

Electronic Supplementary Information

Effect of the Zwitterion Structure on the Thermo-responsive Behaviour of Poly(Sulfobetaine Methacrylate)s

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Methods

Elemental analysis was carried out using a Vario ELIII microanalyzer (Elementar Analysensysteme, Hanau/Germany). High resolution mass spectra (HR-MS) were recorded with a Thermo Scientific ESI-Q-TOFmicro (Quadrupol – Time of Flight). Electrospray ionisation (ESI) and water as solvent was chosen as method. FT-IR spectra were recorded in a N₂ purged atmosphere with a Thermo Nicolet Nexus FT-IR spectrometer equipped with an attenuated total reflection (ATR) Smart Endurance element. Ultraviolet-visible (UV-vis) absorption spectra were recorded by a UV/Vis/NIR Spectrometer Lambda instrument (Perkin Elmer). Fluorescence spectra were recorded using a Luminescence Spectrometer LS 50 B (Perkin Elmer). Optical silica cuvettes with an optical path length $d = 1$ cm were used. Thermogravimetric analysis (TGA) was conducted under N₂ atmosphere using a Netzsch TG 209 F1 apparatus, in the temperature range from 25 °C to 900 °C with a heating rate of 10 K·min⁻¹. Differential scanning calorimetry (DSC) measurements were performed in the temperature range from 25 to 250 °C with a Mettler Toledo DSC 822e at N₂ atmosphere. Heating and cooling rates of 10 K·min⁻¹ were applied during the first and third cycles, while rates of 30 K·min⁻¹, were used during the second cycle.

¹H and ¹³C NMR spectra, ¹H-¹H-Correlation Spectra (COSY), and 1H-¹³C-Hetero-nuclear Multiple Quantum Coherence spectra (HMQC) were recorded with a Bruker Avance 300 spectrometer (300 MHz and 75 MHz, respectively) or with a Bruker Avance 400 spectrometer (400 MHz and 125 MHz, respectively) at ambient temperature in deuterated solvents. ¹³C NMR spectra were recorded in ¹H-broad band decoupling mode and in Attached Proton Test (APT) mode, respectively. Solvent signals were used as internal shift references.

General chemicals and solvents.

4,4'-azobis (4-cyanopentanoic acid) (V501, Wako, 84 %) was crystallised from methanol. 2-(Dimethylamino)ethyl methacrylate (Sigma Aldrich, 98 %), methyl methacrylate (MMA, Sigma Aldrich, 99 %), 2-(piperidin-1-yl)ethan-1-ol (Alfa Aesar, 99 %), 2-morpholinoethan-1-ol (Alfa Aesar, 99 %), 3-(dimethylamino)propan-1-ol (Merck, 98 %), 1,3-propanesultone (TCI, 99 %), 1,4-butane sultone (Acros, 99+ %), 4-methoxyphenol (MEHQ, Acros, 99.9 %), hydroquinone (Fluka, >99 %), acetonitrile (Sigma Aldrich, 99.8 %), diethyl ether (ChemSolute, 99.8 %), methanol (Chemievertrieb Magdeburg, 99 %), nitrobenzene (Fluka, 99 %), trifluoroethanol (TFE, Roth, 99.8 %), anhydrous potassium phosphate (Amresco, 99.9 %), sodium chloride (NaCl, ChemSolute, 99 %), sodium hydroxide (ChemSolute, 98 %), D₂O (Armar, 99.9 atom% D), and molecular sieve 4 Å (Roth) were used as received.

Synthesis of the intermediate methacrylates bearing tertiary amine moieties.

The synthesis of the intermediates was adapted from a patent procedure [Process for preparing (meth)acrylic esters of N,N-substituted amino alcohols; inventors: V. Bette, H. Bergmann, J. Petzoldt and F. Höfer, US 20120077977 A1, by BASF SE]. As described in the patent, the N,N-substituted amino alcohols were reacted with MMA (≥ 400 mol% based on amino alcohol) in the presence of freshly ground anhydrous K₃PO₄ (2.0 mol% based on amino alcohol) as transesterification catalyst, and of hydroquinone monomethyl ether as polymerisation inhibitor (350 ppm based on MMA). In order to push the transesterification to completion, the condensed azeotrope of MMA and methanol was treated with freshly activated (either 200° C at 10⁻³ mbar, or 200 °C in streaming dry nitrogen for 2 h) molecular sieve LTA 4Å (2 mm spherules) to selectively remove the methanol formed. The apparatus consisted of a Schlenk-type round-bottom flask connected to a Soxhlet extractor topped with a Dimroth condenser. After charging the flask with all starting materials and filling the Soxhlet extractor with molecular sieves (covering the entrance of the siphon with a swab of cotton),

the set-up was exposed to reduced pressure (ca. 300 mbar). Subsequently, the mixture was heated to reflux. Using the stop-cock of the Schlenk-type flask as a port (covered with a silicone cap), samples were withdrawn to follow the reaction analytically (TLC; eluent ethyl acetate / hexane / triethylamin 6 / 2 / 0.32 v/v/v). After completion (taking about 3 h), the heating mantle was removed and the whole set-up was aerated. The content of the flask was filtrated through a thin layer of Celite which was washed with additional MMA. The combined filtrates were freed from MMA using a rotary evaporator (40°C). The residue was further purified by ball-tube distillation (130°C, ~0.01mbar) to yield the pure methacrylates in about 90% yield as colorless oils.

2-(piperidin-1-yl)ethan-1-ol gave 2-(piperidin-1-yl)ethyl methacrylate.

¹H NMR (300 MHz, CD₂Cl₂, 298 K): δ (ppm) = 1.35 – 1.60 (m, 6H, -CH₂- piperidine (C3, C4, C5)), 1.92 (s, 3H, =C-CH₃), 2.40 (m, 4H, -CH₂-N-CH₂- piperidine (C2, C6)), 2.59 (t, *J* = 6.0 Hz, 2H, -COO-C-CH₂-), 4.20 (t, *J* = 6.0 Hz, 2H, -COO-CH₂-), 5.54 (s, 1H, CH=C-COO- (cis)), 6.05 (s, 1H, CH=C-COO- (trans)).

2-morpholinoethan-1-ol yielded 2-morpholinoethyl methacrylate.

¹H NMR (300 MHz, CD₂Cl₂, 298 K): δ (ppm) = 1.92 (s, 3H, =C-CH₃), 2.48 (m, 4H, -CH₂-N-CH₂- piperidine (C2, C6)), 2.64 (t, *J* = 5.8 Hz, 2H, -COO-C-CH₂-), 3.64 (m, 4H, -CH₂-O-CH₂- piperidine (C3, C5)), 4.24 (t, *J* = 5.8 Hz, 2H, COO-CH₂), 5.56 (s, 1H, CH=C-COO- (cis)), 6.06 (s, 1H, CH=C-COO- (trans)).

3-(dimethylamino)propyl methacrylate was obtained from 3-(dimethylamino) propan-1-ol.

¹H NMR (300 MHz, CDCl₃, 298 K): δ (ppm) = 1.66 – 1.86 (m, 5H, -CH₂-C-N-, =C-CH₃), 2.10 (s, 6H, -N-(CH₃)₂), 2.23 (t, 2H, *J* = 7.4 Hz, -CH₂-N-), 4.07 (t, *J* = 6.5 Hz, 2H, -COO-CH₂-), 5.42 (s, 1H, CH=C-COO- (cis)), 5.97 (s, 1H, CH=C-COO- (trans)).

¹³C NMR (75 MHz, CDCl₃, 298 K): δ (ppm) = 18.3 (=C-CH₃), 27.0 (-COO-C-CH₂-), 45.4 (-N-(CH₃)₂), 56.3 (-CH₂-N-(CH₃)₂), 63.0 (-COO-CH₂-), 125.1 (=CH₂), 136.5 (=C-COO-), 173.5 (-COO-).

The ¹H and ¹³C NMR spectra of the monomers **2 - 8** shown in Figures S3 - S16 display characteristic features for the various building blocks and functional groups incorporated. Apart from the standard signal pattern characteristic for methacrylic esters of primary alcohols (singlets at about 2.0 ppm, 5.8 ppm and 6.2 ppm, and a triplet around 4.5 ppm), the ¹H spectra of the monomer series share as common characteristic features the triplet at ca. 3.0 ppm, attributed to the protons in α-position of the sulfonate moiety, and the multiplets in the range of 3.3 - 3.8 ppm with complex coupling patterns, which are typical for the protons in α-position of ammonium nitrogens bearing three different substituents. Additionally, the modular molecular variations (cf. Scheme 1) result in specific modular differences in the spectra, as exemplified in Figure 2. For instance, the characteristic multiplet of the rather deshielded central methylene group in ammoniopropanesulfonates **1 - 4** at about 2.3 ppm is replaced by two multiplets between 1.8 and 2.0 ppm for the two central methylene groups in ammoniobutanesulfonates **5 - 8**, while the increased separation from the electron withdrawing ammonium nitrogen shifts the triplet of the α-ester protons in monomers **4 - 8** notably to higher fields compared to monomers **1 - 3** and **4 - 7**, namely from about 4.7 to 4.3 ppm. Also, the various cationic moieties (dimethylammonio-, piperidinio- and morpholinioalkane-sulfonates) give rise to specific patterns of their α-ammonium protons for the group **1 / 4 / 5 / 8**, as well as the pairs **2 / 6** and **3 / 7**.

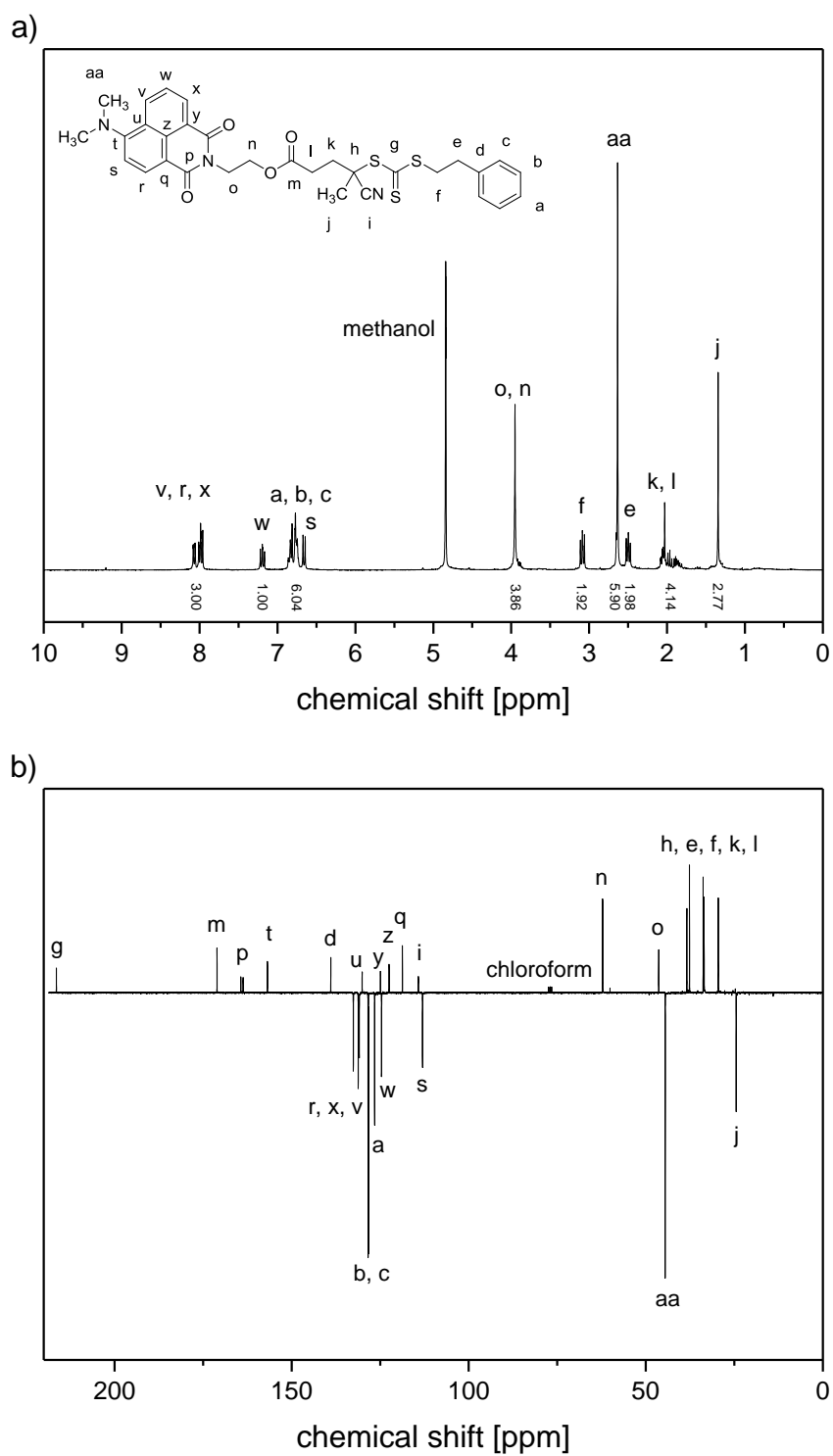


Figure S1. a) ^1H NMR (in CD_3OD) and b) ^{13}C (APT) NMR spectra (in CDCl_3) of **CTA**.

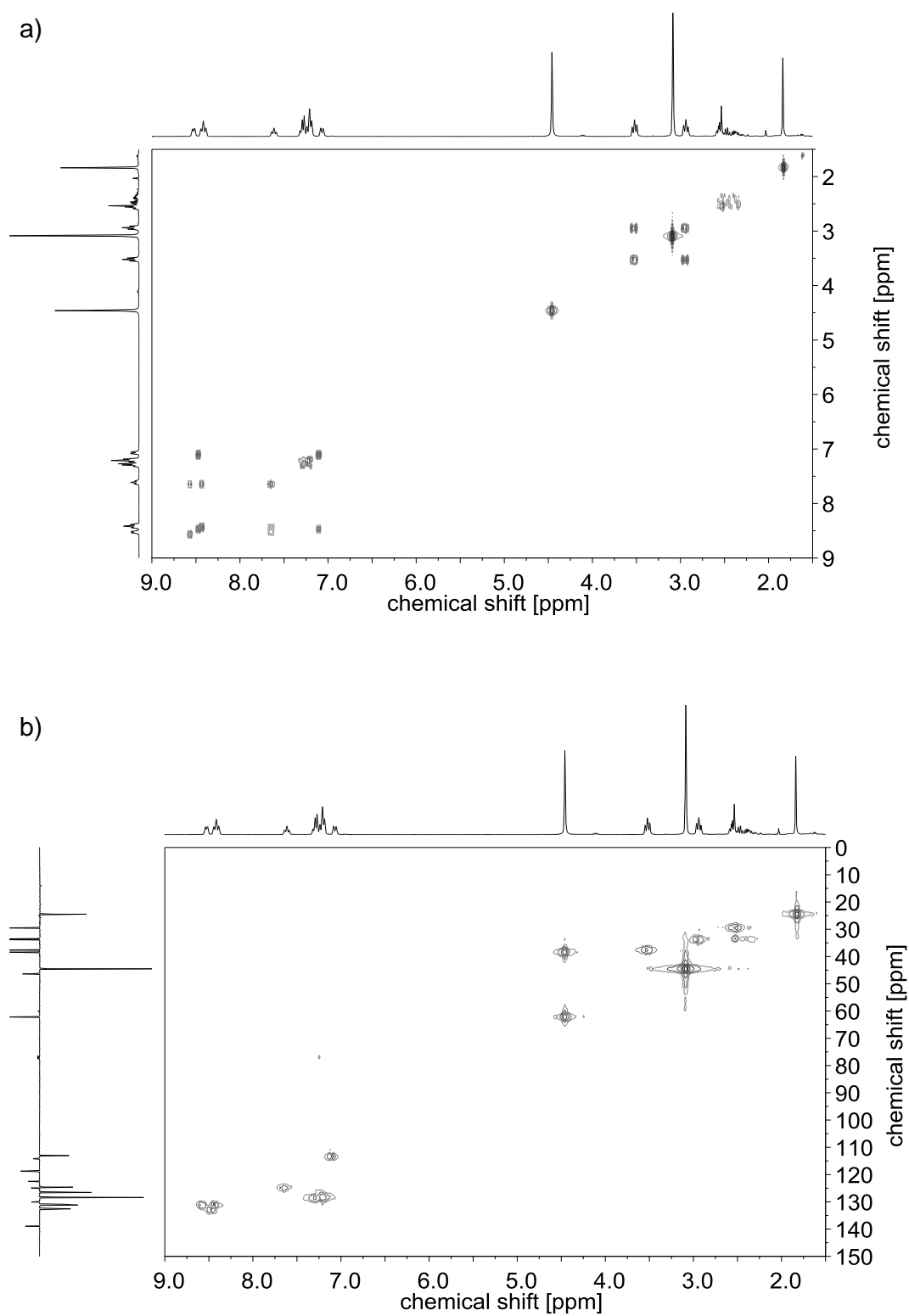


Figure S2. a) ^1H - ^1H -COSY and b) ^1H - ^{13}C -HMQC NMR spectra of **CTA** in CDCl_3 .

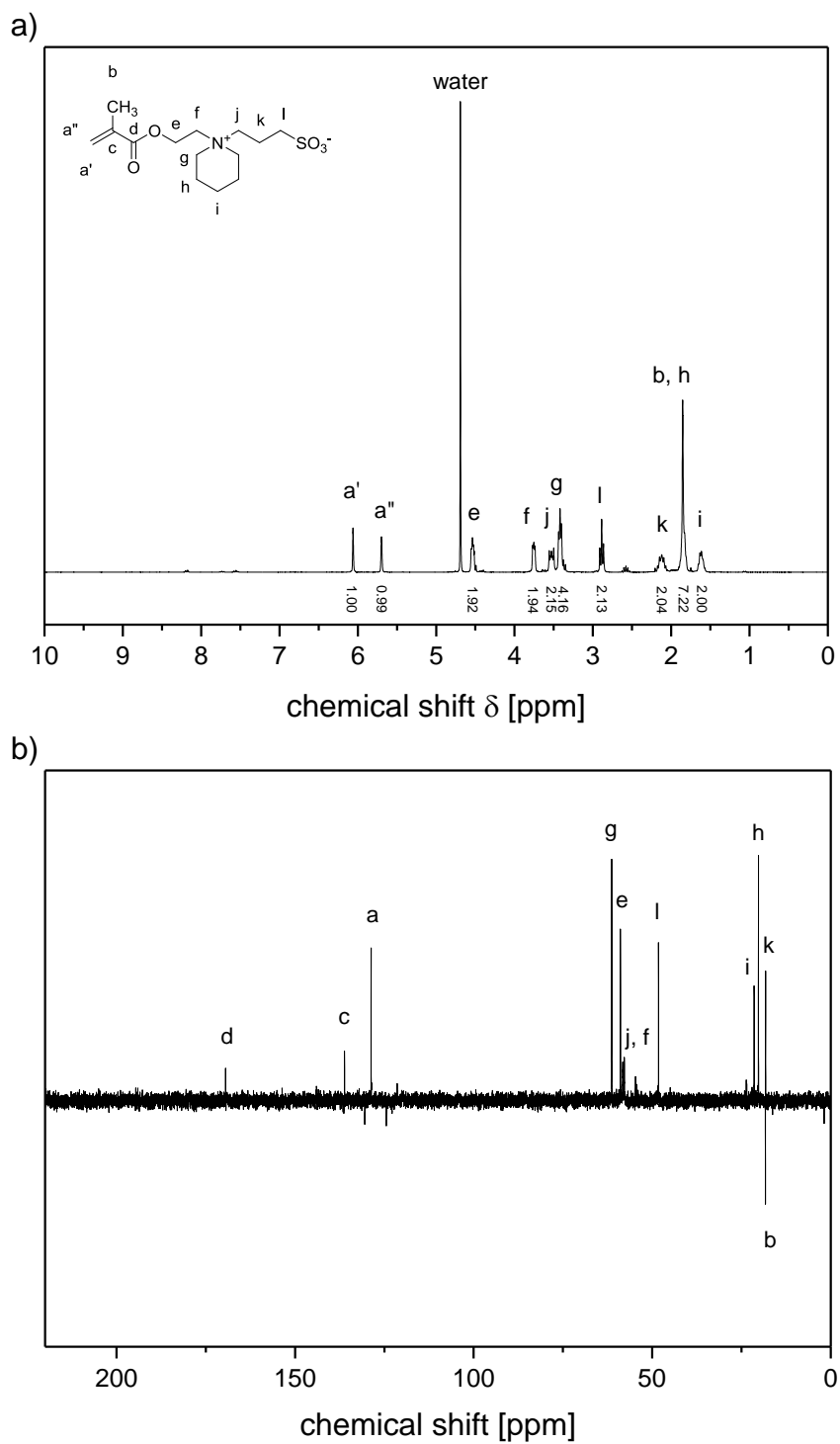
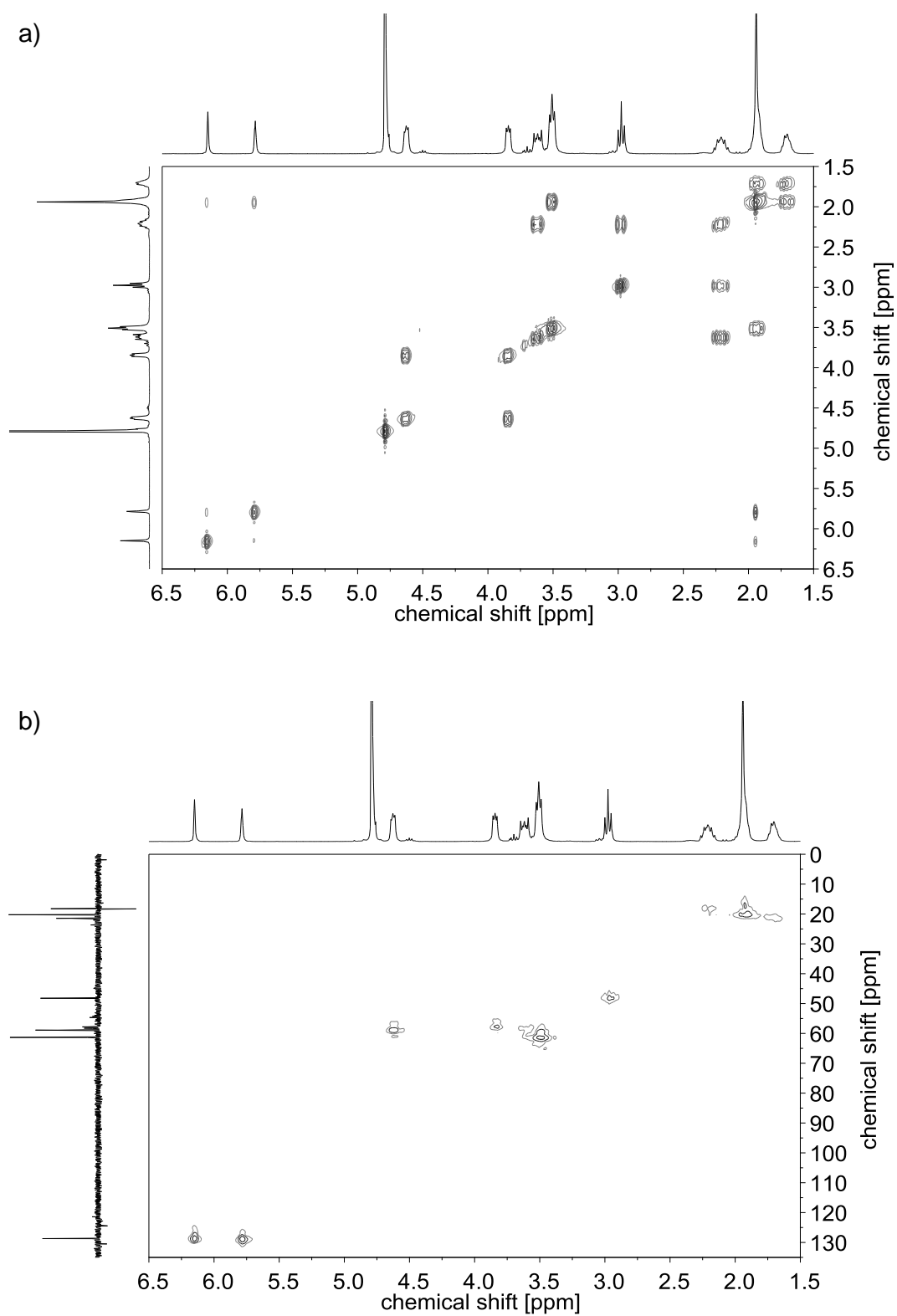


Figure S3. a) ^1H and b) ^{13}C (APT) NMR spectra of **M-2** in D_2O .



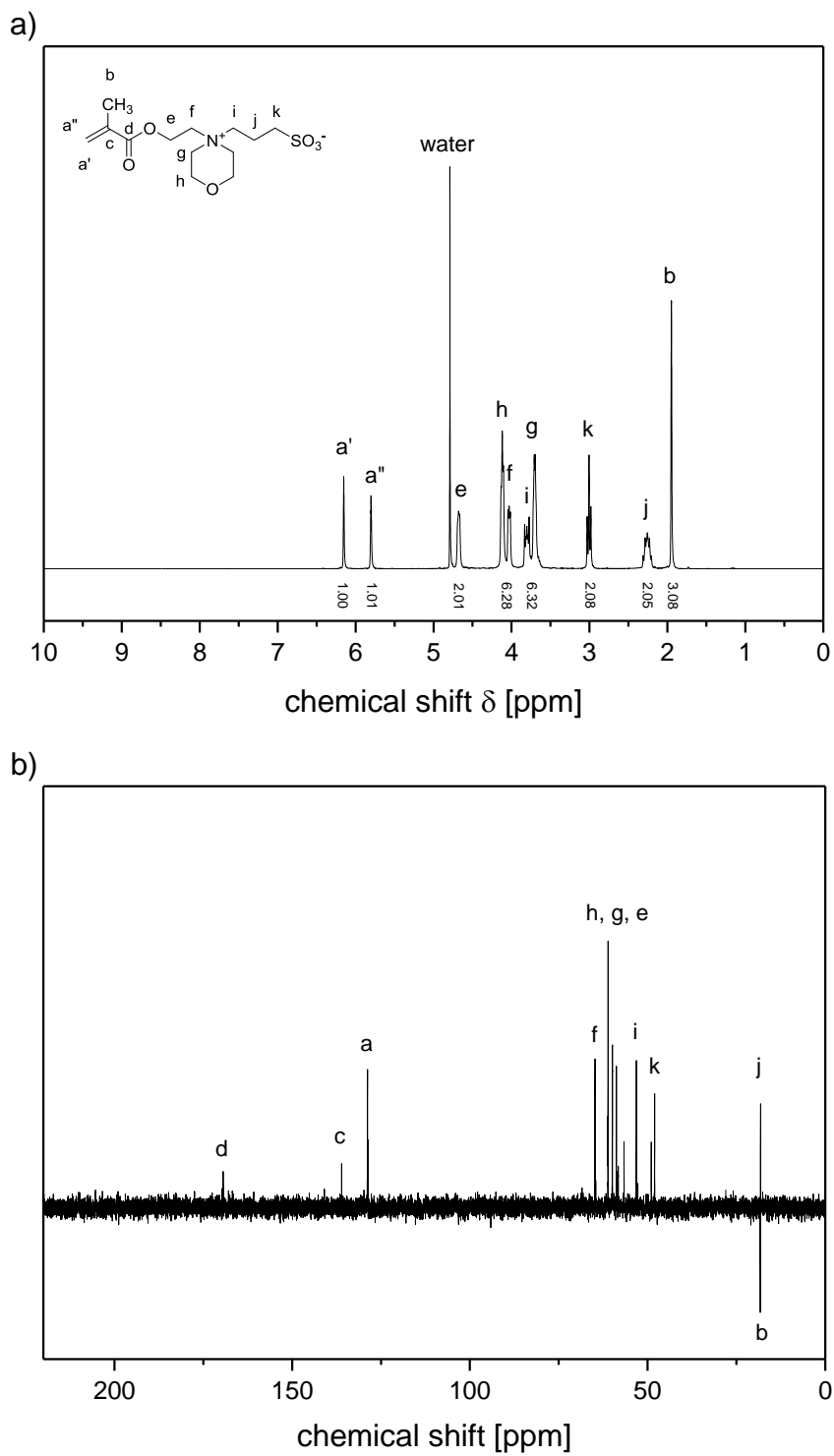


Figure S5. a) ^1H and b) ^{13}C (APT) NMR spectra of **M-3** in D_2O .

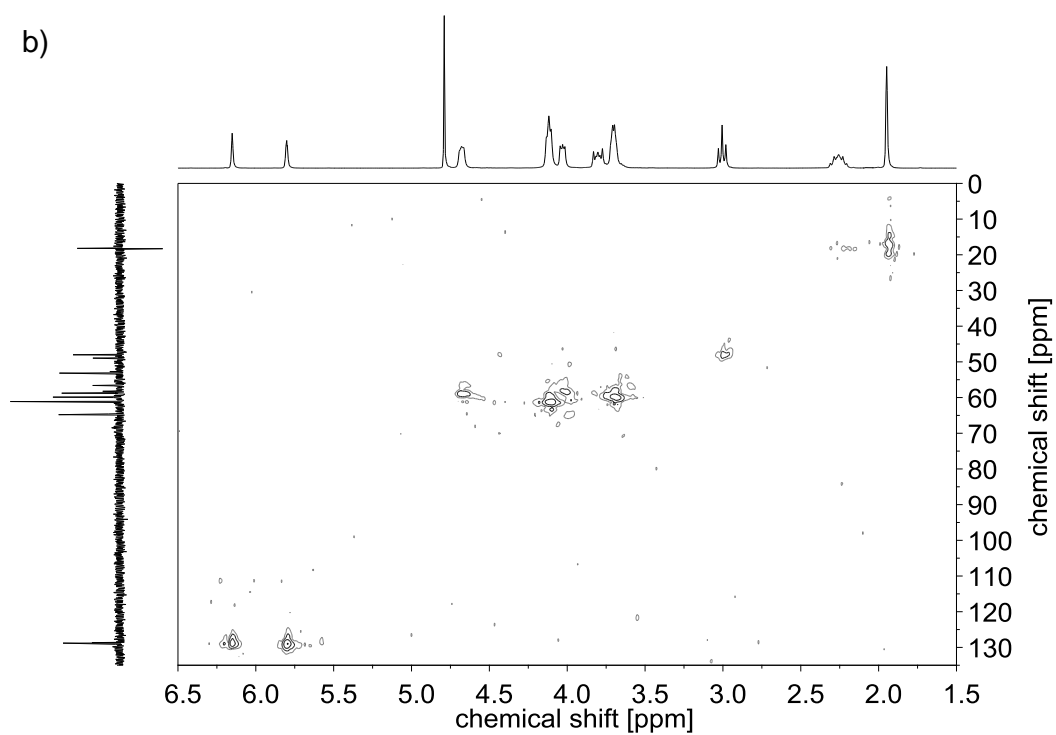
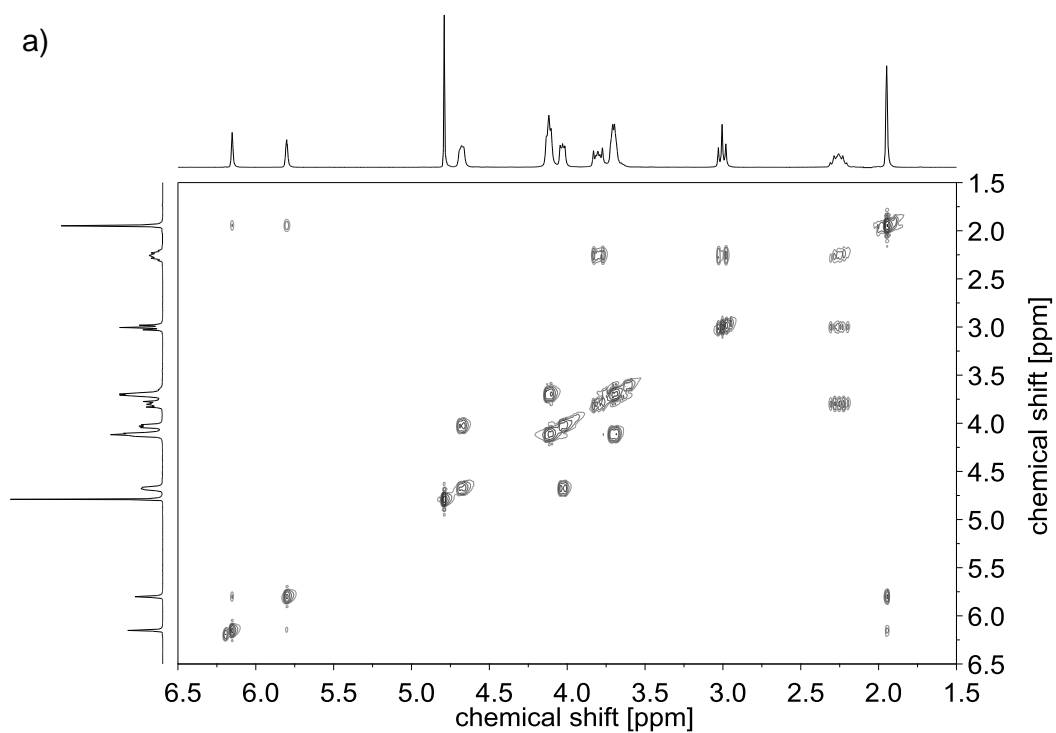


Figure S6. a) ^1H - ^1H -COSY and b) ^1H - ^{13}C -HMQC NMR spectra of **M-3** in D_2O .

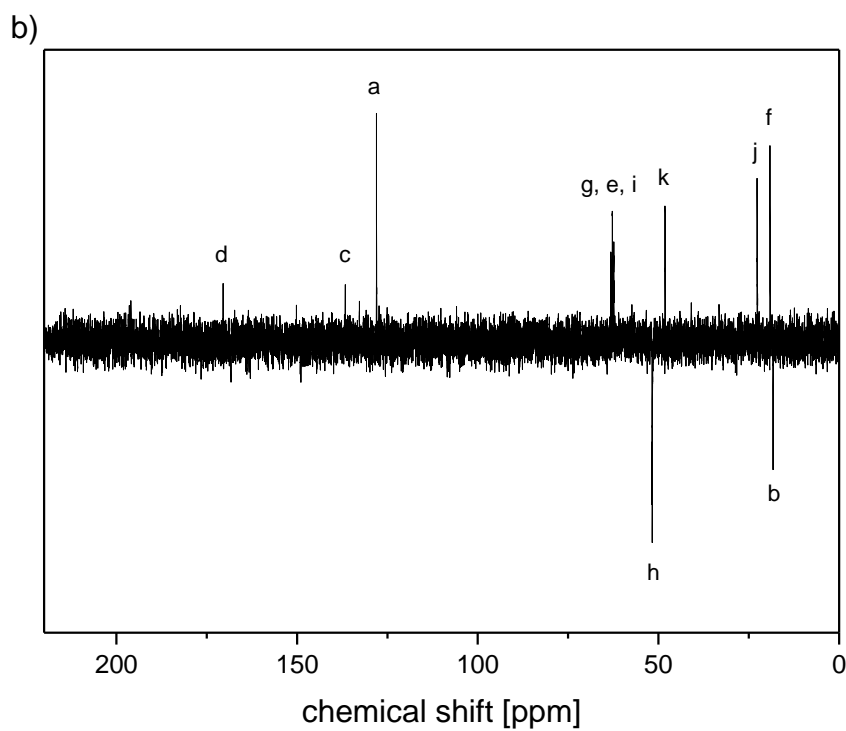
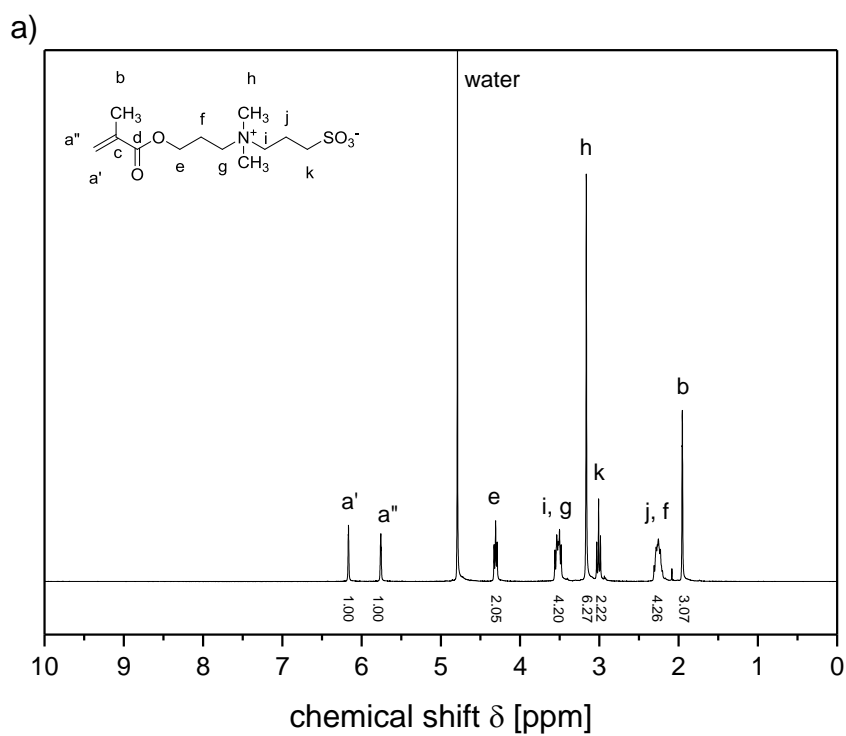


Figure S7. a) ^1H and b) ^{13}C (APT) NMR spectra of **M-4** in D_2O .

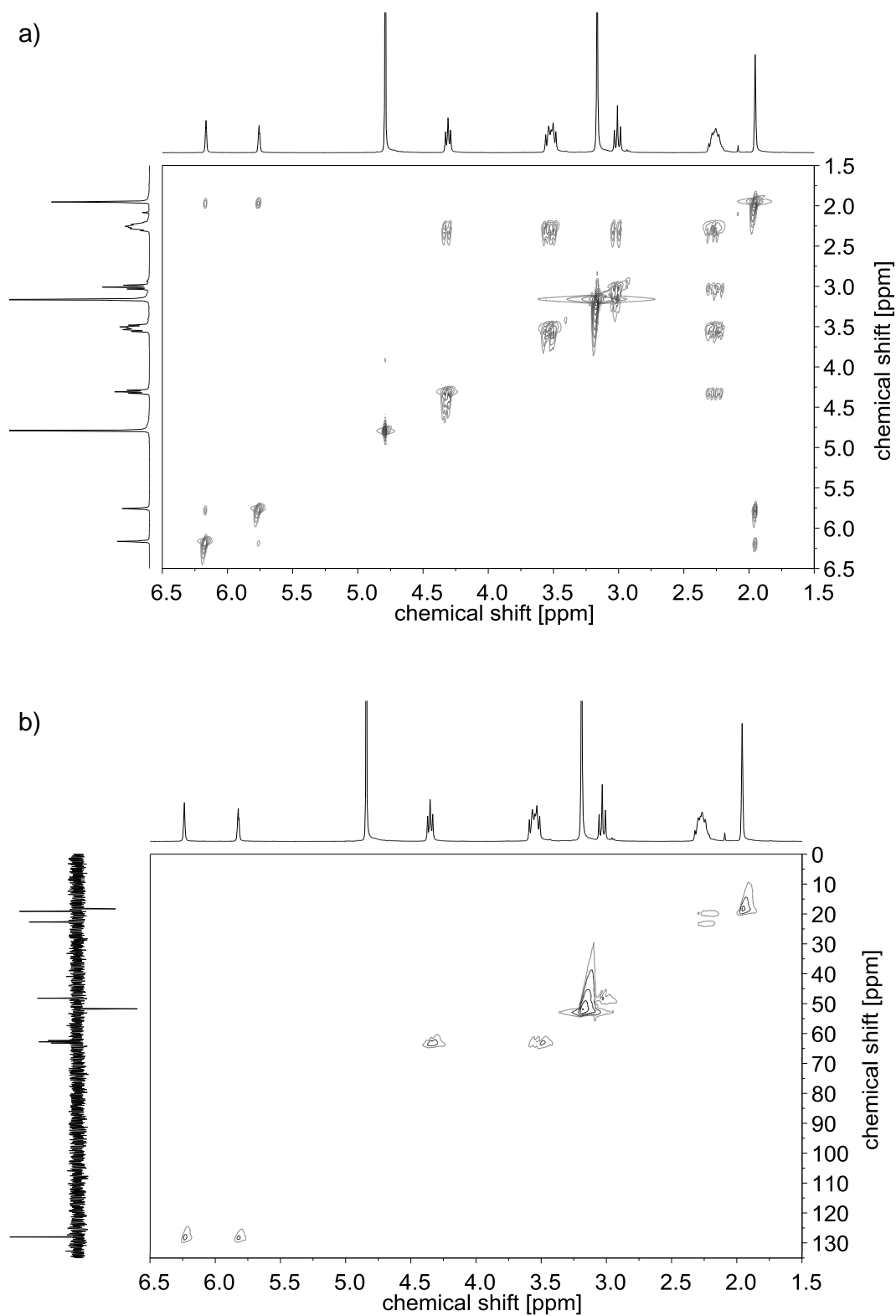


Figure S8. a) ^1H - ^1H -COSY and b) ^1H - ^{13}C -HMQC NMR spectra of **M-4** in D_2O .

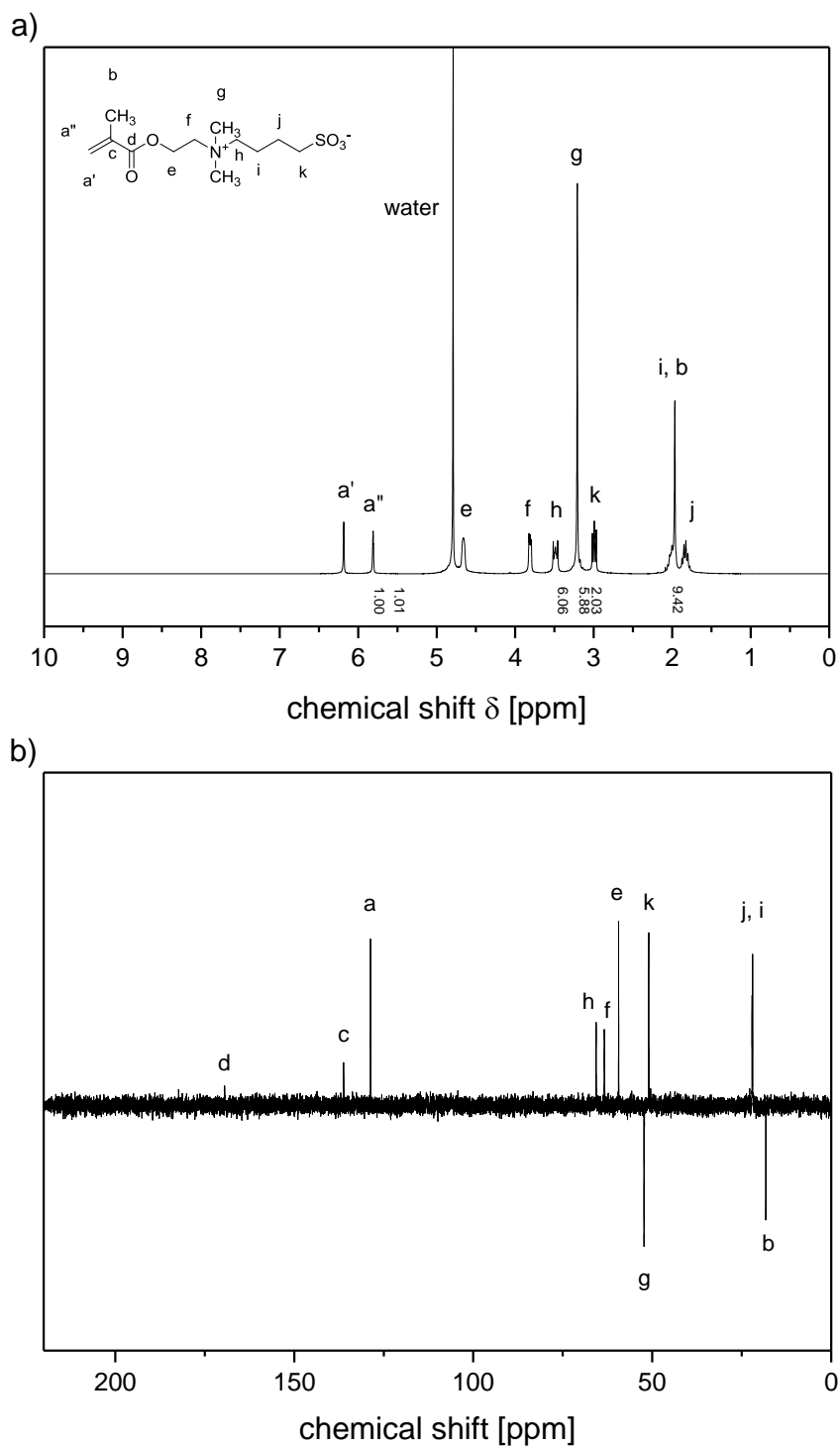


Figure S9. a) ¹H and b) ¹³C (APT) NMR spectra of **M-5** in D₂O.

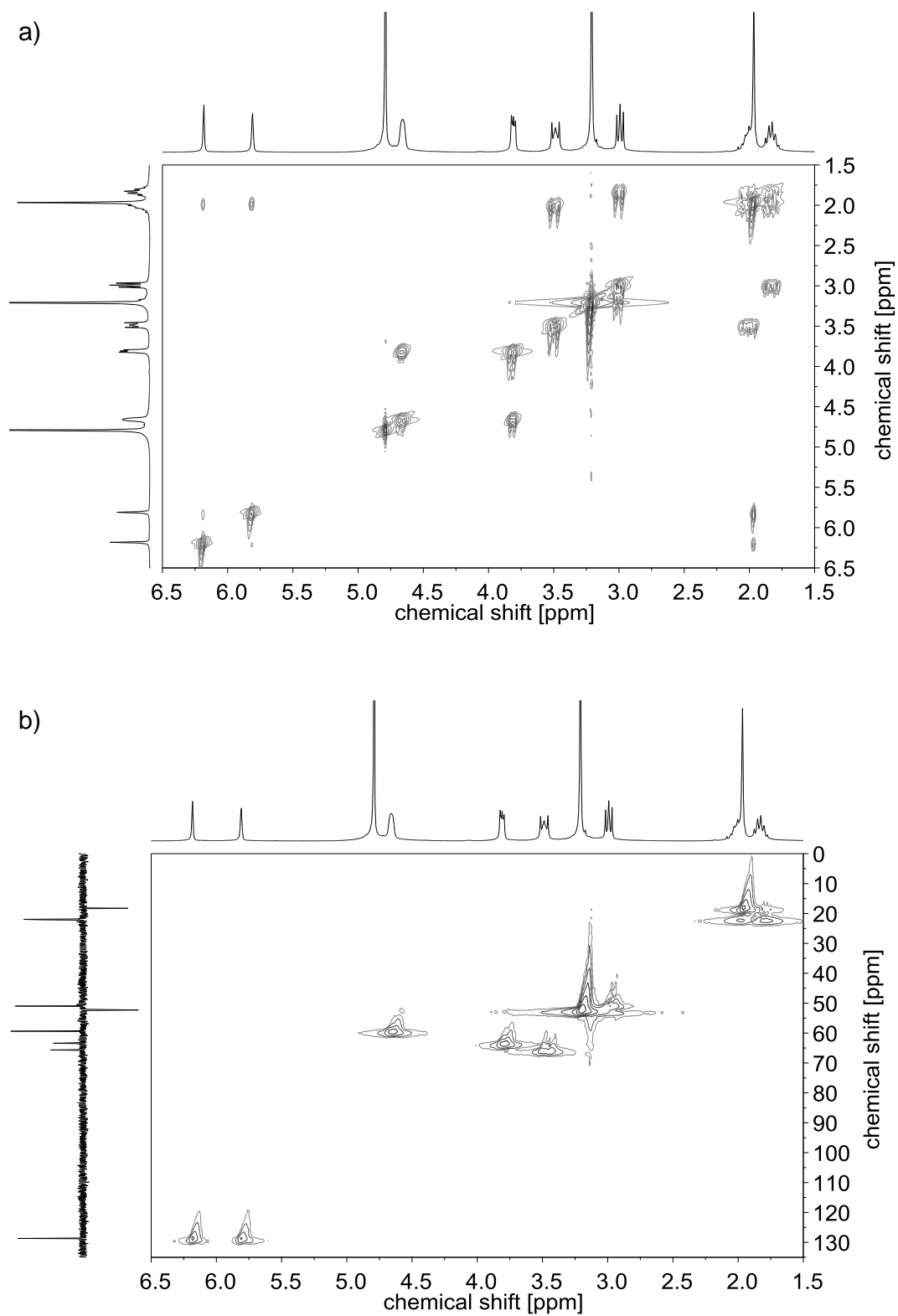


Figure S10. a) ^1H - ^1H -COSY and b) ^1H - ^{13}C -HMQC NMR spectra of **M-5** in D_2O .

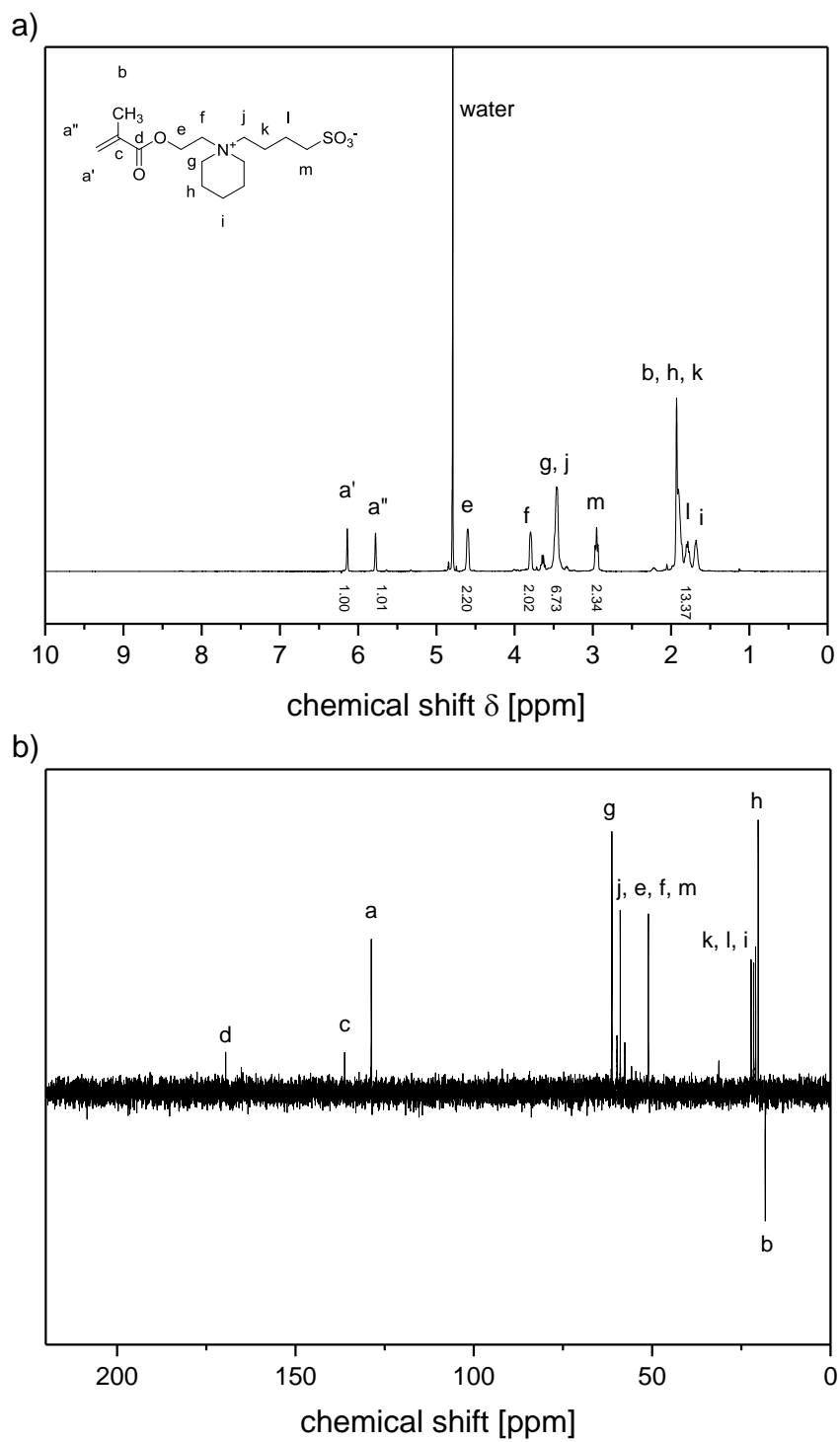


Figure S11. a) ¹H and b) ¹³C (APT) NMR spectra of M-6 in D₂O.

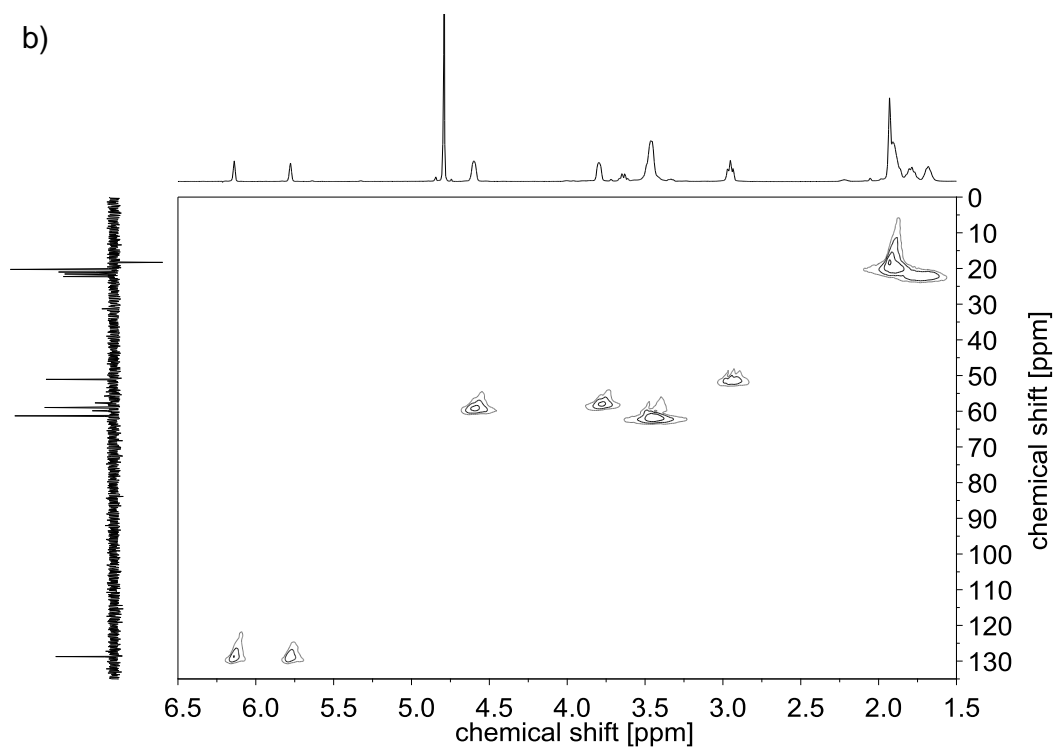
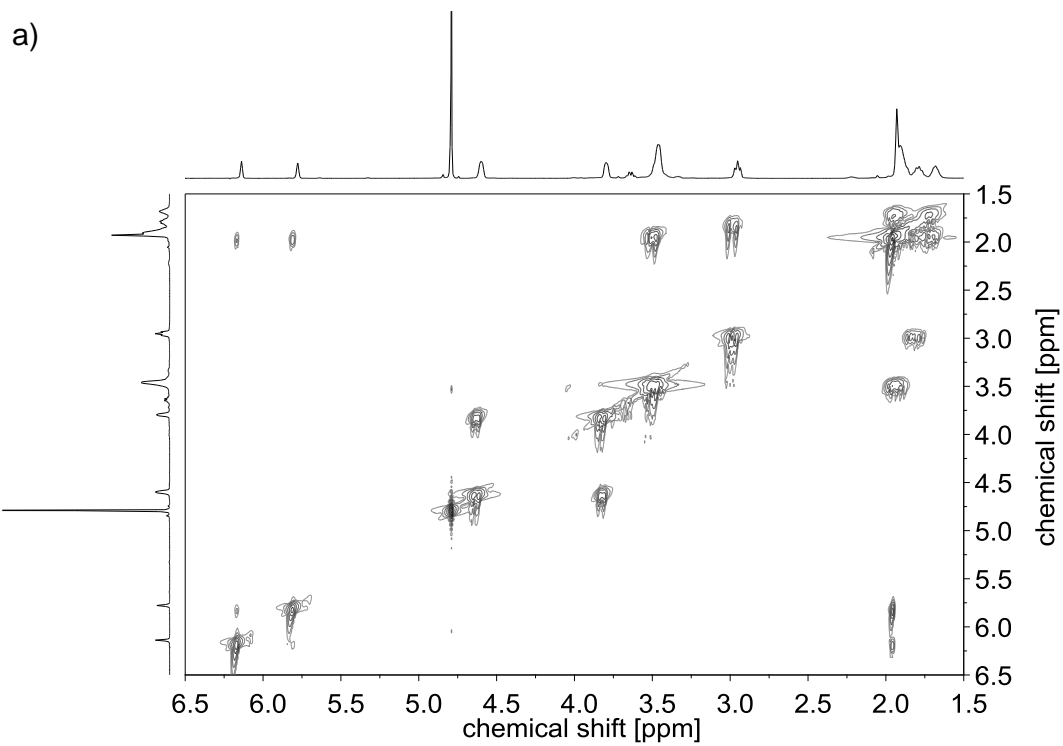


Figure S12. a) ^1H - ^1H -COSY and b) ^1H - ^{13}C -HMQC NMR spectra of **M-6** in D_2O .

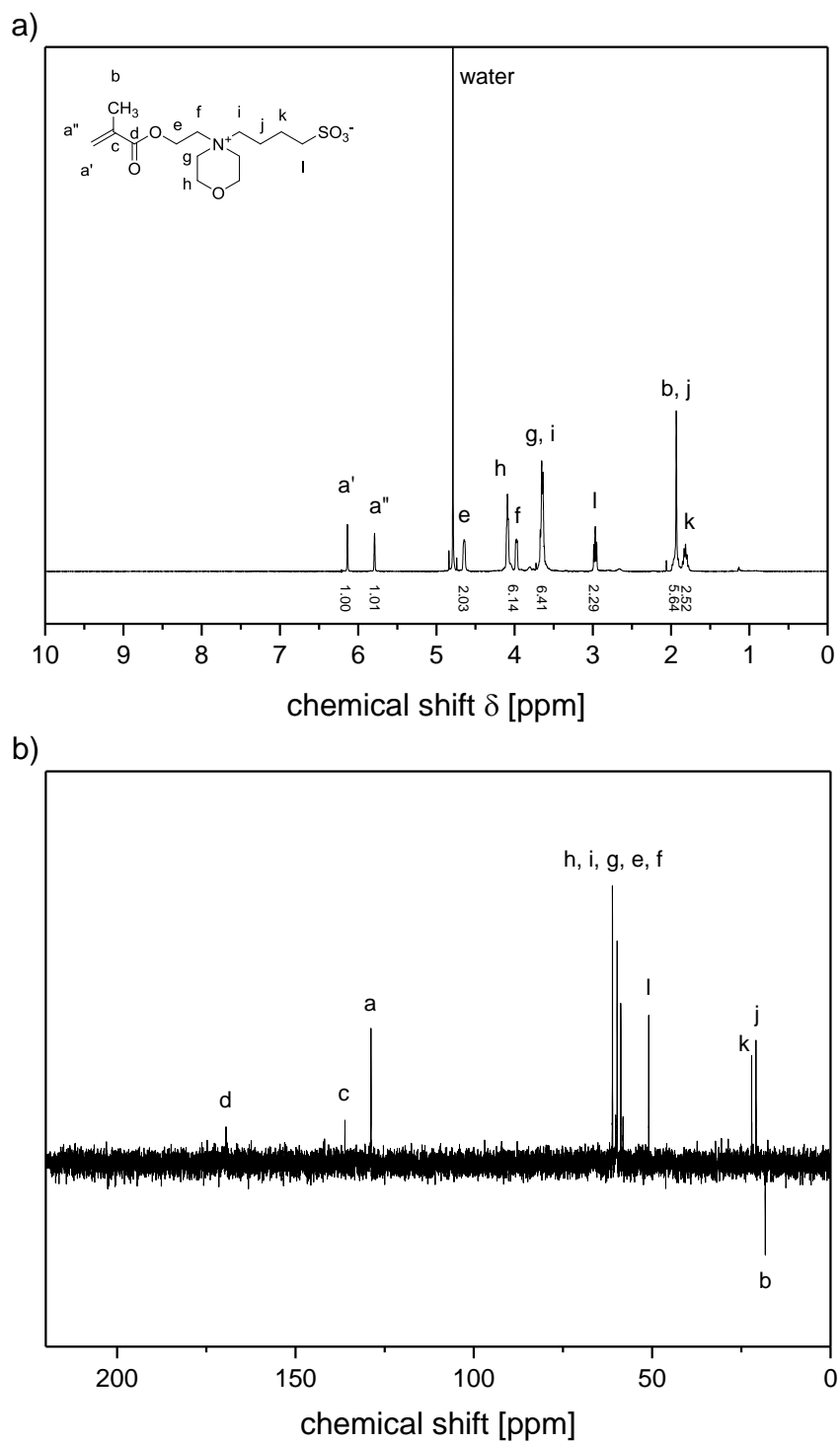


Figure S13. a) ^1H and b) ^{13}C (APT) NMR spectra of **M-7** in D_2O .

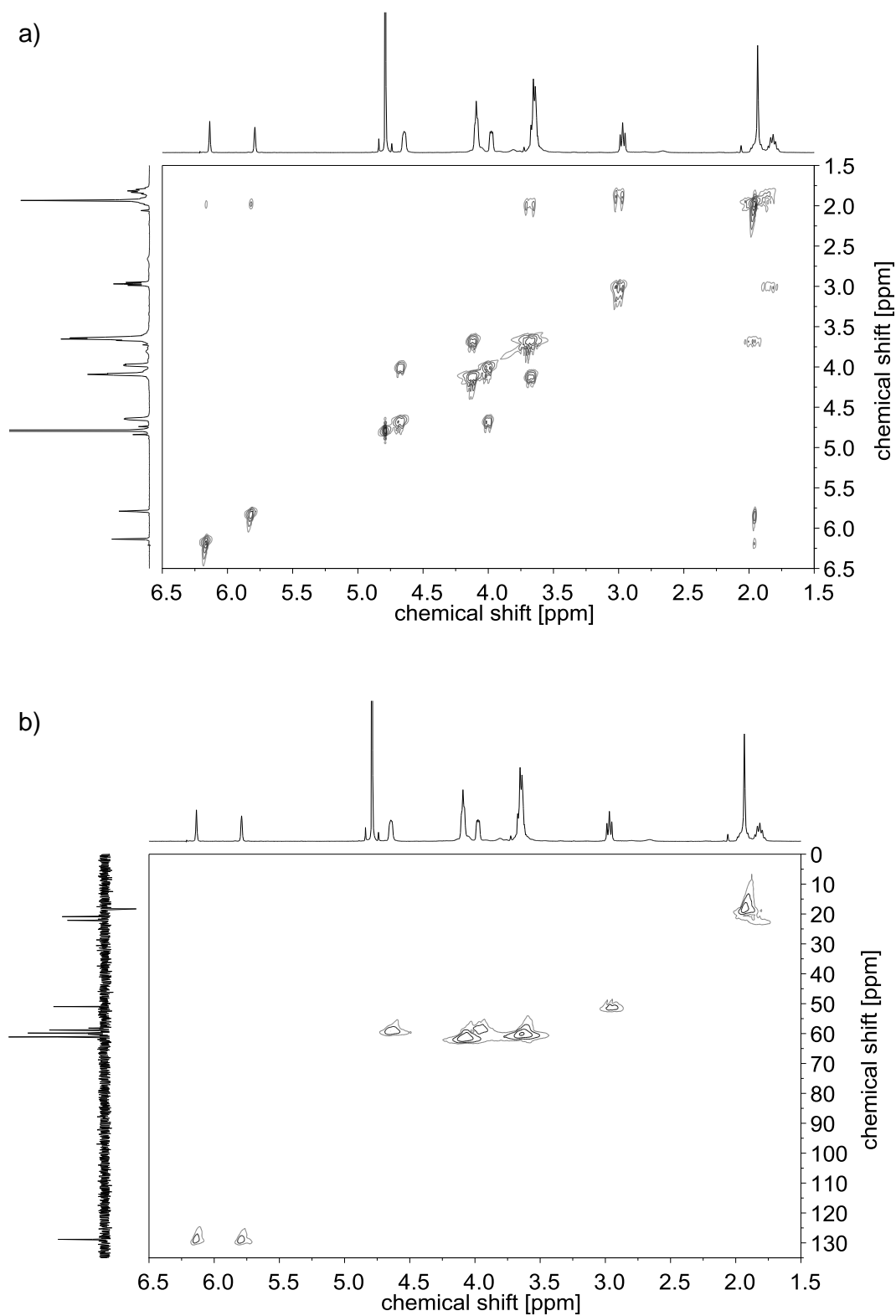


Figure S14. a) 1H - 1H -COSY and b) 1H - ^{13}C -HMQC NMR spectra of **M-7** in D_2O .

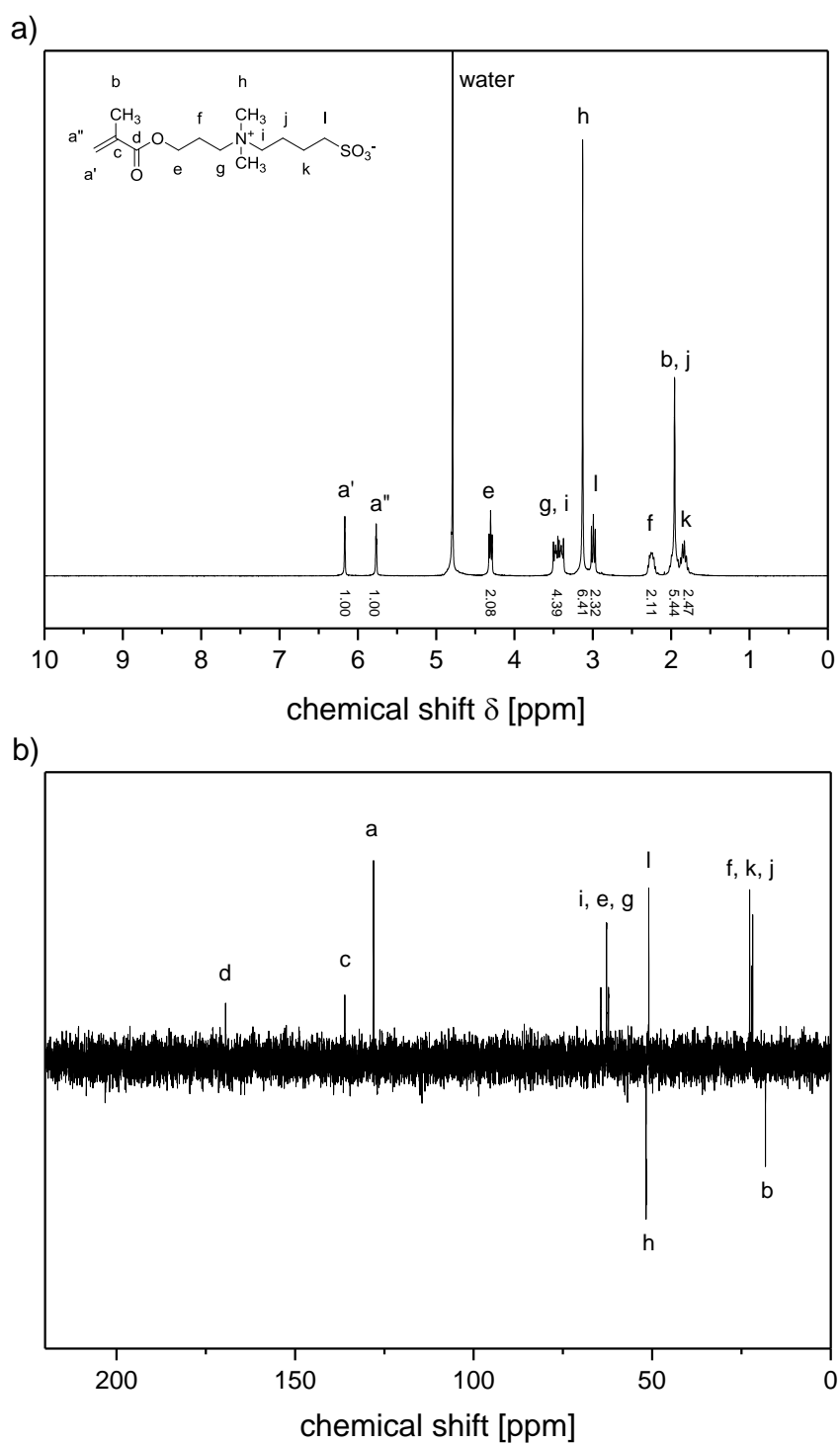
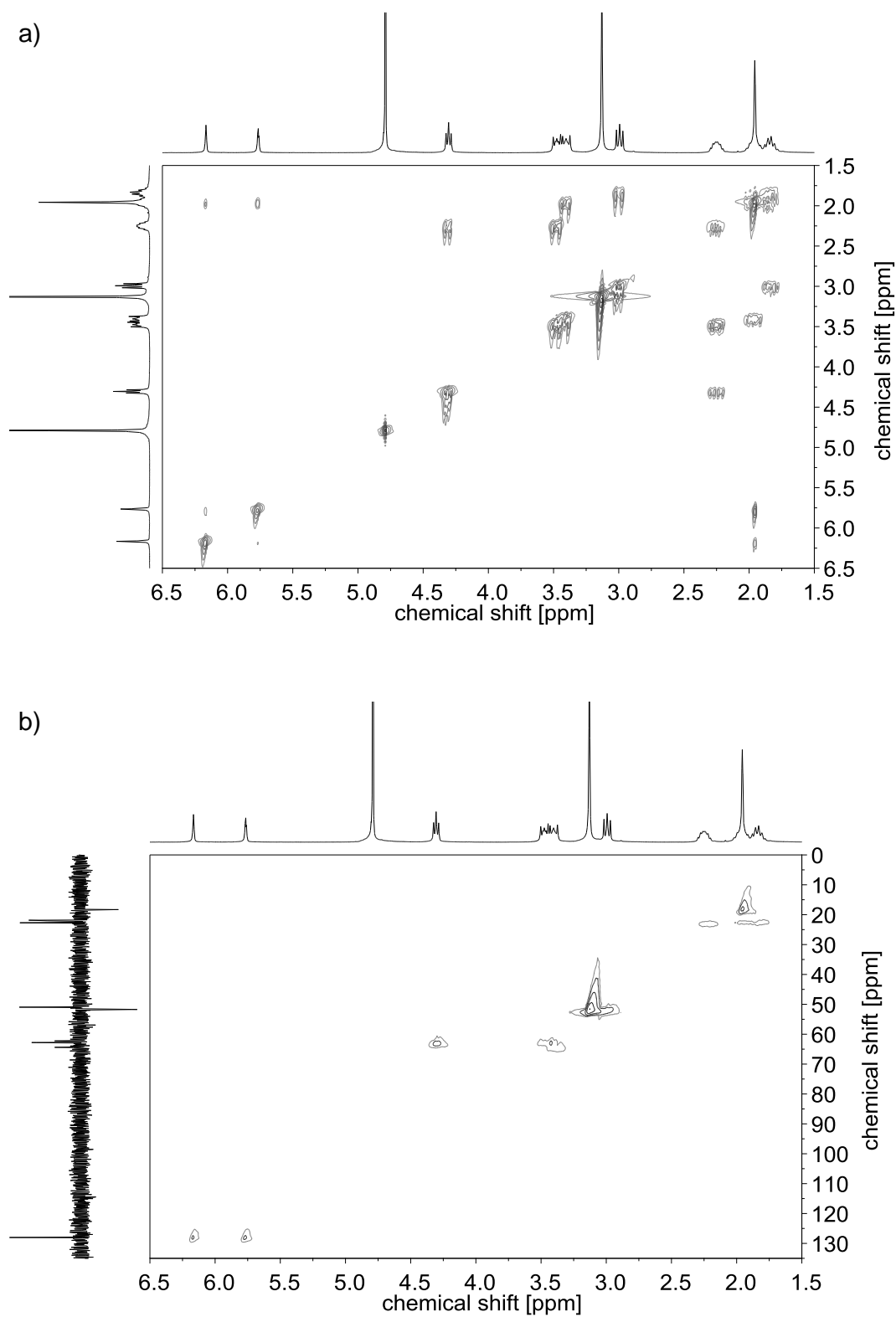


Figure S15. a) ¹H and b) ¹³C (APT) NMR spectra of **M-8** in D₂O.



Exemplary procedures of the RAFT polymerizations of zwitterionic monomers 1–8

Example for polymerisation of monomer 1

Exemplarily, **1** (5.000 g, $1.8 \cdot 10^{-2}$ mol), **CTA** (0.018 g, $3.0 \cdot 10^{-5}$ mol), and V-501 (0.002 g, $6.0 \cdot 10^{-6}$ mol) were dissolved in TFE (9 ml) and purged with N₂. The reaction mixture was polymerised at 75 °C for 15 h yielding **P-1₅₇₅** (yield 4.200 g, 84 %). TGA (the onset of decomposition): 305 °C. DSC: no thermal transition.

¹H NMR (400 MHz, in dilute aqueous NaCl (0.9 g·L⁻¹) in D₂O, 298 K): δ (ppm) = 0.6 – 2.5 (broad 7H, -CH₃ and -CH₂- on/in backbone, -CH₂-C-SO₃⁻), 2.9 – 3.1 (2H, -CH₂-SO₃⁻), 3.2 – 3.4 (6H, -N⁺-(CH₃)₂), 3.6 – 4.0 (4H, -CH₂-N⁺-CH₂-), 4.4 – 4.7 (2H, -COO-CH₂-).

FT-IR (selected bands in cm⁻¹): 3039 ν(N⁺-CH₃), 2977 ν(CH₂), 1740 ν(C=O), 1173 ν_{as}(SO₃⁻), 1036 ν_s(SO₃⁻).

UV-vis absorbance maxima: in TFE (λ_{max} = 266, 296, and 444 nm), and in water (λ_{max} = 254, 283, and 430 nm).

Fluorescence emission maxima: in TFE (λ_{PL} = 537 nm), and in water (λ_{PL} = 548 nm).

Example for polymerisation of monomer 2

Exemplarily, **2** (1.000 g, $3.2 \cdot 10^{-3}$ mol), **CTA** (0.003 g, $5.4 \cdot 10^{-6}$ mol), and V-501 (0.001 g, $1.1 \cdot 10^{-6}$ mol) were dissolved in TFE (2 ml) and purged with N₂. The reaction mixture was polymerised at 75 °C for 18 h yielding **P-2₄₈₅** (yield 0.810 g, 81 %). TGA (the onset of decomposition): 295 °C. DSC: no thermal transition.

¹H NMR (400 MHz, in dilute aqueous NaCl (0.9 g·L⁻¹) in D₂O, 298 K): δ (ppm) = 0.5 – 2.5 (broad 13H, -CH₃ and -CH₂- on/in backbone, -CH₂-CH₂-CH₂- piperidine (C4, C3, C5), CH₂-C-SO₃⁻), 2.8 – 3.1 (2H, -CH₂-SO₃⁻), 3.1 – 4.0 (8H, -CH₂-N⁺-CH₂- piperidine (C2, C6), -N⁺-CH₂-, -COO-C-CH₂-), 4.6 – 4.7 (2H, -COO-CH₂-).

FT-IR (selected bands in cm⁻¹): 3002 ν(N⁺-CH₃), 2968 ν(CH₂), 1728 ν(C=O), 1162 ν_{as}(SO₃⁻), 1034 ν_s(SO₃⁻).

UV-vis absorbance maxima: in TFE (λ_{max} = 268, 286, and 442 nm), and in water (λ_{max} = 258, 288, and 439 nm).

Fluorescence emission maxima: in TFE (λ_{PL} = 534 nm), and in water (λ_{PL} = 532 nm).

Example for polymerisation of monomer 3

Exemplarily, **3** (1.000 g, $3.1 \cdot 10^{-3}$ mol), **CTA** (0.019 g, $3.1 \cdot 10^{-5}$ mol), and V-501 (0.002 g, $6.2 \cdot 10^{-6}$ mol) were dissolved in TFE (2 ml) and purged with N₂. The reaction mixture was polymerised at 75 °C for 2.75 h yielding **P-3₉₅** (yield 0.960 g, 96 %). TGA (the onset of decomposition): 280 °C. DSC: no thermal transition.

¹H NMR (300 MHz, in dilute aqueous NaCl (0.9 g·L⁻¹) in D₂O, 298 K): δ (ppm) = 0.5 – 2.5 (broad 7H, -CH₃ and -CH₂- on/in backbone, -CH₂-C-SO₃⁻), 2.8 – 3.3 (2H, -CH₂-SO₃⁻), 3.3 – 4.4 (12H, -CH₂-CH₂-N⁺-CH₂-CH₂- morpholine (C2, C3, C5, C6), -CH₂-N⁺-CH₂-), 4.4 – 4.7 (2H, -COO-CH₂-).

FT-IR (selected bands in cm⁻¹): 3021 ν(N⁺-CH₃), 2951 ν(CH₂), 1726 ν(C=O), 1172 ν_{as}(SO₃⁻), 1036 ν_s(SO₃⁻).

UV-vis absorbance maxima: in TFE ($\lambda_{\max} = 269, 310, \text{ and } 444 \text{ nm}$), and in water ($\lambda_{\max} = 254, 295, \text{ and } 444 \text{ nm}$).

Fluorescence emission maxima: in TFE ($\lambda_{\text{PL}} = 537 \text{ nm}$), and in water ($\lambda_{\text{PL}} = 547 \text{ nm}$).

Example for polymerisation of monomer 4

Exemplarily, **4** (2.000 g, $6.8 \cdot 10^{-3} \text{ mol}$), **CTA** (0.007 g, $1.1 \cdot 10^{-5} \text{ mol}$), and V-501 (0.001 g, $2.3 \cdot 10^{-6} \text{ mol}$) were dissolved in TFE (4 ml) and purged with N_2 . The reaction mixture was polymerised at $75 \text{ }^\circ\text{C}$ for 12 h yielding **P-4₅₈₅** (yield 1.900 g, 95 %). TGA (the onset of decomposition): $295 \text{ }^\circ\text{C}$. DSC: no thermal transition.

$^1\text{H NMR}$ (300 MHz, in dilute aqueous NaCl ($0.9 \text{ g} \cdot \text{L}^{-1}$) in D_2O , 298 K): δ (ppm) = 0.5 – 2.5 (broad 9H, $-\text{CH}_3$ and $-\text{CH}_2-$ on/in backbone, $-\text{CH}_2-\text{C}-\text{SO}_3^-$, $-\text{COO}-\text{C}-\text{CH}_2-$), 2.9 – 3.1 (2H, $\text{CH}_2-\text{SO}_3^-$), 3.1 – 3.4 (6H, $-\text{N}^+(\text{CH}_3)_2$), 3.4 – 3.8 (4H, $-\text{CH}_2-\text{N}^+-\text{CH}_2-$), 3.9 – 4.3 (2H, $-\text{COO}-\text{CH}_2-$).

FT-IR (selected bands in cm^{-1}): 3036 $\nu(\text{N}^+-\text{CH}_3)$, 2966 $\nu(\text{CH}_2)$, 1720 $\nu(\text{C}=\text{O})$, 1150 $\nu_{\text{as}}(\text{SO}_3^-)$, 1033 $\nu_{\text{s}}(\text{SO}_3^-)$.

UV-vis absorbance maxima: in TFE ($\lambda_{\max} = 263, 307, \text{ and } 445 \text{ nm}$), and in water ($\lambda_{\max} = 254, 296, \text{ and } 444 \text{ nm}$).

Fluorescence emission maxima: in TFE ($\lambda_{\text{PL}} = 538 \text{ nm}$), and in water ($\lambda_{\text{PL}} = 545 \text{ nm}$).

Example for polymerisation of monomer 5

Exemplarily, **5** (1.000 g, $3.4 \cdot 10^{-3} \text{ mol}$), **CTA** (0.026 g, $4.3 \cdot 10^{-5} \text{ mol}$), and V-501 (0.002 g, $8.5 \cdot 10^{-6} \text{ mol}$) were dissolved in TFE (2 ml) and purged with N_2 . The reaction mixture was polymerised at $75 \text{ }^\circ\text{C}$ for 2 h yielding **P-5₈₀** (yield 0.960 g, 96 %). TGA (the onset of decomposition): $295 \text{ }^\circ\text{C}$. DSC: no thermal transition.

$^1\text{H NMR}$ (300 MHz, in dilute aqueous NaCl ($0.9 \text{ g} \cdot \text{L}^{-1}$) in D_2O , 298 K): δ (ppm) = 0.5 – 2.5 (broad 9H, $-\text{CH}_3$ and $-\text{CH}_2-$ on/in backbone, $-\text{CH}_2-\text{CH}_2-\text{C}-\text{SO}_3^-$), 2.8 – 3.1 (2H, $\text{CH}_2-\text{SO}_3^-$), 3.1 – 3.4 (6H, $-\text{N}^+(\text{CH}_3)_2$), 3.4 – 4.0 (4H, $-\text{CH}_2-\text{N}^+-\text{CH}_2-$), 4.4 – 5.0 (2H, $-\text{COO}-\text{CH}_2-$).

FT-IR (selected bands in cm^{-1}): 3030 $\nu(\text{N}^+-\text{CH}_3)$, 2967 $\nu(\text{CH}_2)$, 1724 $\nu(\text{C}=\text{O})$, 1146 $\nu_{\text{as}}(\text{SO}_3^-)$, 1035 $\nu_{\text{s}}(\text{SO}_3^-)$.

UV-vis absorbance maxima: in TFE ($\lambda_{\max} = 260, 306, \text{ and } 444 \text{ nm}$), and in water ($\lambda_{\max} = 252, 296, \text{ and } 436 \text{ nm}$).

Fluorescence emission maxima: in TFE ($\lambda_{\text{PL}} = 539 \text{ nm}$), and in water ($\lambda_{\text{PL}} = 545 \text{ nm}$).

Example for polymerisation of monomer 6

Exemplarily, **6** (1.900 g, $5.7 \cdot 10^{-3} \text{ mol}$), **CTA** (0.006 g, $9.5 \cdot 10^{-6} \text{ mol}$), and V-501 (0.001 g, $1.9 \cdot 10^{-6} \text{ mol}$) were dissolved in TFE (4 ml) and purged with N_2 . The reaction mixture was polymerised at $75 \text{ }^\circ\text{C}$ for 15 h yielding **P-6₅₀₀** (yield 1.600 g, 83 %). TGA (the onset of decomposition): $290 \text{ }^\circ\text{C}$. DSC: no thermal transition.

$^1\text{H NMR}$ (300 MHz, in dilute aqueous NaCl ($0.9 \text{ g} \cdot \text{L}^{-1}$) in D_2O , 298 K): δ (ppm) = 0.5 – 2.5 (broad 15H, $-\text{CH}_3$ and $-\text{CH}_2-$ on/in backbone, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ piperidine (C4, C3, C5), $\text{CH}_2-\text{CH}_2-\text{C}-\text{SO}_3^-$), 2.8 – 3.1 (2H, $-\text{CH}_2-\text{SO}_3^-$), 3.1 – 4.0 (8H, $-\text{CH}_2-\text{N}^+-\text{CH}_2-$ piperidine (C2, C6), $-\text{N}^+-\text{CH}_2-$, $-\text{COO}-\text{C}-\text{CH}_2-$), 4.4 – 4.7 (2H, $-\text{COO}-\text{CH}_2-$).

FT-IR (selected bands in cm^{-1}): 3027 $\nu(\text{N}^+\text{-CH}_3)$, 2951 $\nu(\text{CH}_2)$, 1724 $\nu(\text{C=O})$, 1170 $\nu_{\text{as}}(\text{SO}_3^-)$, 1034 $\nu_{\text{s}}(\text{SO}_3^-)$.

UV-vis absorbance maxima: in TFE ($\lambda_{\text{max}} = 262, 305, \text{ and } 439 \text{ nm}$), and in water ($\lambda_{\text{max}} = 260, 296, \text{ and } 444 \text{ nm}$).

Fluorescence emission maxima: in TFE ($\lambda_{\text{PL}} = 534 \text{ nm}$), and in water ($\lambda_{\text{PL}} = 537 \text{ nm}$).

Example for polymerisation of monomer 7

Exemplarily, **7** (1.000 g, $3.0 \cdot 10^{-3} \text{ mol}$), **CTA** (0.018 g, $3.0 \cdot 10^{-5} \text{ mol}$), and V-501 (0.002 g, $6.0 \cdot 10^{-6} \text{ mol}$) were dissolved in TFE (2 ml) and purged with N_2 . The reaction mixture was polymerised at 75 °C for 3 h yielding **P-7₈₅** (yield 0.700 g, 70 %). TGA (the onset of decomposition): 250 °C. DSC: no thermal transition.

^1H NMR (400 MHz, in dilute aqueous NaCl ($0.9 \text{ g} \cdot \text{L}^{-1}$) in D_2O , 298 K): δ (ppm) = 0.5 – 2.5 (broad 9H, $-\text{CH}_3$ and $-\text{CH}_2-$ on/in backbone, $-\text{CH}_2\text{-CH}_2\text{-C-SO}_3^-$), 2.8 – 3.3 (2H, $\text{CH}_2\text{-SO}_3^-$), 3.3 – 4.4 (12H, $-\text{CH}_2\text{-CH}_2\text{-N}^+\text{-CH}_2\text{-CH}_2-$ morpholine (C2, C3, C5, C6), $-\text{CH}_2\text{-N}^+\text{-CH}_2-$), 4.4 – 4.7 (2H, $-\text{COO-CH}_2-$).

FT-IR (selected bands in cm^{-1}): 3011 $\nu(\text{N}^+\text{-CH}_3)$, 2967 $\nu(\text{CH}_2)$, 1724 $\nu(\text{C=O})$, 1169 $\nu_{\text{as}}(\text{SO}_3^-)$, 1035 $\nu_{\text{s}}(\text{SO}_3^-)$.

UV-vis absorbance maxima: in TFE ($\lambda_{\text{max}} = 263, 306, \text{ and } 442 \text{ nm}$), and in water ($\lambda_{\text{max}} = 260, 295, \text{ and } 444 \text{ nm}$).

Fluorescence emission maxima: in TFE ($\lambda_{\text{PL}} = 534 \text{ nm}$), and in water ($\lambda_{\text{PL}} = 541 \text{ nm}$).

Example for polymerisation of monomer 8

Exemplarily, **8** (5.000 g, $1.6 \cdot 10^{-2} \text{ mol}$), **CTA** (0.099 g, $1.6 \cdot 10^{-4} \text{ mol}$), and V-501 (0.009 g, $3.3 \cdot 10^{-5} \text{ mol}$) were dissolved in TFE (9 ml) and purged with N_2 . The reaction mixture was polymerised at 75 °C for 19 h yielding **P-8₁₀₀** (yield 4.900 g, 98 %). TGA: onset of decomposition at 300 °C. DSC: no thermal transition.

^1H NMR (300 MHz, in dilute aqueous NaCl ($0.9 \text{ g} \cdot \text{L}^{-1}$) in D_2O , 298 K): δ (ppm) = 0.5 – 2.5 (broad 11H, $-\text{CH}_3$ and $-\text{CH}_2-$ on/in backbone, $-\text{CH}_2\text{-CH}_2\text{-C-SO}_3^-$, $-\text{COO-C-CH}_2-$), 2.9 – 3.1 (2H, $-\text{CH}_2\text{-SO}_3^-$), 3.1 – 3.3 (6H, $-\text{N}^+\text{-(CH}_3)_2$), 3.3 – 3.6 (4H, $-\text{CH}_2\text{-N}^+\text{-CH}_2-$), 3.9 – 4.3 (2H, COO-CH_2-).

FT-IR (selected bands in cm^{-1}): 3033 $\nu(\text{N}^+\text{-CH}_3)$, 2967 $\nu(\text{CH}_2)$, 1722 $\nu(\text{C=O})$, 1165 $\nu_{\text{as}}(\text{SO}_3^-)$, 1034 $\nu_{\text{s}}(\text{SO}_3^-)$.

UV-vis absorbance maxima: in TFE ($\lambda_{\text{max}} = 264, 306, \text{ and } 449 \text{ nm}$), and in water ($\lambda_{\text{max}} = 256, 285, \text{ and } 447 \text{ nm}$).

Fluorescence emission maxima: in TFE ($\lambda_{\text{PL}} = 538 \text{ nm}$), and in water ($\lambda_{\text{PL}} = 545 \text{ nm}$).

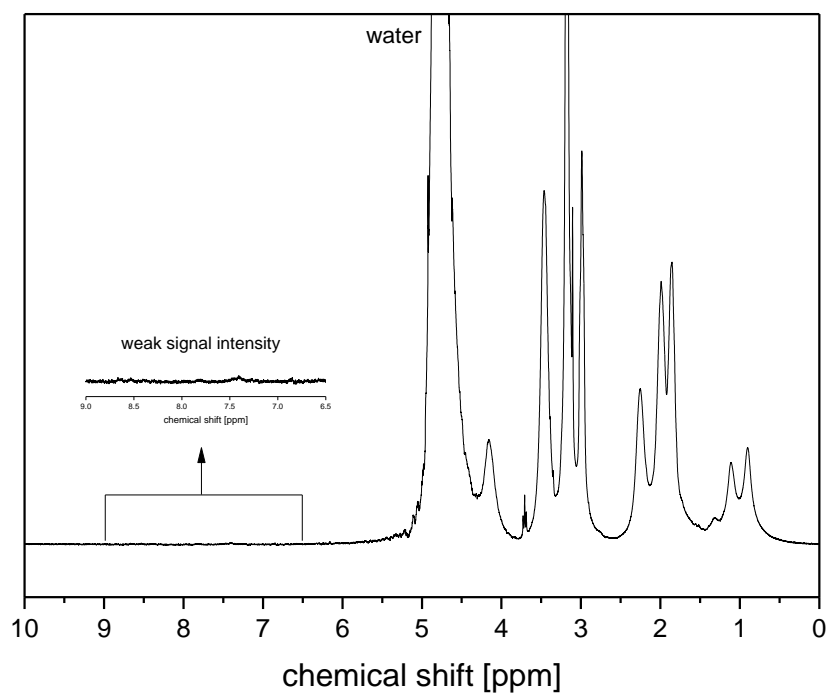


Figure S17. Limits of end group analysis by ^1H NMR exemplified for **P-8290**, spectrum taken in D_2O . The inset shows the magnified, barely visible weak signals of the Z and R-groups between 6.5 and 9.0 ppm.

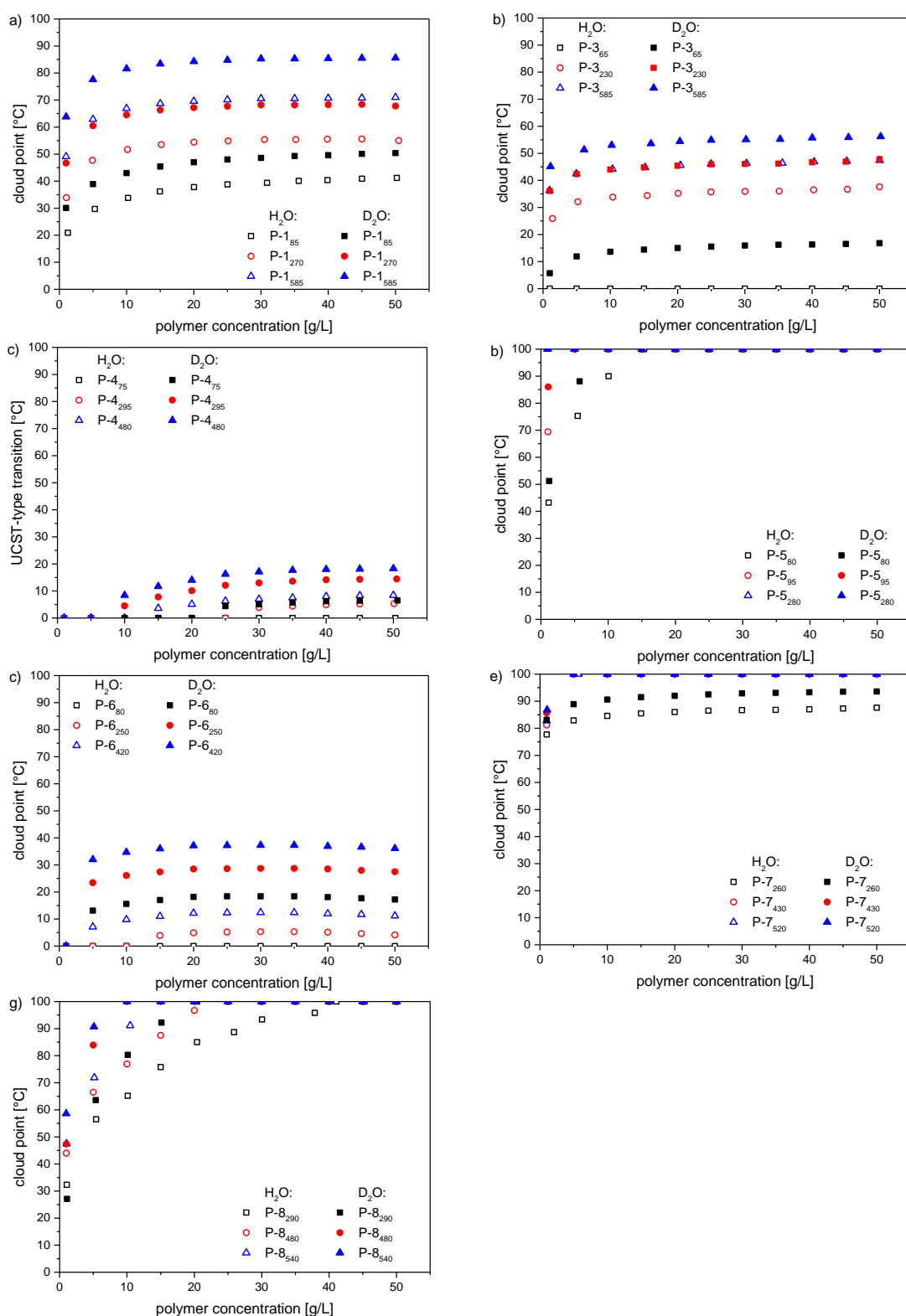


Figure S18. Concentration dependence of UCST-type cloud points in H₂O (open symbols) and D₂O (full symbols) of polysulfobetaines with varying molar mass: a) P-1), b) P-3, c) P-4, d) P-5, e) P-6, f) P-7, g) P-8.

Note that the phase transition of P-2 in H₂O and in D₂O is below 0 °C.

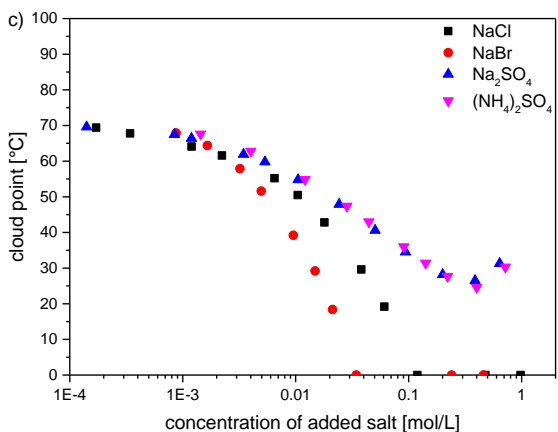
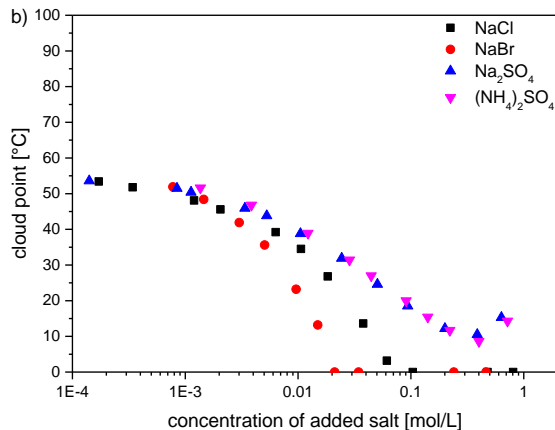
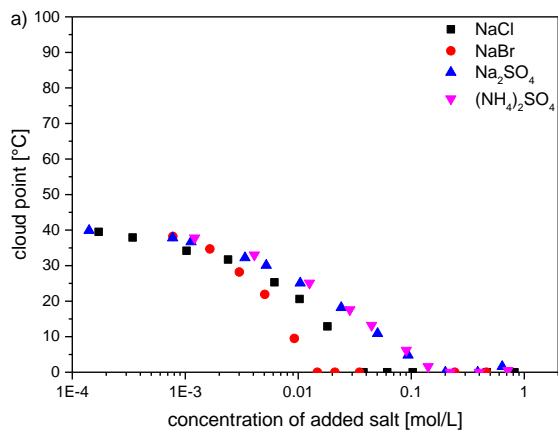


Figure S19. UCST-type cloud points of the polymers of **P-1** series in H₂O (50 g/L) containing inorganic salts as function of molar mass: a) **P-185**, b) **P-1270**, c) **P-1585**.

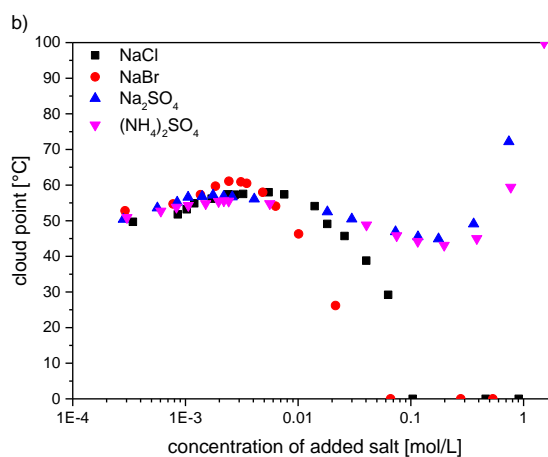
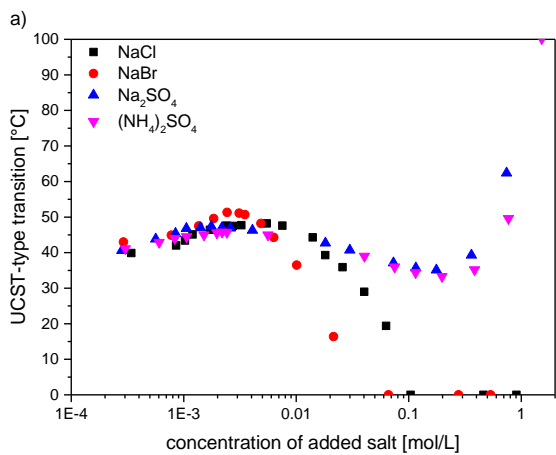


Figure S20. UCST-type cloud points of the polymers of **P-3** series in H₂O (50 g/L) containing inorganic salts as function of molar mass: a) **P-3230**, b) **P-3585**.

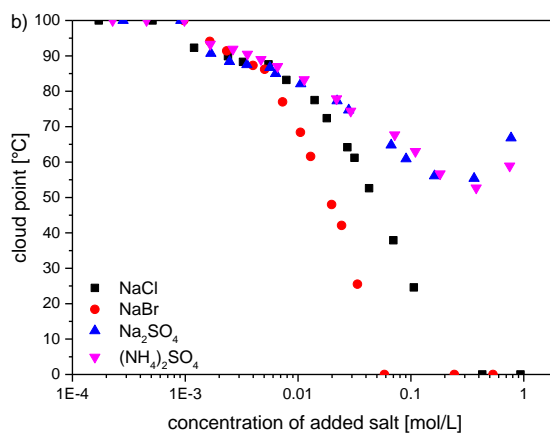
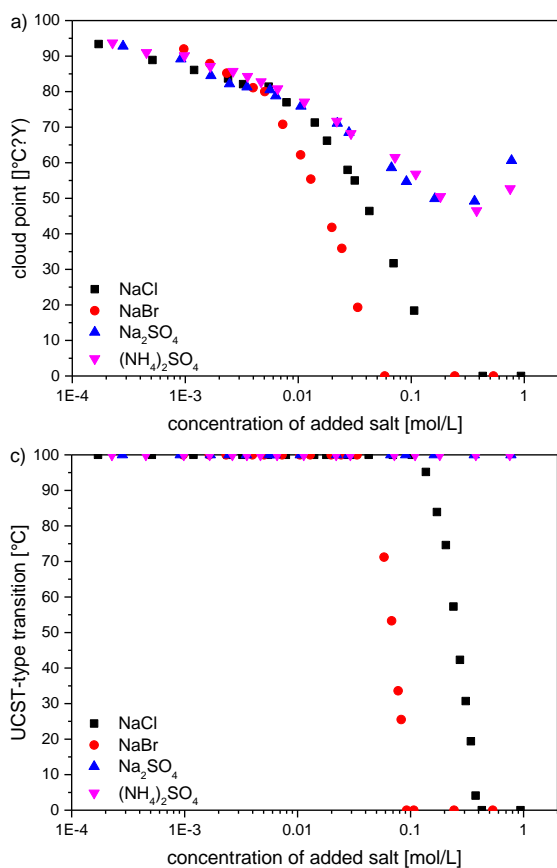


Figure S21.
UCST-type cloud points of the polymers of **P-5** series in H₂O (50 g/L) containing inorganic salts as function of molar mass:
a) **P-5₈₀**, b) **P-5₉₅**, c) **P-5₂₈₀**.

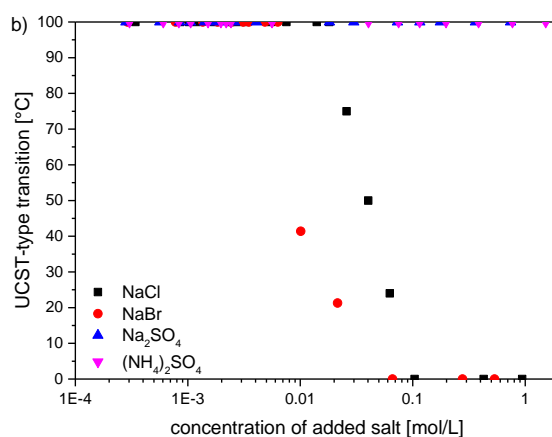
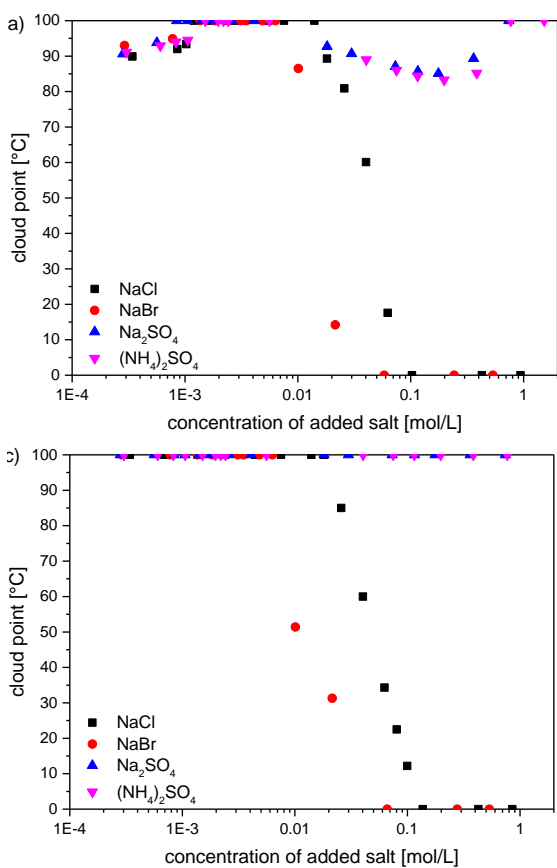


Figure S22.
UCST-type cloud points of the polymers of **P-7** series in H₂O (50 g/L) containing inorganic salts as function of molar mass:
a) **P-7₂₆₀**, b) **P-7₄₃₀**, c) **P-7₅₂₀**.

