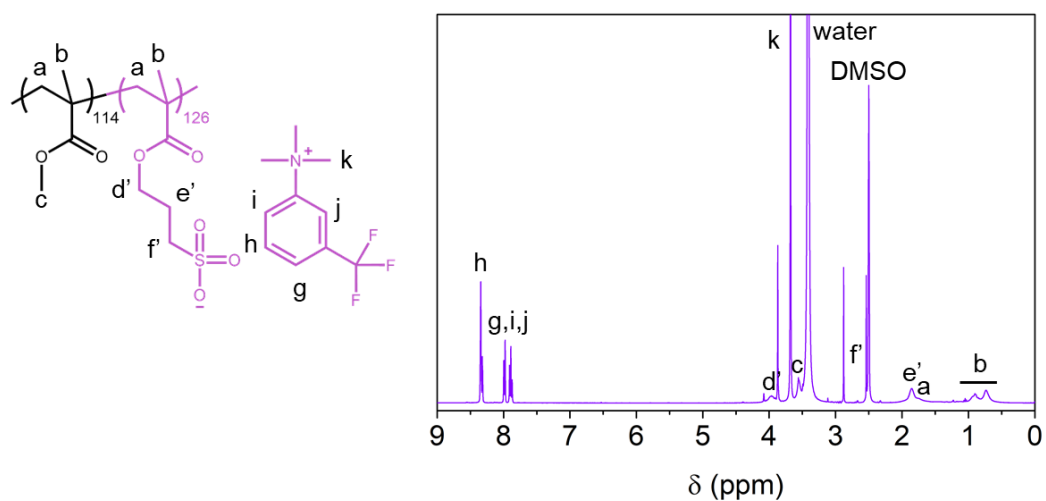


**Figure S9-6:**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{DMSO-}d_6$ ) of  $\text{PMMA}_{114}\text{-}b\text{-PSPMA-EMIM}_{126}$ .

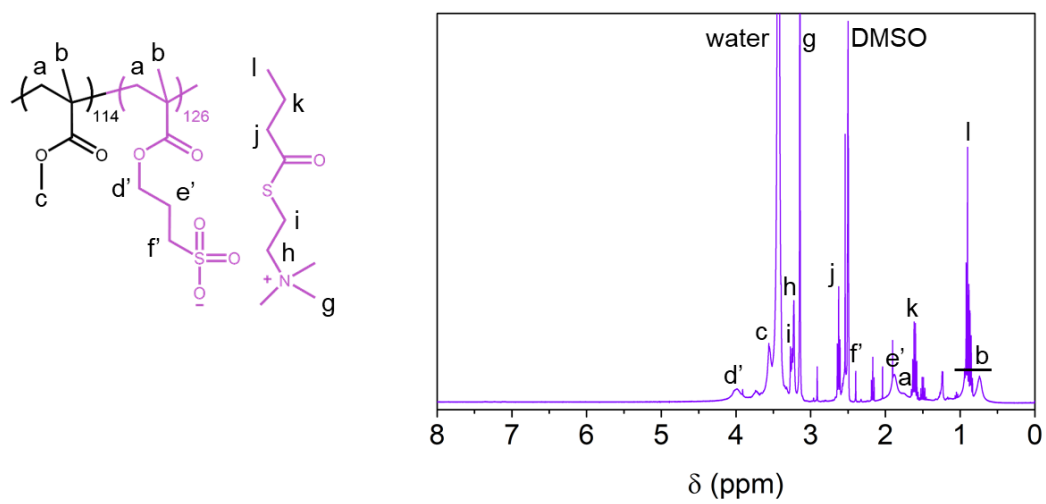




**Figure S9-7:**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{DMSO-}d_6$ ) of  $\text{PMMA}_{114}\text{-}b\text{-PSPMA-PhTEA}_{126}$ .

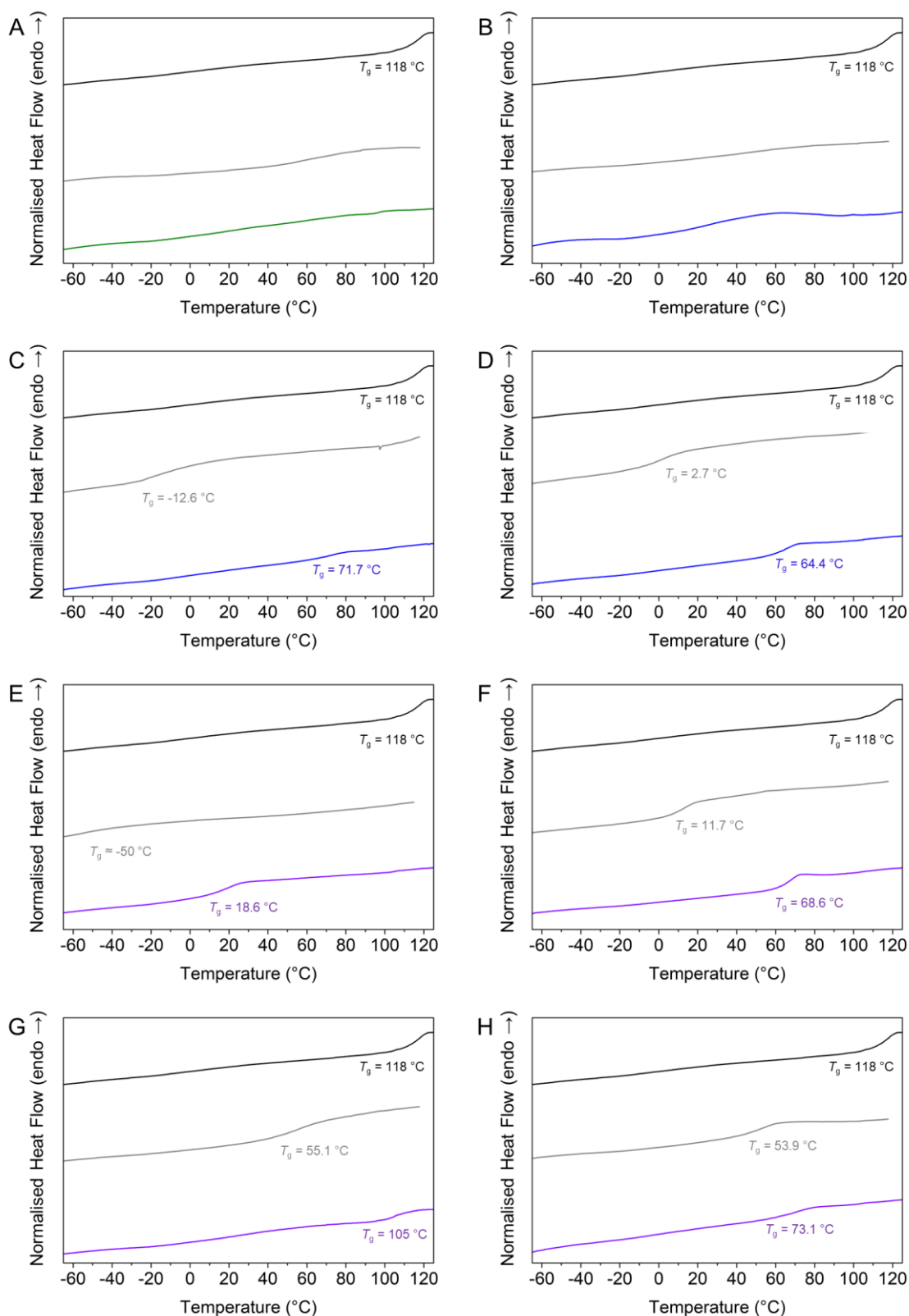


**Figure S9-8:**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{DMSO-}d_6$ ) of  $\text{PMMA}_{114}\text{-}b\text{-PSPMA-FPhTMA}_{126}$ .



**Figure S9-9:** <sup>1</sup>H NMR spectrum (400 MHz, DMSO-*d*<sub>6</sub>) of PMMA<sub>114</sub>-*b*-PSPMA-BTC<sub>126</sub>.

## S10: Thermal characterisation of block copolymers



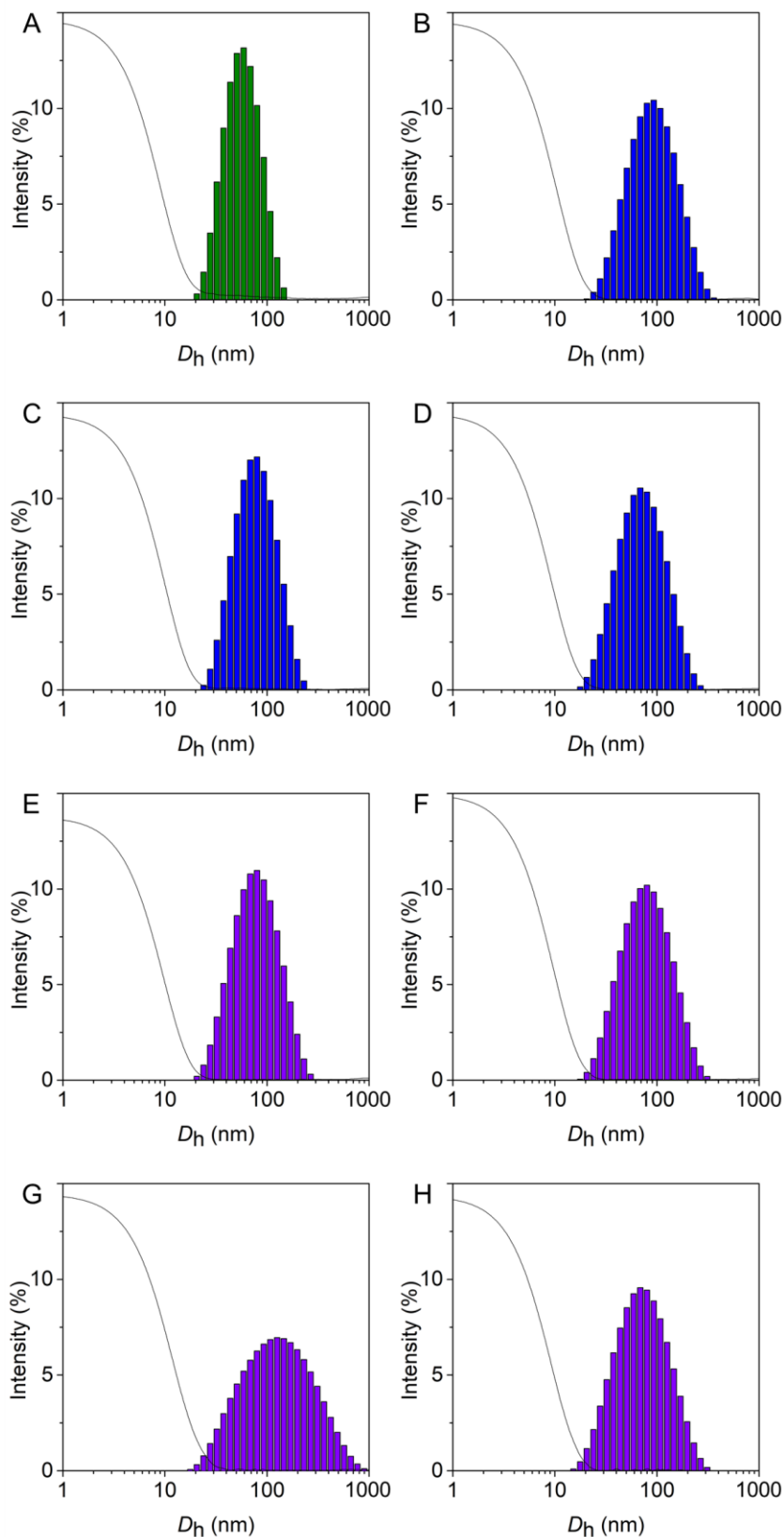
**Figure S10:** Comparative DSC thermograms of PMMA<sub>114</sub> macro-CTA (black), PMMA<sub>114</sub>-b-PSPMA-R<sub>126</sub> block copolymers (green, blue or violet) and their corresponding PSPMA-R<sub>126</sub> homopolymers analogues (grey). Counterions are (A) Na<sup>+</sup>, (B) TMA<sup>+</sup>, (C) TEA<sup>+</sup>, (D) TBA<sup>+</sup>, (E) EMIM<sup>+</sup>, (F) PhTEA<sup>+</sup>, (G) FPhTMA<sup>+</sup> and (H) BTC<sup>+</sup>.

**Table S5:** Glass transition temperatures of the amphiphilic block copolymers.

block copolymer	$T_g$ (°C)
PMMA <sub>114</sub>	118
PMMA <sub>114</sub> - <i>b</i> -PBSPMA <sub>126</sub>	18.1
PMMA <sub>114</sub> - <i>b</i> -PSPMA-Na <sub>126</sub>	n.a.
PMMA <sub>114</sub> - <i>b</i> -PSPMA-TMA <sub>126</sub>	n.a.
PMMA <sub>114</sub> - <i>b</i> -PSPMA-TEA <sub>126</sub>	71.7
PMMA <sub>114</sub> - <i>b</i> -PSPMA-TBA <sub>126</sub>	64.4
PMMA <sub>114</sub> - <i>b</i> -PSPMA-EMIM <sub>126</sub>	18.6
PMMA <sub>114</sub> - <i>b</i> -PSPMA-PhTEA <sub>126</sub>	68.6

Determined from DSC using a 20 °C min<sup>-1</sup> heating rate.

## S11: DLS and $\zeta$ -potential on block copolymers in aqueous media



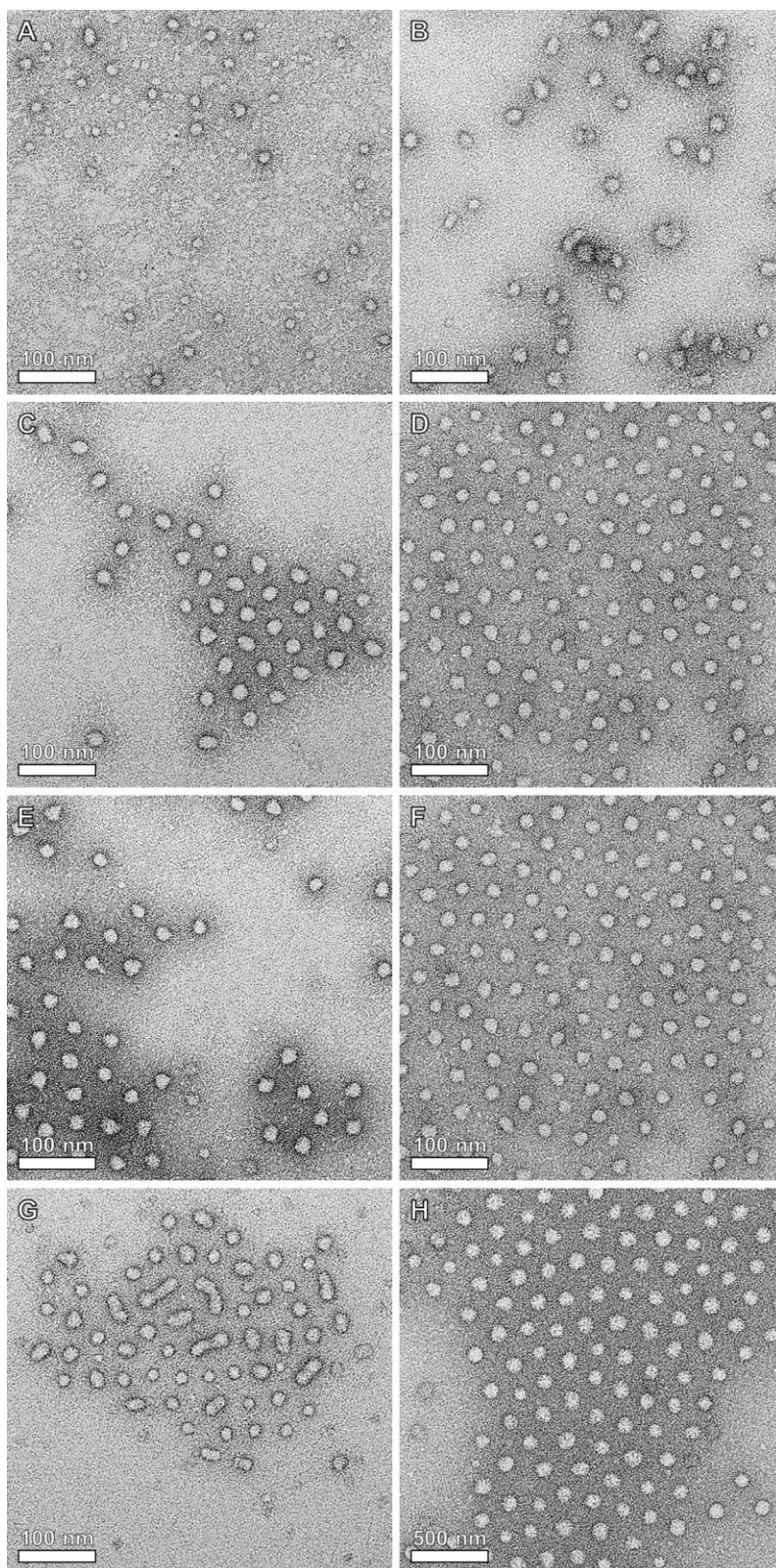
**Figure S11:** Comparative DLS intensity plots (bars) and correlograms (solid lines) of (A) PMMA<sub>114</sub>-*b*-PSPMA-Na<sub>126</sub>, (B) PMMA<sub>114</sub>-*b*-PSPMA-TMA<sub>126</sub>, (C) PMMA<sub>114</sub>-*b*-PSPMA-TEA<sub>126</sub>, (D) PMMA<sub>114</sub>-*b*-PSPMA-TBA<sub>126</sub>, (E) PMMA<sub>114</sub>-*b*-PSPMA-EMIM<sub>126</sub>, (F) PMMA<sub>114</sub>-*b*-PSPMA-PhTEA<sub>126</sub>, (G) PMMA<sub>114</sub>-*b*-PSPMA-FPhTMA<sub>126</sub>, and (H) PMMA<sub>114</sub>-*b*-PSPMA-BTC<sub>126</sub>.

**Table S6:** Characteristics of the micelles obtained after self-assembly of the PMMA<sub>114</sub>-*b*-PSPMA-R<sub>116</sub> BCPs in aqueous media.

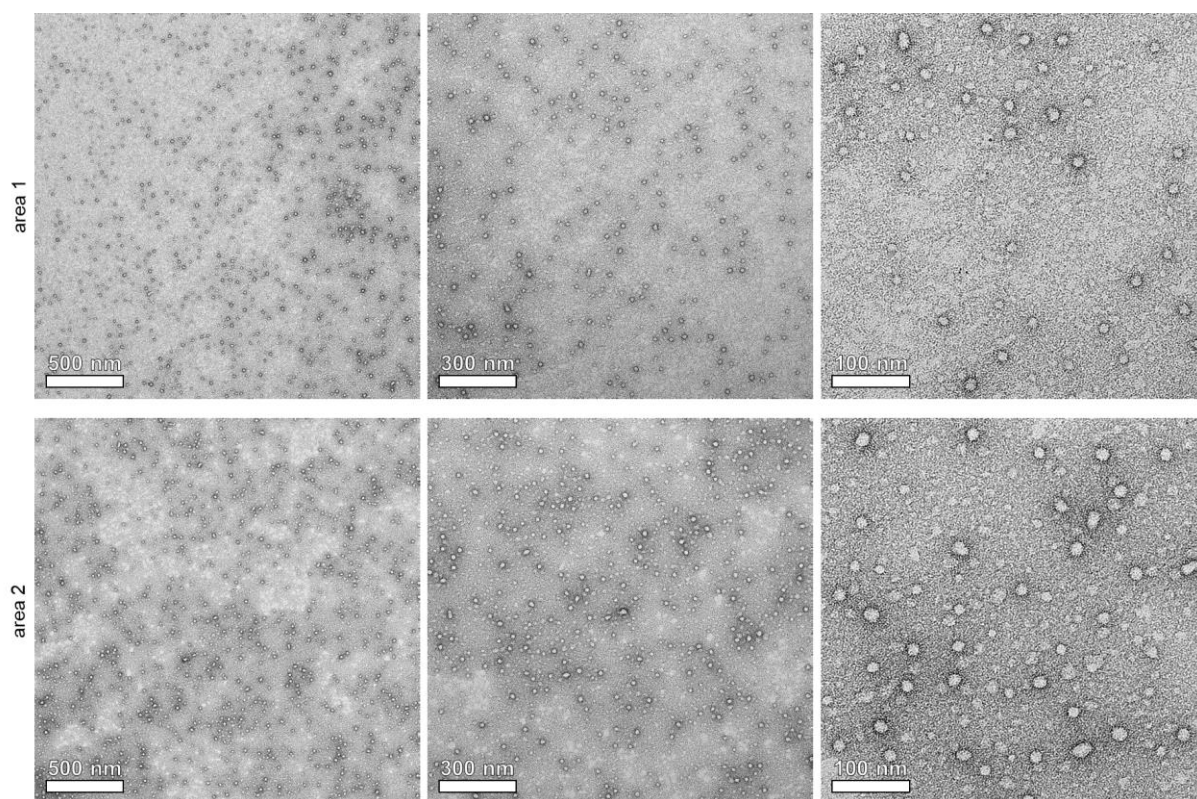
	$D_h$ (nm)	PDI	$\zeta$ (mV)
PMMA <sub>114</sub> - <i>b</i> -PSPMA-Na <sub>126</sub>	60 ± 4	0.215 ± 0.071	-47.5 ± 1.4
PMMA <sub>114</sub> - <i>b</i> -PSPMA-TMA <sub>126</sub>	75 ± 1	0.244 ± 0.007	-42.0 ± 1.0
PMMA <sub>114</sub> - <i>b</i> -PSPMA-TEA <sub>126</sub>	68 ± 1	0.218 ± 0.009	-41.6 ± 1.2
PMMA <sub>114</sub> - <i>b</i> -PSPMA-TBA <sub>126</sub>	59 ± 1	0.268 ± 0.040	-36.2 ± 2.6
PMMA <sub>114</sub> - <i>b</i> -PSPMA-EMIM <sub>126</sub>	64 ± 1	0.246 ± 0.002	-40.0 ± 2.4
PMMA <sub>114</sub> - <i>b</i> -PSPMA-PhTEA <sub>126</sub>	63 ± 1	0.265 ± 0.003	-37.2 ± 1.5
PMMA <sub>114</sub> - <i>b</i> -PSPMA-FPhTMA <sub>126</sub>	95 ± 1	0.383 ± 0.414	-36.2 ± 0.3
PMMA <sub>114</sub> - <i>b</i> -PSPMA-BTC <sub>126</sub>	58 ± 1	0.269 ± 0.005	-35.2 ± 0.7

Determined by DLS/ $\zeta$ -potential measurements at 25 °C on 1 g L<sup>-1</sup> solutions in 10 mM KNO<sub>3</sub> and measured in triplicate.

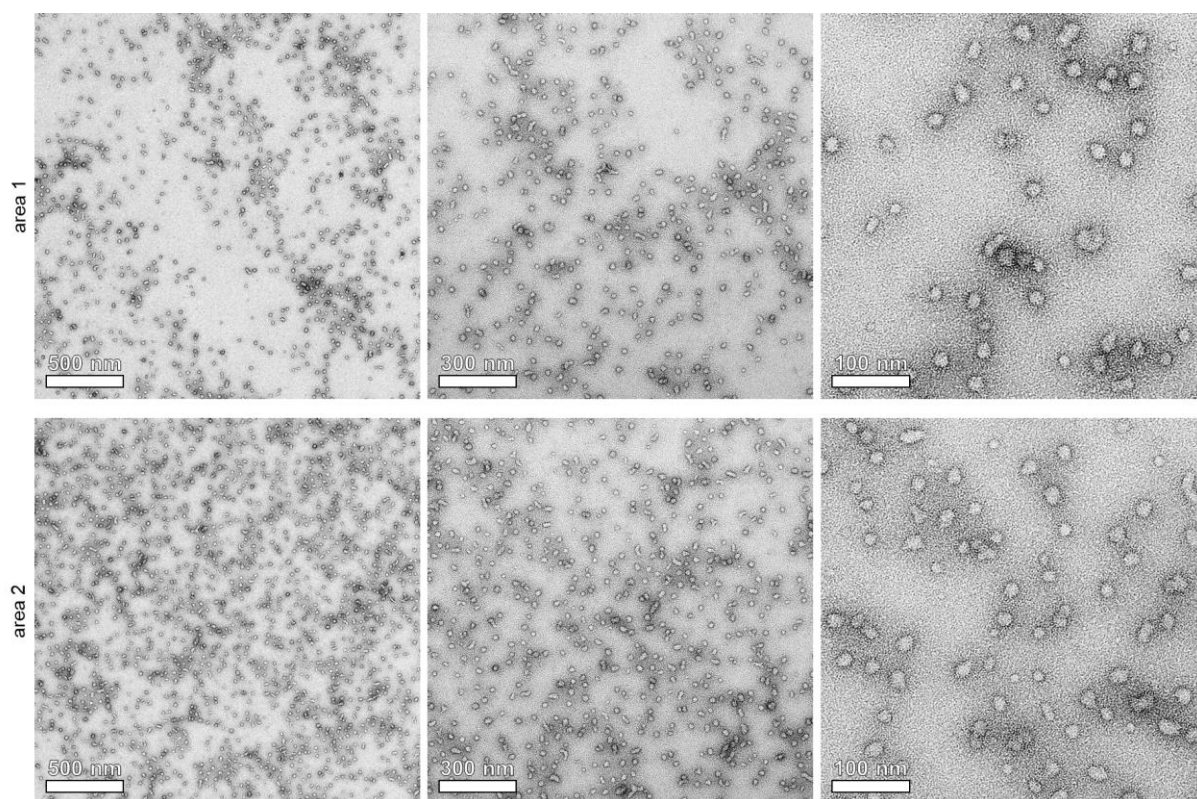
## S12: TEM on block copolymers in aqueous media



**Figure S12-1:** Comparative TEM images of uranyl acetate-stained polymer micelles self-assembled from aqueous solutions of (A)  $\text{PMMA}_{114}\text{-}b\text{-PSPMA-Na}_{126}$ , (B)  $\text{PMMA}_{114}\text{-}b\text{-PSPMA-TMA}_{126}$ , (C)  $\text{PMMA}_{114}\text{-}b\text{-PSPMA-TEA}_{126}$ , (D)  $\text{PMMA}_{114}\text{-}b\text{-PSPMA-TBA}_{126}$ , (E)  $\text{PMMA}_{114}\text{-}b\text{-PSPMA-EMIM}_{126}$ , (F)  $\text{PMMA}_{114}\text{-}b\text{-PSPMA-PhTEA}_{126}$ , (G)  $\text{PMMA}_{114}\text{-}b\text{-PSPMA-FPhTMA}_{126}$ , and (H)  $\text{PMMA}_{114}\text{-}b\text{-PSPMA-BTC}_{126}$  in 10 mM  $\text{KNO}_3$ .

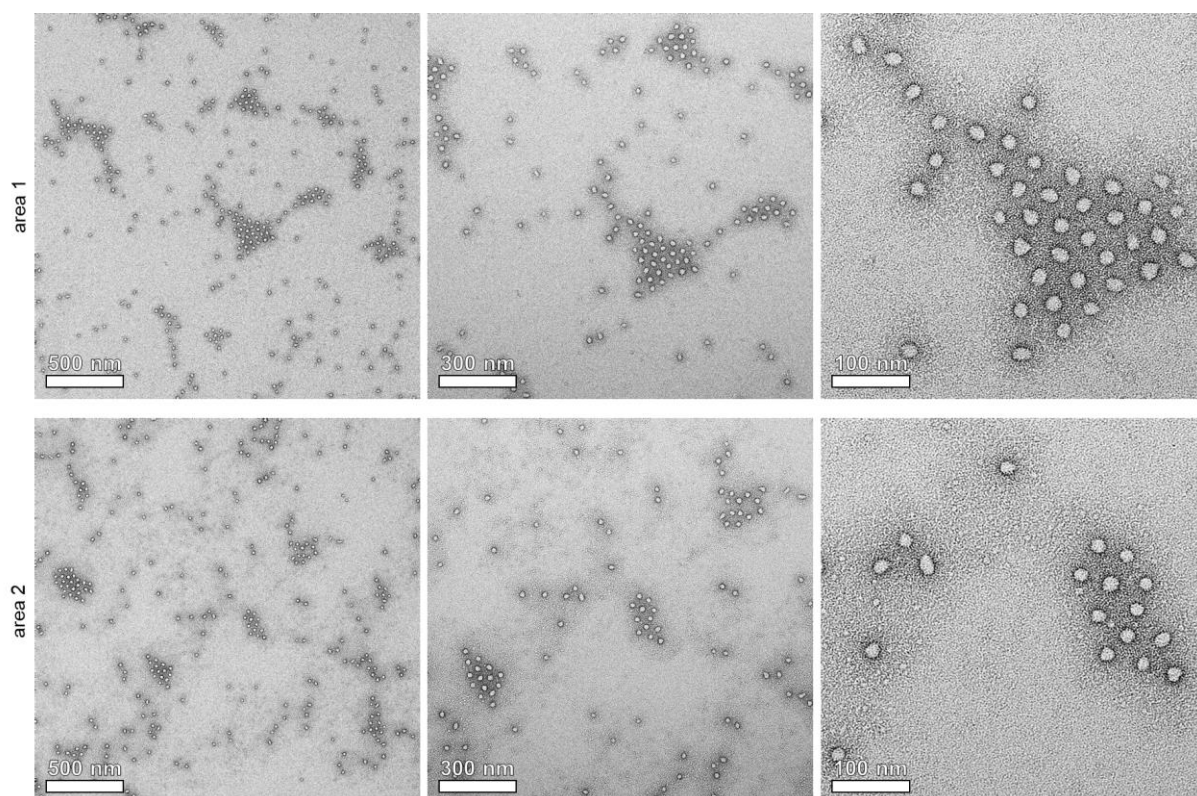


**Figure S12-2:** TEM images of uranyl acetate-stained polymer micelles self-assembled from a solution of PMMA<sub>114</sub>-*b*-PSPMA-Na<sub>126</sub> in 10 mM KNO<sub>3</sub>.

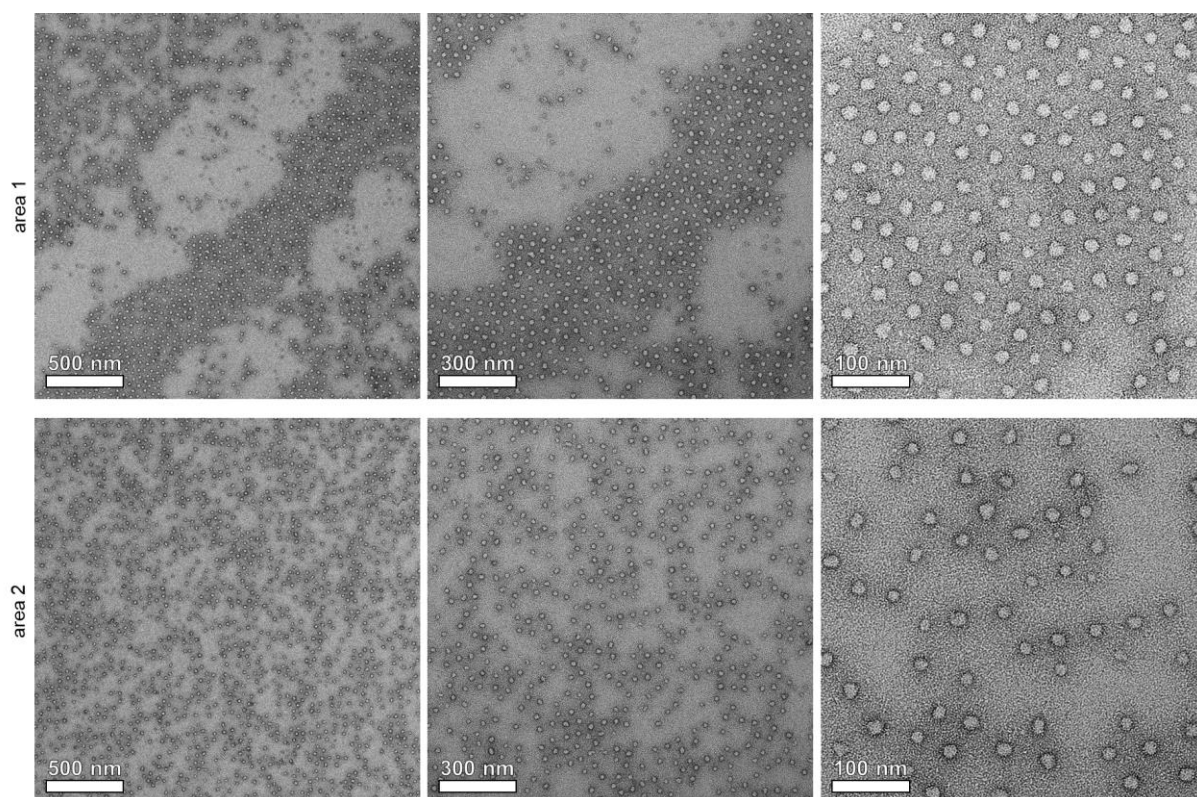


**Figure S12-3:** TEM images of uranyl acetate-stained polymer micelles self-assembled from a solution of PMMA<sub>114</sub>-*b*-PSPMA-TMA<sub>126</sub> in 10 mM KNO<sub>3</sub>.

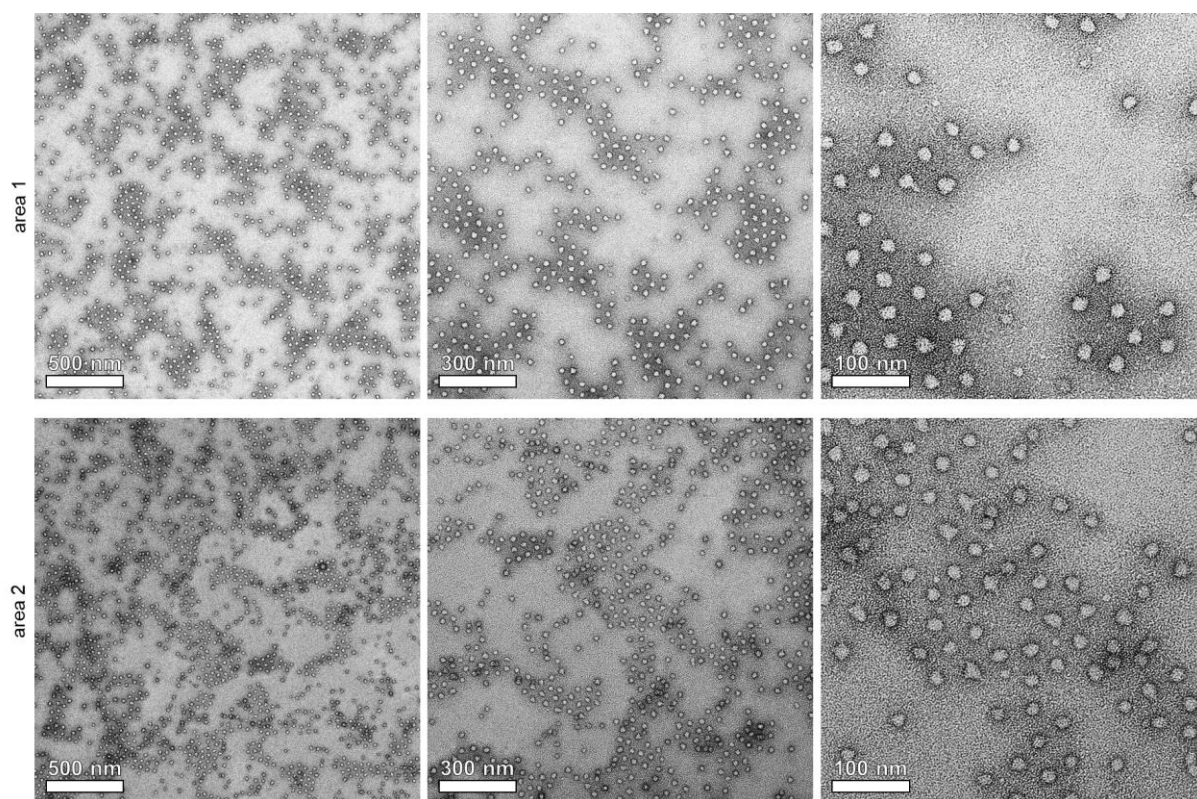




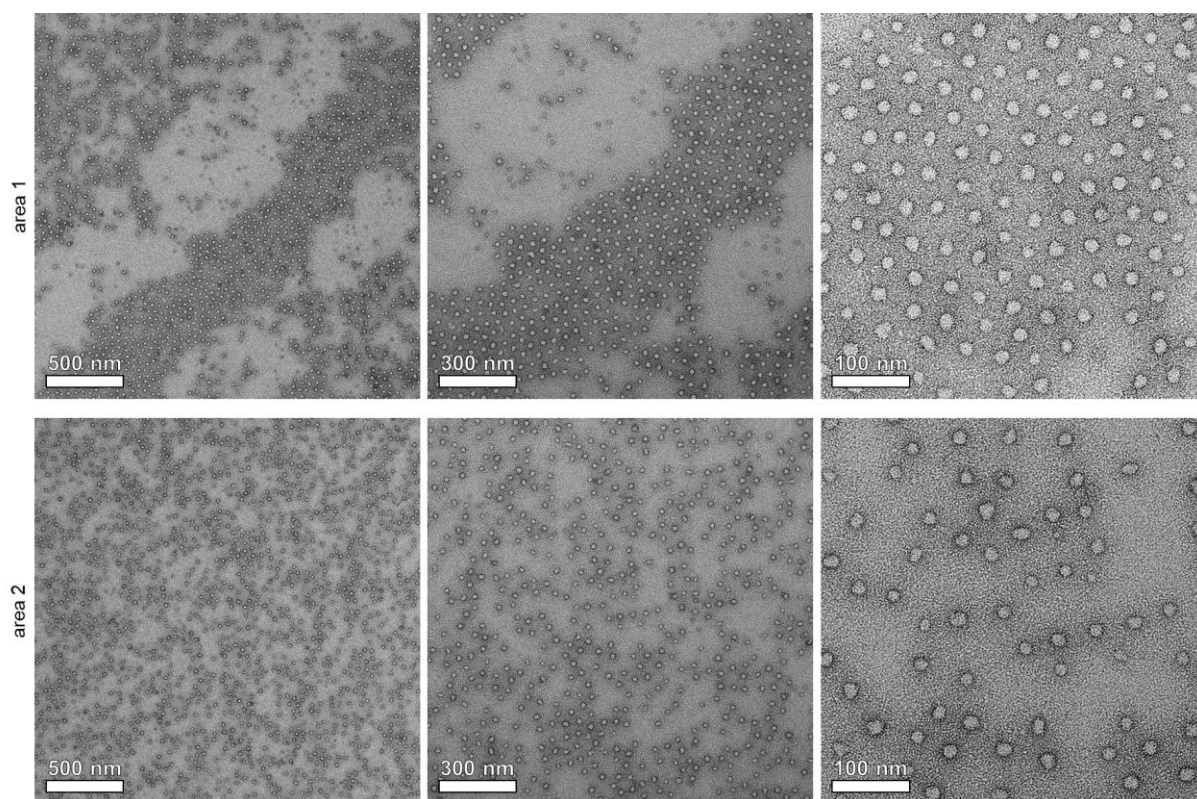
**Figure S12-4:** TEM images of uranyl acetate-stained polymer micelles self-assembled from a solution of PMMA<sub>114</sub>-*b*-PSPMA-TEA<sub>126</sub> in 10 mM KNO<sub>3</sub>.



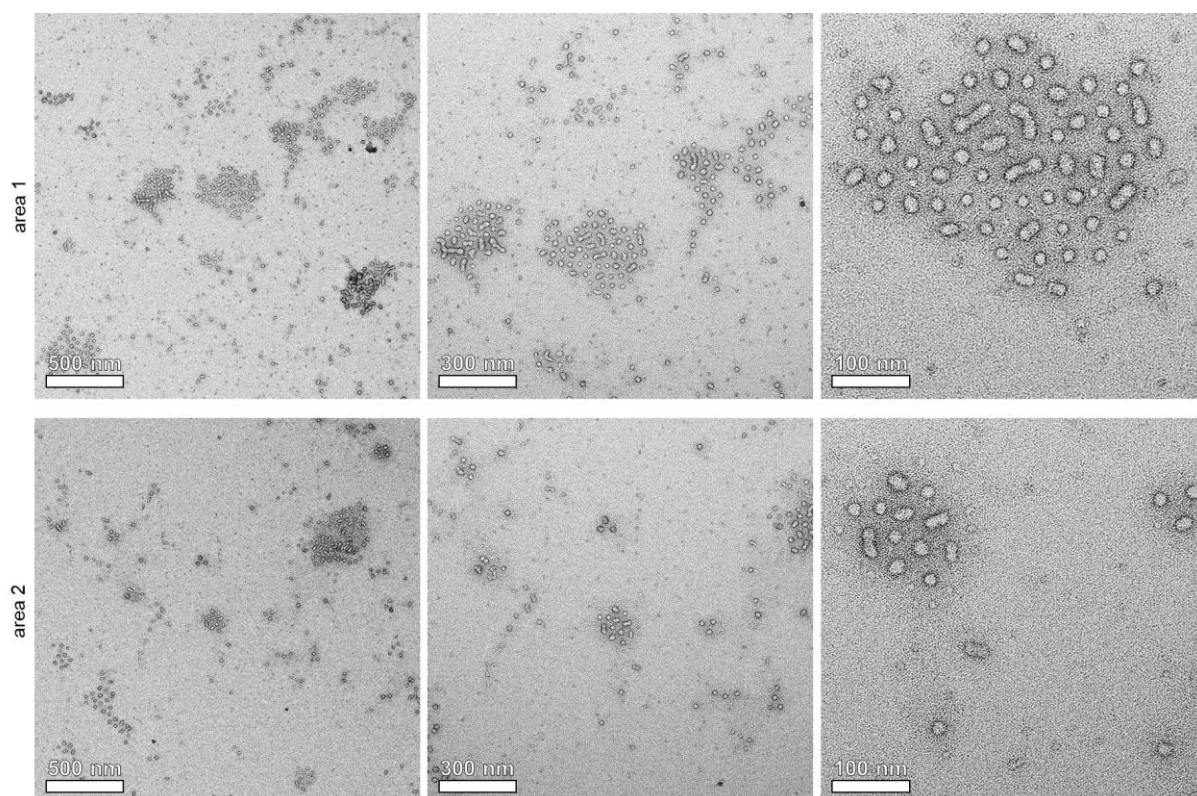
**Figure S12-5:** TEM images of uranyl acetate-stained polymer micelles self-assembled from a solution of PMMA<sub>114</sub>-*b*-PSPMA-TBA<sub>126</sub> in 10 mM KNO<sub>3</sub>.



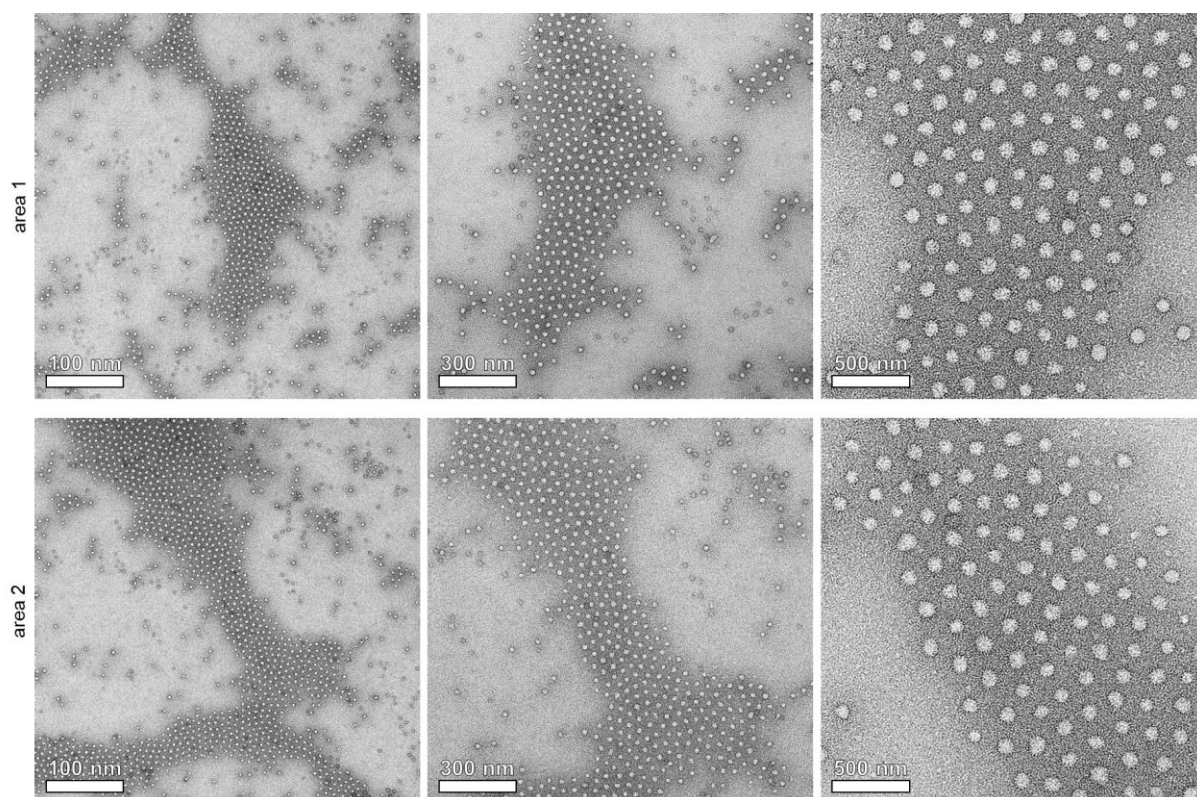
**Figure S12-6:** TEM images of uranyl acetate-stained polymer micelles self-assembled from a solution of PMMA<sub>114</sub>-*b*-PSPMA-EMIM<sub>126</sub> in 10 mM KNO<sub>3</sub>.



**Figure S12-7:** TEM images of uranyl acetate-stained polymer micelles self-assembled from a solution of PMMA<sub>114</sub>-*b*-PSPMA-PhTEA<sub>126</sub> in 10 mM KNO<sub>3</sub>.

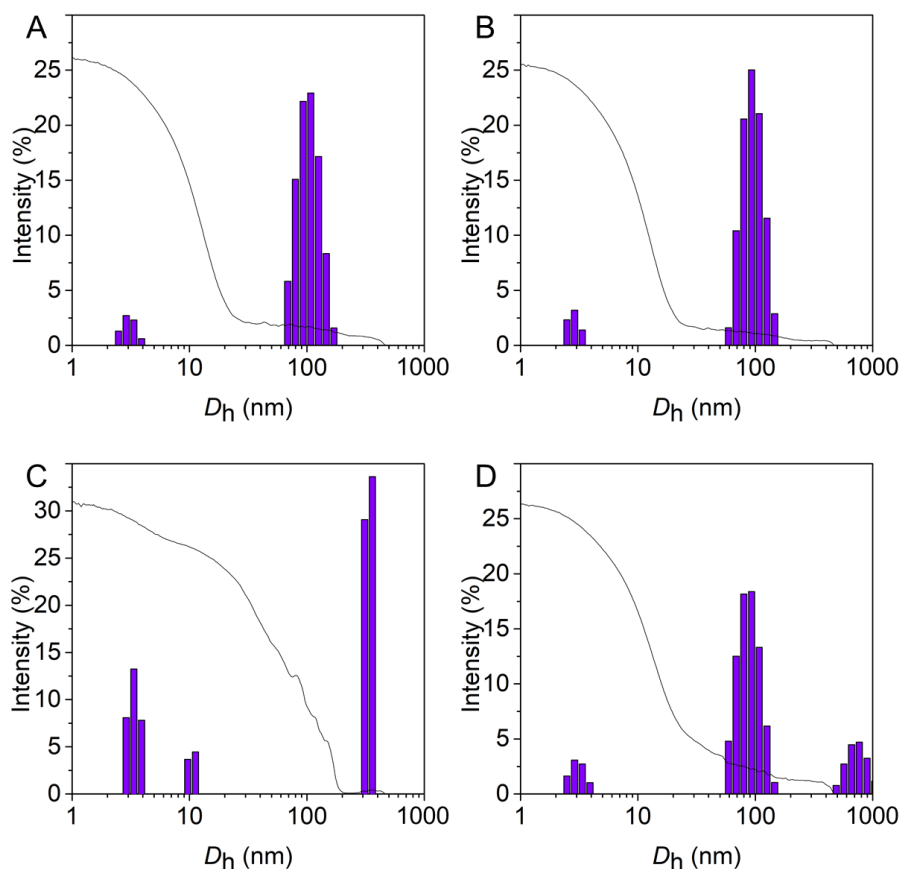


**Figure S12-8:** TEM images of uranyl acetate-stained polymer micelles self-assembled from a solution of PMMA<sub>114</sub>-*b*-PSPMA-FPhTMA<sub>126</sub> in 10 mM KNO<sub>3</sub>.



**Figure S12-9:** TEM images of uranyl acetate-stained polymer micelles self-assembled from a solution of PMMA<sub>114</sub>-*b*-PSPMA-BTC<sub>126</sub> in 10 mM KNO<sub>3</sub>.

### S13: DLS on block copolymers in methanol



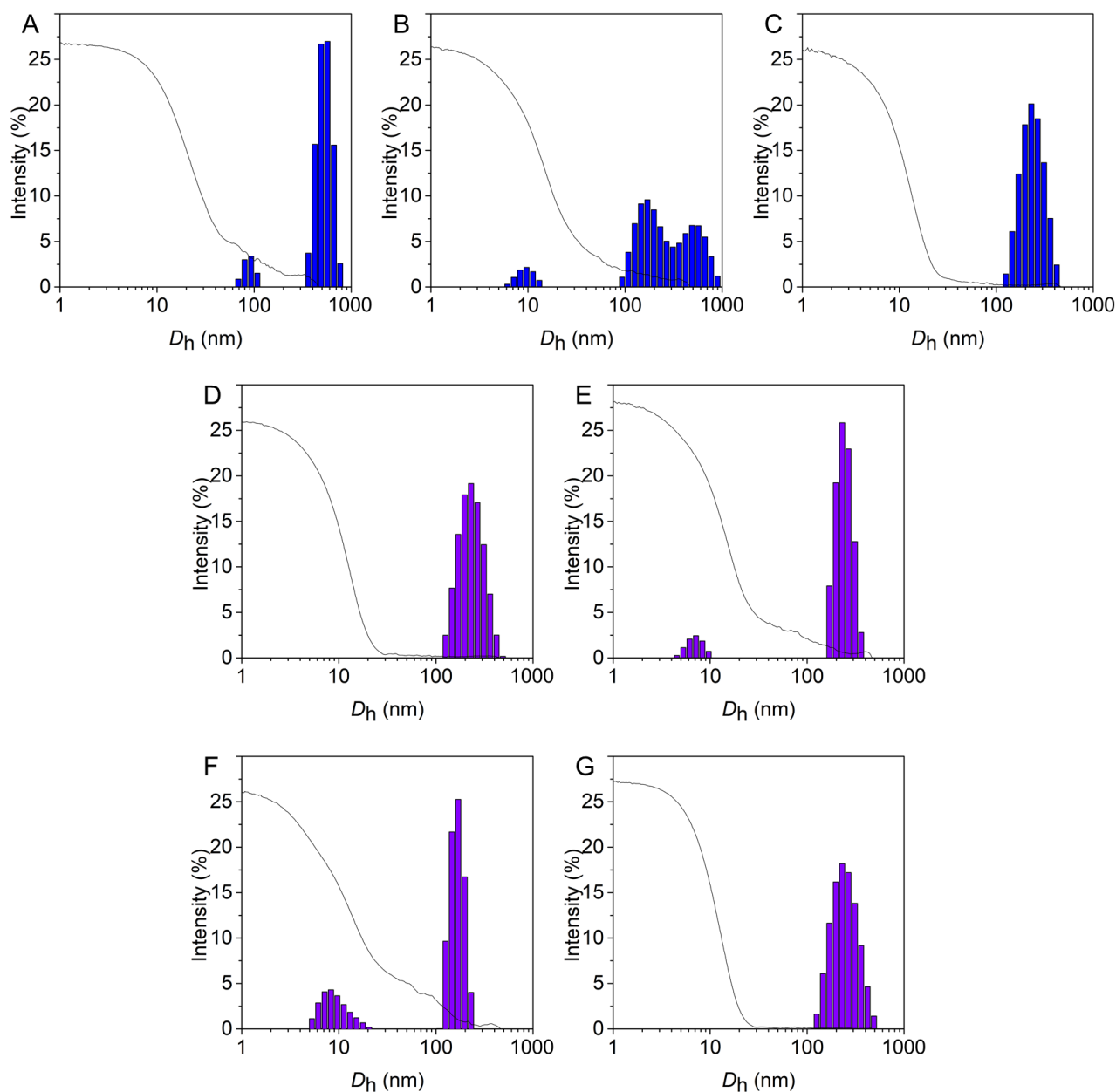
**Figure S13:** Comparative DLS intensity plots (bars) and correlograms (solid lines) of polymer micelles self-assembled from (A) PMMA<sub>114</sub>-*b*-PSPMA-EMIM<sub>126</sub>, (B) PMMA<sub>114</sub>-*b*-PSPMA-PhTEA<sub>126</sub>, (C) PMMA<sub>114</sub>-*b*-PSPMA-FPhTMA<sub>126</sub> and (D) PMMA<sub>114</sub>-*b*-PSPMA-BTC<sub>126</sub> in methanol.

**Table S7:** Characteristics of the micelles obtained after self-assembly of the PMMA<sub>114</sub>-*b*-PSPMA-R<sub>116</sub> BCPs in methanol.

	$D_h$ (nm)	PDI
PMMA <sub>114</sub> - <i>b</i> -PSPMA-EMIM <sub>126</sub>	107 ± 4	0.336 ± 0.006
PMMA <sub>114</sub> - <i>b</i> -PSPMA-PhTEA <sub>126</sub>	95 ± 4	0.341 ± 0.021
PMMA <sub>114</sub> - <i>b</i> -PSPMA- FPhTMA <sub>126</sub>	1417 ± 386	n.a.
PMMA <sub>114</sub> - <i>b</i> -PSPMA-BTC <sub>126</sub>	204 ± 90	0.507 ± 0.042

Determined by DLS at 25 °C on 1 g L<sup>-1</sup> solutions in methanol and measured in triplicate.

## S14: DLS on block copolymers in ethanol



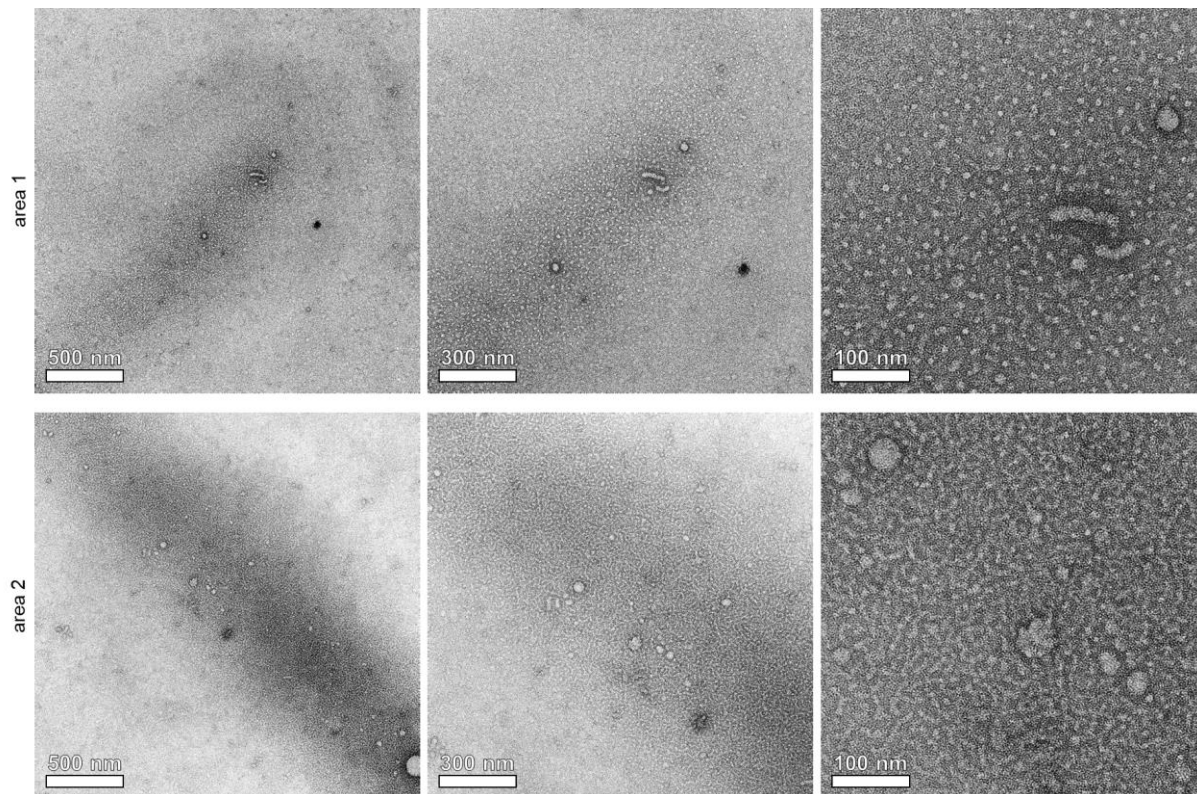
**Figure S14:** Comparative DLS intensity plots (bars) and correlograms (solid lines) of polymer micelles self-assembled from (A)  $\text{PMMA}_{114}\text{-}b\text{-PSPMA-TMA}_{126}$ , (B)  $\text{PMMA}_{114}\text{-}b\text{-PSPMA-TEA}_{126}$ , (C)  $\text{PMMA}_{114}\text{-}b\text{-PSPMA-TBA}_{126}$  (D)  $\text{PMMA}_{114}\text{-}b\text{-PSPMA-EMIM}_{126}$ , (E)  $\text{PMMA}_{114}\text{-}b\text{-PSPMA-PhTEA}_{126}$ , (F)  $\text{PMMA}_{114}\text{-}b\text{-PSPMA-FPhTMA}_{126}$  and (G)  $\text{PMMA}_{114}\text{-}b\text{-PSPMA-BTC}_{126}$  in ethanol.

**Table S8:** Characteristics of the micelles obtained after self-assembly of the PMMA<sub>114</sub>-*b*-PSPMA-R<sub>116</sub> BCPs in ethanol.

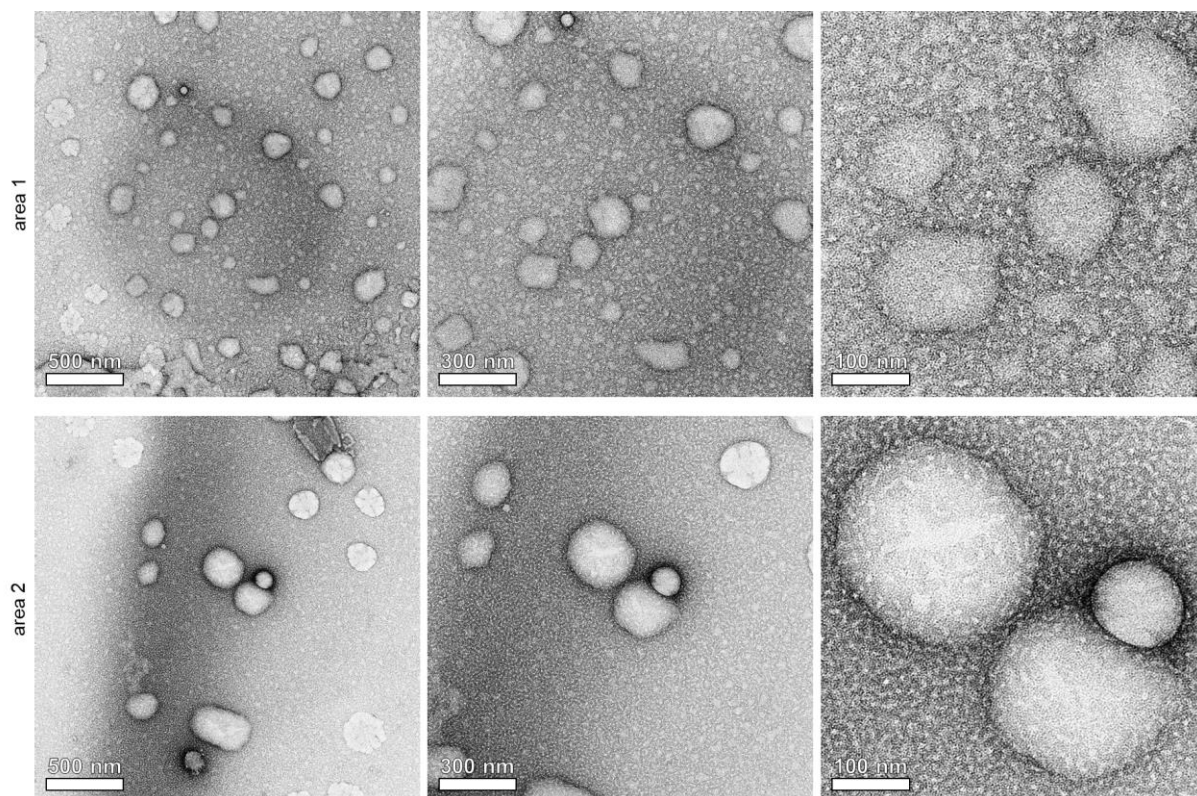
	$D_h$ (nm)	PDI
PMMA <sub>114</sub> - <i>b</i> -PSPMA-TMA <sub>126</sub>	1001 ± 139	0.736 ± 0.144
PMMA <sub>114</sub> - <i>b</i> -PSPMA-TEA <sub>126</sub>	337 ± 49	0.616 ± 0.056
PMMA <sub>114</sub> - <i>b</i> -PSPMA-TBA <sub>126</sub>	237 ± 4	0.377 ± 0.059
PMMA <sub>114</sub> - <i>b</i> -PSPMA-EMIM <sub>126</sub>	212 ± 15	0.339 ± 0.051
PMMA <sub>114</sub> - <i>b</i> -PSPMA-PhTEA <sub>126</sub>	358 ± 38	0.466 ± 0.027
PMMA <sub>114</sub> - <i>b</i> -PSPMA- FPhTMA <sub>126</sub>	449 ± 3	0.611 ± 0.106
PMMA <sub>114</sub> - <i>b</i> -PSPMA-BTC <sub>126</sub>	232 ± 1	0.050 ± 0.048

Determined by DLS at 25 °C on 1 g L<sup>-1</sup> solutions in ethanol and measured in triplicate.

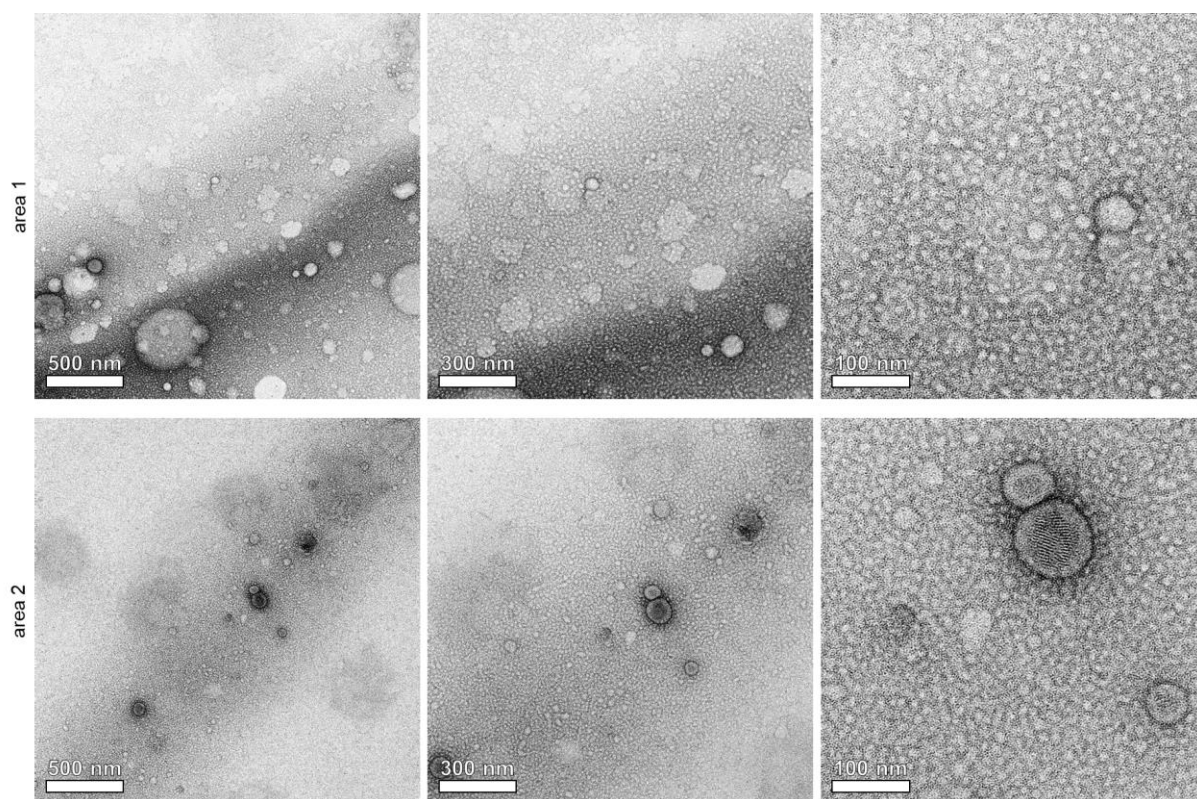
**S15: TEM on block copolymers in methanol**



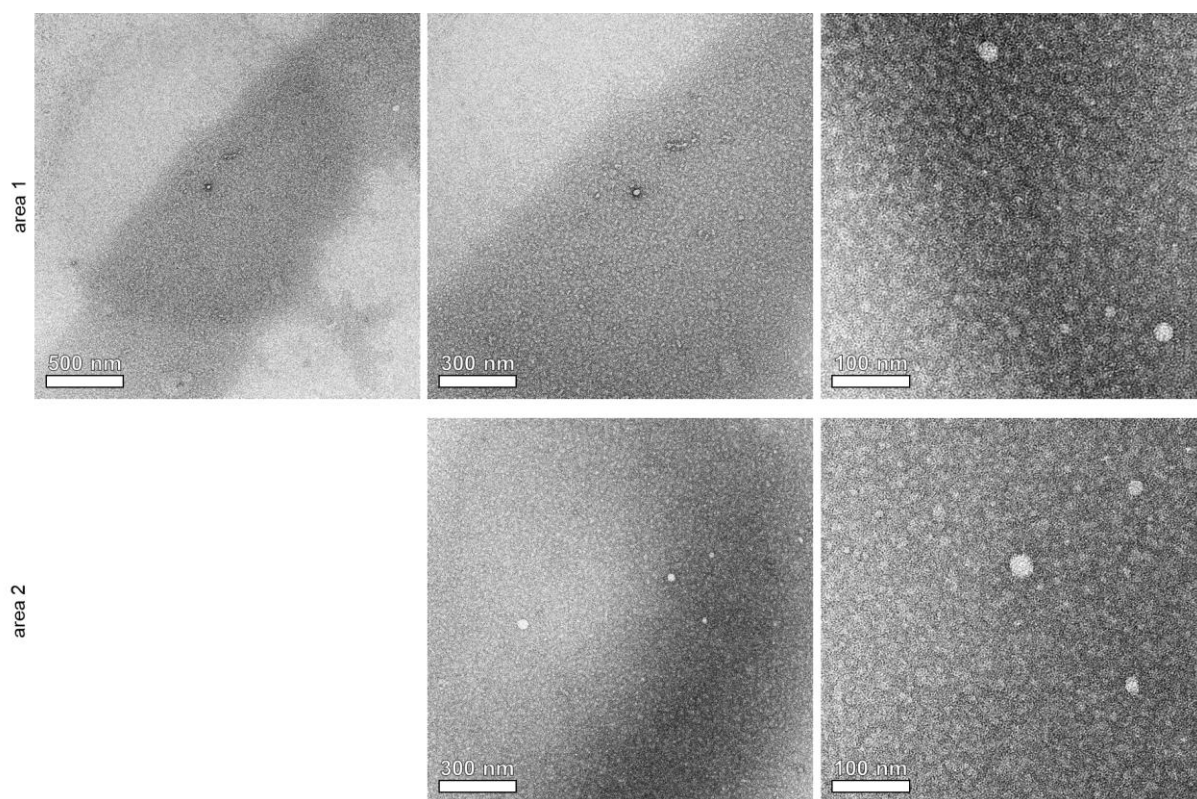
**Figure S15-1:** TEM images of uranyl acetate-stained polymer micelles self-assembled from a solution of PMMA<sub>114</sub>-*b*-PSPMA-EMIM<sub>126</sub> in methanol.



**Figure S15-2:** TEM images of uranyl acetate-stained polymer micelles self-assembled from a solution of PMMA<sub>114</sub>-*b*-PSPMA-PhTEA<sub>126</sub> in methanol.



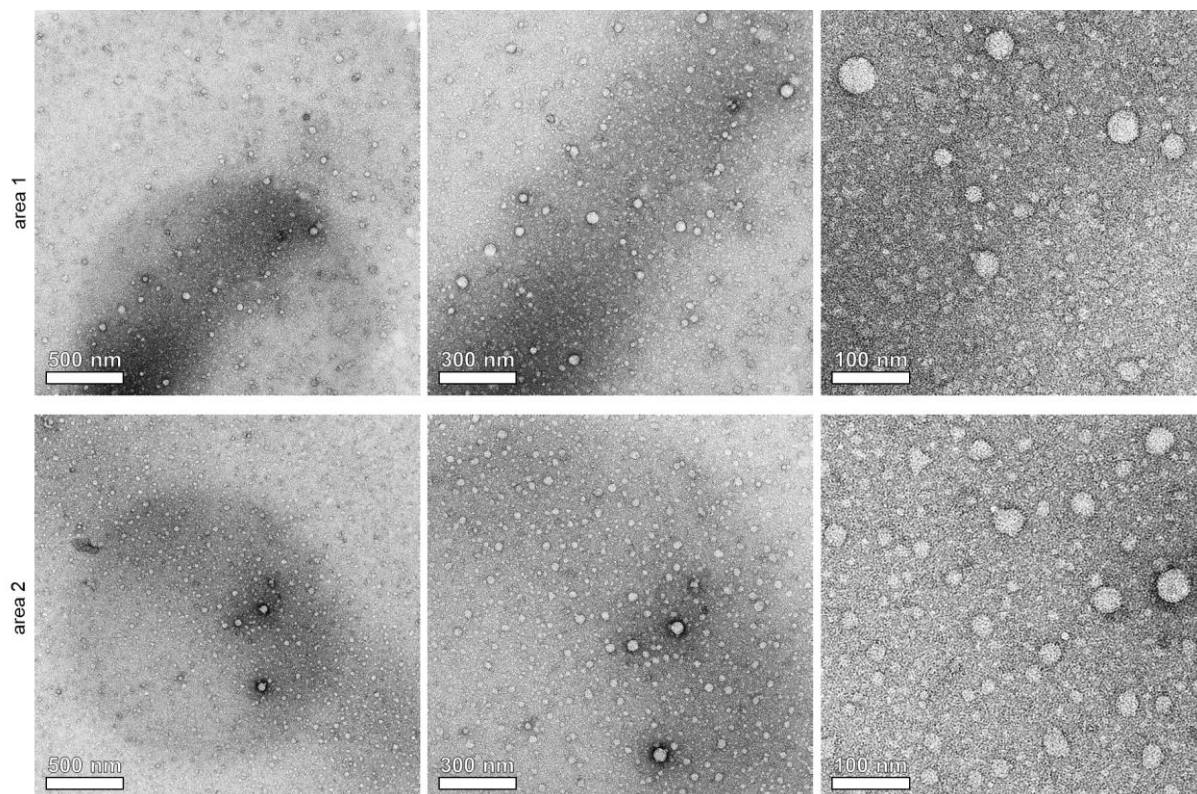
**Figure S15-3:** TEM images of uranyl acetate-stained polymer micelles self-assembled from a solution of PMMA<sub>114</sub>-*b*-PSPMA-FPhTMA<sub>126</sub> in methanol.



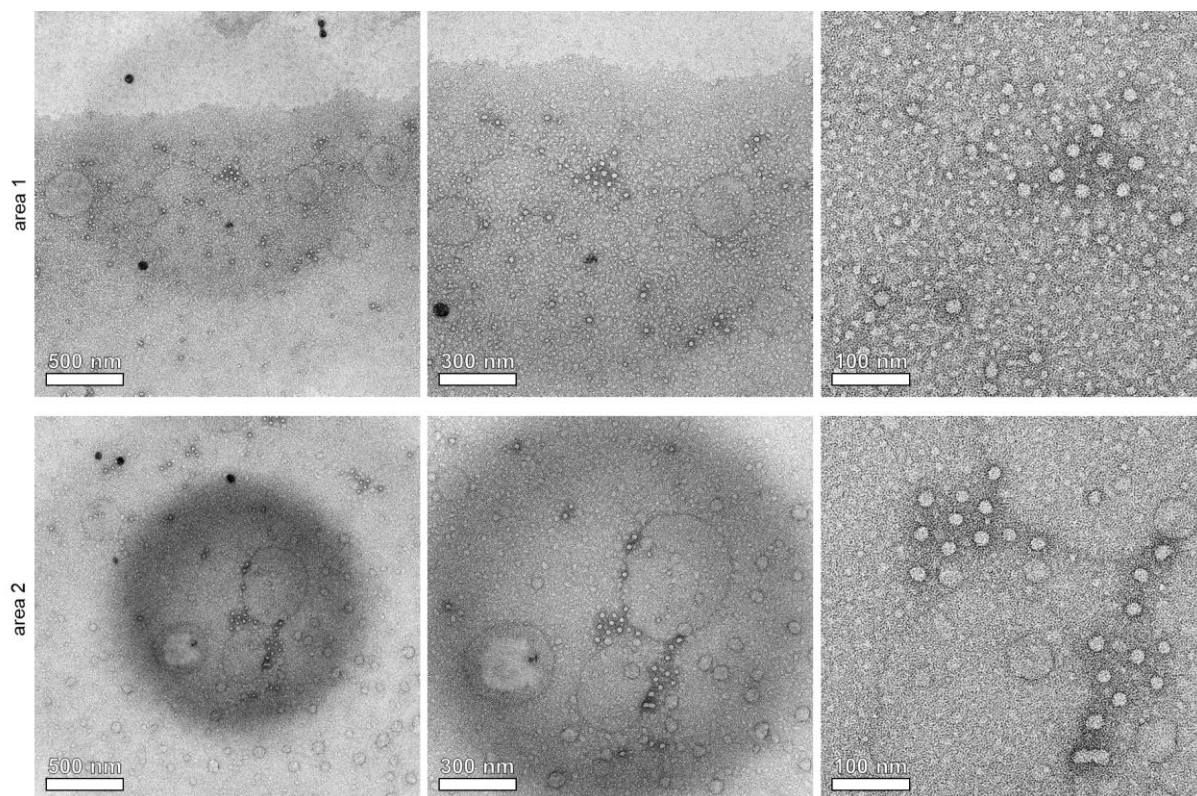
**Figure S15-4:** TEM images of uranyl acetate-stained polymer micelles self-assembled from a solution of PMMA<sub>114</sub>-*b*-PSPMA-BTC<sub>126</sub> in methanol.



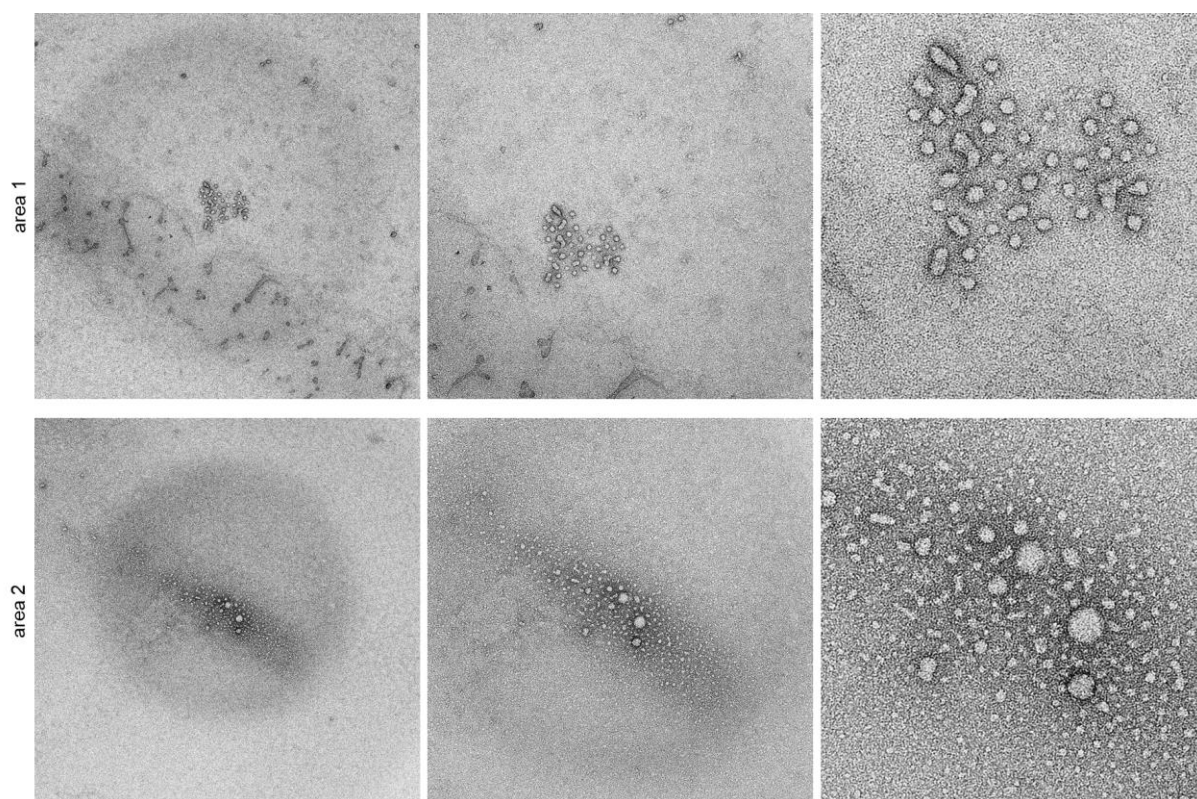
**S16: TEM on block copolymers in ethanol**



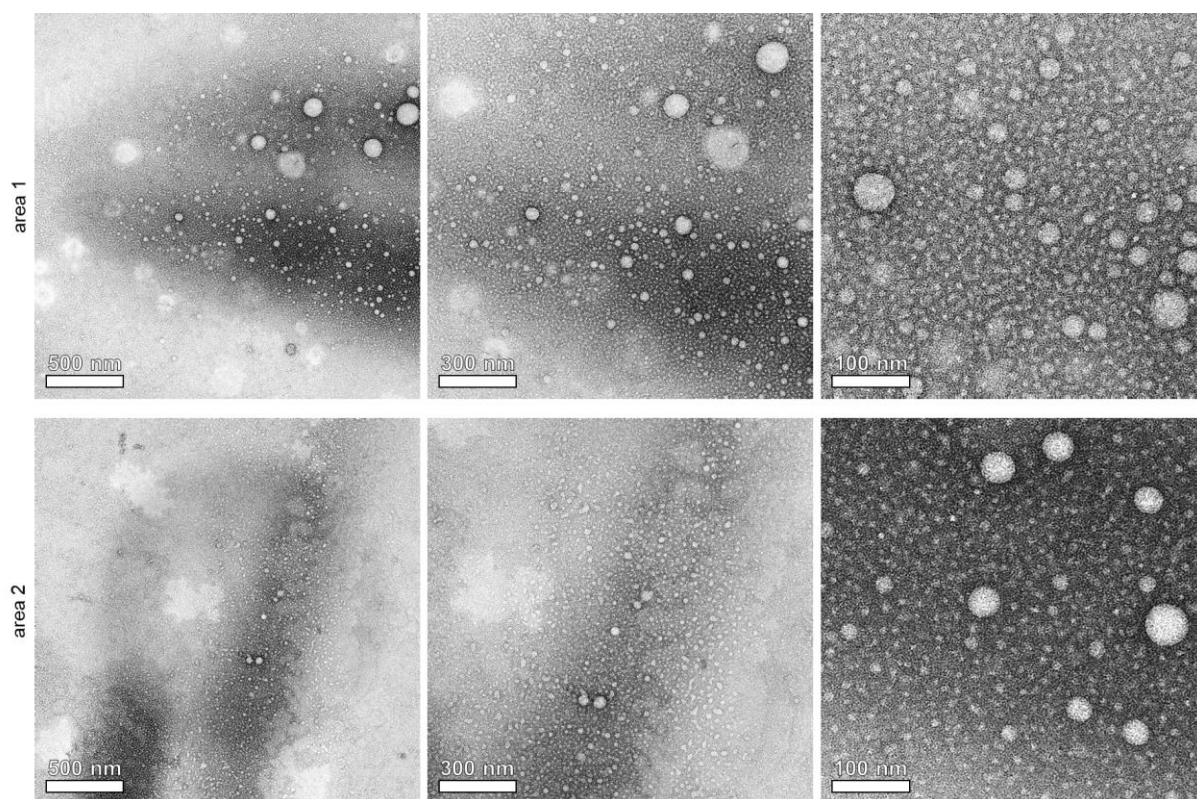
**Figure S16-1:** TEM images of uranyl acetate-stained polymer micelles self-assembled from a solution of PMMA<sub>114</sub>-*b*-PSPMA-TMA<sub>126</sub> in ethanol.



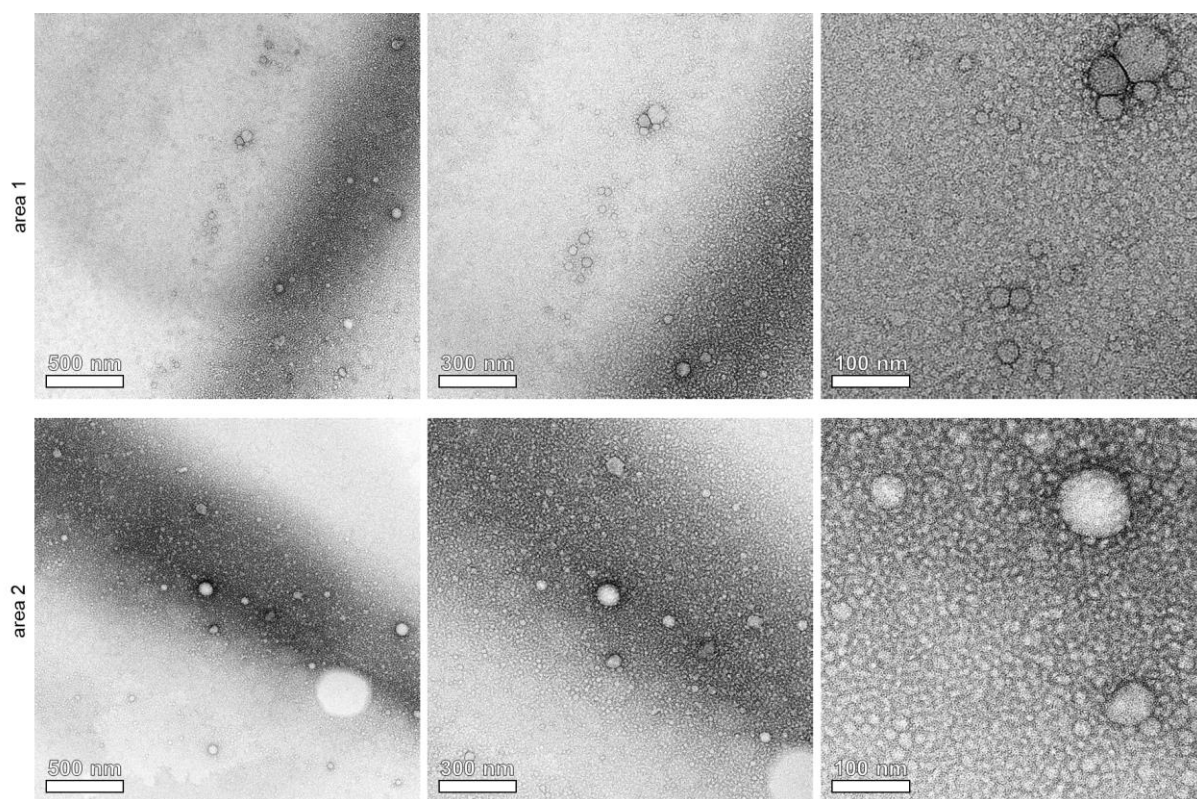
**Figure S16-2:** TEM images of uranyl acetate-stained polymer micelles self-assembled from a solution of PMMA<sub>114</sub>-*b*-PSPMA-TEA<sub>126</sub> in ethanol.



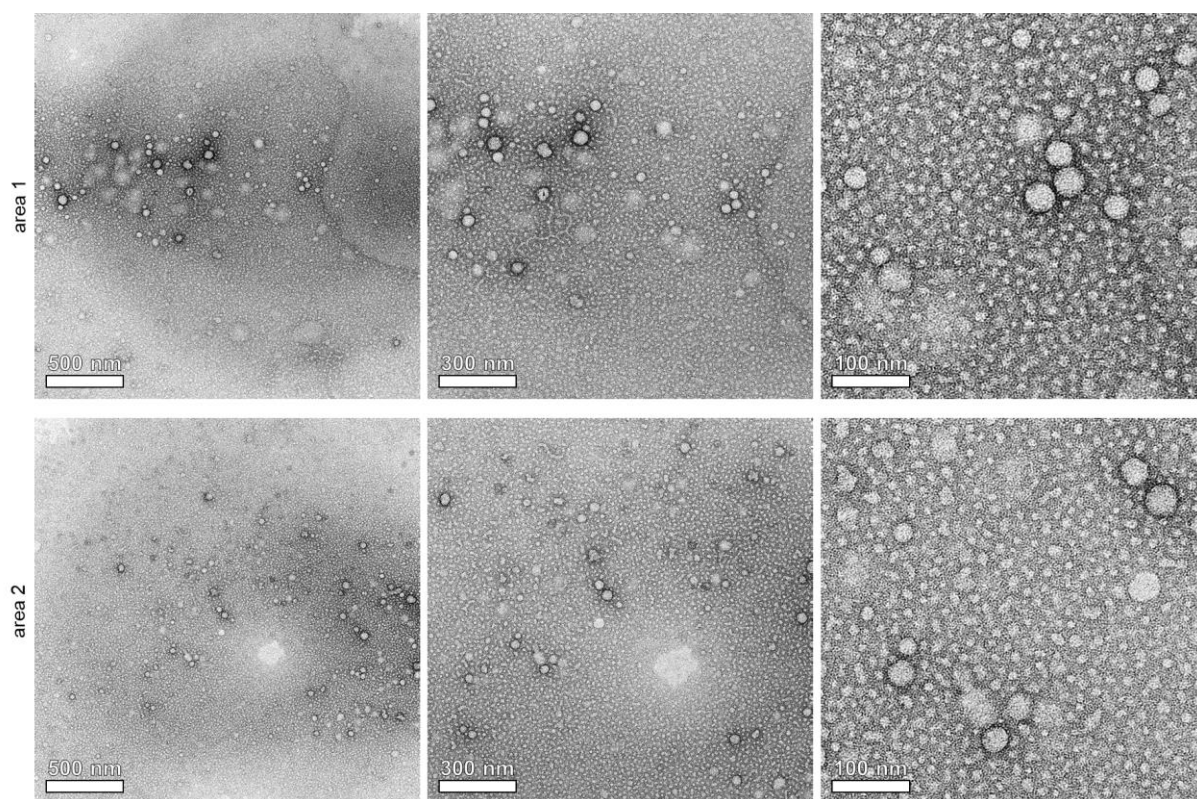
**Figure S16-3:** TEM images of uranyl acetate-stained polymer micelles self-assembled from a solution of PMMA<sub>114</sub>-*b*-PSPMA-TBA<sub>126</sub> in ethanol.



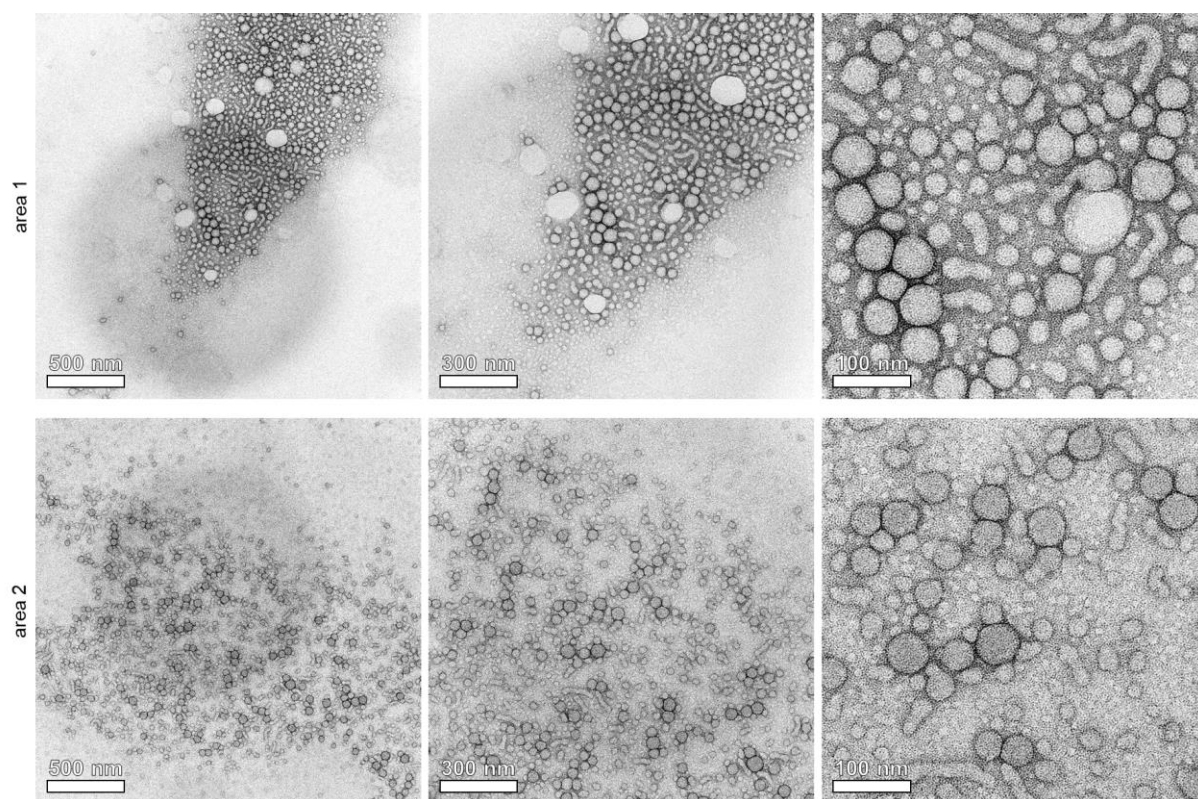
**Figure S16-4:** TEM images of uranyl acetate-stained polymer micelles self-assembled from a solution of PMMA<sub>114</sub>-*b*-PSPMA-EMIM<sub>126</sub> in ethanol.



**Figure S16-5:** TEM images of uranyl acetate-stained polymer micelles self-assembled from a solution of PMMA<sub>114</sub>-*b*-PSPMA-PhTEA<sub>126</sub> in ethanol.



**Figure S16-6:** TEM images of uranyl acetate-stained polymer micelles self-assembled from a solution of PMMA<sub>114</sub>-*b*-PSPMA-FPhTMA<sub>126</sub> in ethanol.



**Figure S16-7:** TEM images of uranyl acetate-stained polymer micelles self-assembled from a solution of  $\text{PMMA}_{114}\text{-}b\text{-PSPMA-BTC}_{126}$  in ethanol.

## Supporting References

[1] *Polym. Chem.* **2019**, 10, 6109