

Supporting Information - Permanently positive charged and Betainic Poly(ethylene oxid)- copolymers for calcium phosphate mineralization

analytical data

C1. FTIR (ATR, 298 K): 3023 cm^{-1} , C–N asymmetric stretching vibration, 2962 cm^{-1} , C–H stretching of R–CH₃; 1724 cm^{-1} , C=O stretching vibration; 1643 cm^{-1} , C=O stretching vibration; 1481 cm^{-1} , C–H scissor vibration; 1283 cm^{-1} and 1153 cm^{-1} , C–N stretching vibration. ¹H NMR (300 MHz, D₂O, 298 K) δ ppm 0.66 - 1.47 (m, 3 H) 1.56 - 2.39 (m, 2 H) 3.28 (br. s., 9 H) 3.83 (br. s., 2 H) 4.27 - 4.64 (m, 2 H). EA experiment (calculated): C 44.1% (50.6%), H 9.6% (7.7%), N 5.8% (8.1%). Value dn/dc = 0.143 mL/g. $M_n(\text{GPC})$ = 40.7 kg/mol, PDI = 4.15.

C2. FTIR (ATR, 298 K): 3023 cm^{-1} , C–N asymmetric stretching vibration, 2962 cm^{-1} , C–H stretching of R–CH₃; 1724 cm^{-1} , C=O stretching vibration; 1643 cm^{-1} , C=O stretching vibration; 1481 cm^{-1} , C–H scissor vibration; 1283 cm^{-1} and 1153 cm^{-1} , C–N stretching vibration. ¹H NMR (300 MHz, D₂O, 298 K) δ ppm 0.67 - 1.45 (m, 3 H) 1.47 - 2.49 (m, 2 H) 3.29 (br. s., 9 H) 3.58 - 4.12 (m, 3 H) 4.20 - 4.63 (m, 2 H). EA experiment (calculated): C 44.5% (50.6%), H 8.6% (7.7%), N 5.5% (8.1%). Value dn/dc = 0.145 mL/g. $M_n(\text{GPC})$ = 136.5 kg/mol, PDI = 6.01, $M_n(^1\text{H NMR})$ = 98.8 kg/mol.

C3. FTIR (ATR, 298 K): 3023 cm^{-1} , C–N asymmetric stretching vibration, 2962 cm^{-1} , C–H stretching of R–CH₃; 1724 cm^{-1} , C=O stretching vibration; 1643 cm^{-1} , C=O stretching vibration; 1481 cm^{-1} , C–H scissor vibration; 1283 cm^{-1} and 1153 cm^{-1} , C–N stretching vibration. ¹H NMR (300 MHz, D₂O, 298 K) δ ppm 0.65 - 1.43 (m, 6 H) 1.50 - 2.48 (m, 4 H) 3.29 (br. s., 18 H) 3.70 (s, 5 H) 4.22 - 4.64 (m, 4 H). EA experiment (calculated): C 43.8% (50.6%), H 9.7% (7.7%), N

5.3% (8.1%). Value $dn/dc = 0.132$ mL/g. $M_n(\text{GPC}) = 61.7$ kg/mol, $PDI = 5.56$. $M_n(^1\text{H NMR}) = 300.0$ kg/mol.

C1^{CN}. FTIR (ATR, 298 K): 3027 cm^{-1} , C–N asymmetric stretching vibration; 2248 cm^{-1} , CN stretching vibration; 1724 cm^{-1} and 1625 cm^{-1} , C=O stretching; 1463 cm^{-1} , C–H scissor vibration; 1149 cm^{-1} C–N stretching vibration. $^1\text{H NMR}$ (300 MHz, D₂O, 298 K) δ ppm 0.62 - 1.58 (m, 3 H) 2.27 (br. s., 4 H) 2.73 (br. s., 2 H) 3.26 (br. s., 6 H) 3.58 (br. s., 2 H) 3.70 - 4.10 (m, 2 H) 4.20 - 4.68 (m, 1 H). EA experiment (calculated): C 53.1% (55.3%), H 9.0% (8.1%), N 10.1% (10.7%). Value $dn/dc = 0.149$ mL/g. GPC $M_n(\text{GPC}) = 90.2$ kg/mol, $PDI = 3.7$.

C2^{CN}. FTIR (ATR, 298 K): 3027 cm^{-1} , C–N asymmetric stretching vibration; 2248 cm^{-1} , CN stretching vibration; 1724 cm^{-1} and 1625 cm^{-1} , C=O stretching; 1415 cm^{-1} , C–H deformation of CH₂; 1091 cm^{-1} , C–N stretching vibration. $^1\text{H NMR}$ (300 MHz, D₂O, 298 K) δ ppm 0.61 - 1.43 (m, 3 H) 1.63 - 2.40 (m, 4 H) 2.59 - 2.85 (m, 2 H) 3.25 (br. s., 6 H) 3.47 - 3.73 (m, 3 H) 3.87 (br. s., 2 H) 4.34 - 4.60 (m, 2 H). EA experiment (calculated): C 17.4% (55.3%), H 6.9% (8.1%), N 16.5% (10.7%). Value $dn/dc = 0.158$ mL/g. $M_n(\text{GPC}) = 82.2$ kg/mol, $PDI = 5.47$. $M_n(^1\text{H NMR}) = 67.3$ kg/mol.

C3^{CN}. FTIR (ATR, 298 K): 3027 cm^{-1} , C–N asymmetric stretching vibration; 2248 cm^{-1} , CN stretching vibration; 1724 cm^{-1} and 1625 cm^{-1} , C=O stretching; 1415 cm^{-1} , C–H deformation of CH₂; 1091 cm^{-1} , C–N stretching vibration. $^1\text{H NMR}$ (300 MHz, D₂O, 298 K) δ ppm 0.56 - 1.45 (m, 8 H) 1.58 - 2.38 (m, 8 H) 2.54 - 2.84 (m, 5 H) 3.07 - 3.40 (m, 12 H) 3.45 - 3.72 (m, 6 H) 3.74 - 3.98 (m, 5 H) 4.26 - 4.60 (m, 3 H). EA experiment (calculated): C 20.4% (55.3%), H 9.1% (8.1%), N 15.8% (10.7%). Value $dn/dc = 0.159$ mL/g. $M_n(\text{GPC}) = 119.0$ kg/mol, $PDI = 4.02$. $M_n(^1\text{H NMR}) = 85.8$ kg/mol.

C4^{CN}. FTIR (ATR, 298 K): 3027 cm⁻¹, C–N asymmetric stretching vibration; 2248 cm⁻¹, CN stretching vibration; 1724 cm⁻¹ and 1625 cm⁻¹, C=O stretching; 1463 cm⁻¹, C–H scissor vibration; 1149 cm⁻¹ C–N stretching vibration. ¹H NMR (300 MHz, D₂O, 298 K) δ ppm 0.56 - 1.43 (m, 7 H) 1.52 - 2.46 (m, 8 H) 2.68 (br. s., 4 H) 3.21 (br. s., 12 H) 3.58 (br. s., 6 H) 3.82 (br. s., 6 H) 4.23 - 4.63 (m, 3 H). EA experiment (calculated): C 50.4% (55.3%), H 8.1% (8.1%), N 10.0% (10.7%). M_n(GPC) = 111.3 g/mol, PDI = 4.83. M_n(¹H NMR) = 1293.3 kg/mol.

A1. FTIR (ATR, 298 K): 3046 cm⁻¹, C–N stretching vibration; 2969 cm⁻¹, C–H stretching of R–CH₃; 1724 cm⁻¹ and 1650 cm⁻¹, C=O stretching vibration; 1481 cm⁻¹, C–H symmetrical deformation vibration of N–CH₃; 1419 cm⁻¹, C–H deformation vibration of CH₂; 1153 cm⁻¹, C–N stretching vibration; 1037 cm⁻¹, symmetric stretching vibration of SO₃. ¹H NMR (300 MHz, D₂O + KCl, 298 K) δ ppm 0.56 - 1.47 (m, 6 H) 1.50 - 2.36 (m, 5 H) 2.86 - 3.12 (m, 2 H) 3.15 - 3.50 (m, 9 H) 3.62 - 3.97 (m, 2 H) 3.99 - 4.32 (m, 2 H) 4.33 - 4.62 (m, 2 H). EA experiment (calculated): C 39.3% (50.6%), H 6.6% (7.7%), N 4.0% (3.7%), S 6.9% (8.5%). Value dn/dc = 0.150 mL/g.

A2. FTIR (ATR, 298 K): 3046 cm⁻¹, C–N stretching vibration; 2969 cm⁻¹, C–H stretching of R–CH₃; 1724 cm⁻¹ and 1650 cm⁻¹, C=O stretching vibration; 1481 cm⁻¹, C–H symmetrical deformation vibration of N–CH₃; 1419 cm⁻¹, C–H deformation vibration of CH₂; 1153 cm⁻¹, C–N stretching vibration; 1037 cm⁻¹, symmetric stretching vibration of SO₃. ¹H NMR (300 MHz, D₂O + KCl, 298 K) δ ppm 0.38 - 1.47 (m, 6 H) 1.50 - 2.38 (m, 5 H) 2.86 - 3.10 (m, 2 H) 3.13 - 3.41 (m, 9 H) 3.65 - 3.94 (m, 2 H) 3.99 - 4.32 (m, 2 H) 4.34 - 4.64 (m, 2 H). EA experiment (calculated): C 43.9% (50.6%), H 7.8% (7.7%), N 4.7% (3.7%), S 9.5% (8.5%). Value dn/dc = 0.134 mL/g. M_n(¹H NMR) = 764.0 kg/mol.

A3. FTIR (ATR, 298 K): 3046 cm^{-1} , C–N stretching vibration; 2969 cm^{-1} , C–H stretching of R–CH₃; 1724 cm^{-1} and 1650 cm^{-1} , C=O stretching vibration; 1481 cm^{-1} , C–H symmetrical deformation vibration of N–CH₃; 1419 cm^{-1} , C–H deformation vibration of CH₂; 1153 cm^{-1} , C–N stretching vibration; 1037 cm^{-1} , symmetric stretching vibration of SO₃. ¹H NMR (300 MHz, D₂O + KCl, 298 K) δ ppm 0.49 - 1.48 (m, 12 H) 2.13 (br. s., 11 H) 3.00 (br. s., 5 H) 3.15 - 3.43 (m, 18 H) 3.66 - 3.96 (m, 5 H) 3.99 - 4.34 (m, 4 H) 4.35 - 4.65 (m, 3 H). EA experiment (calculated): C 46.5% (50.6%), H 7.7% (7.7%), N 3.8% (3.7%), S 8.6% (8.5%). Value dn/dc = 0.137 mL/g. $M_n(^1\text{H NMR}) = 443.3 \text{ kg/mol}$.

A4. FTIR (ATR, 298 K): 3046 cm^{-1} , C–N stretching vibration; 2969 cm^{-1} , C–H stretching of R–CH₃; 1724 cm^{-1} and 1650 cm^{-1} , C=O stretching vibration; 1481 cm^{-1} , C–H symmetrical deformation vibration of N–CH₃; 1419 cm^{-1} , C–H deformation vibration of CH₂; 1153 cm^{-1} , C–N stretching vibration; 1103 cm^{-1} , asymmetric stretching deformation of SO₃; 1037 cm^{-1} , symmetric stretching vibration of SO₃. ¹H NMR (300 MHz, D₂O + KCl, 298 K) δ ppm 0.57 - 1.44 (m, 12 H) 1.56 - 2.30 (m, 12 H) 2.90 - 3.10 (m, 5 H) 3.12 - 3.38 (m, 18 H) 3.64 - 3.93 (m, 8 H) 4.02 - 4.30 (m, 4 H) 4.37 - 4.62 (m, 4 H). EA experiment (calculated): C 37.4% (50.6%), H 7.4% (7.7%), N 6.9% (3.7%), S 11.7% (8.5%). Value dn/dc = 0.165 mL/g. $M_n(^1\text{H NMR}) = 2429.4 \text{ kg/mol}$.

A1^{CN}. FTIR (ATR, 298 K): 3046 cm^{-1} , C–N stretching vibration; 2252 cm^{-1} , CN stretching vibration; 1724 cm^{-1} and 1646 cm^{-1} , C=O stretching vibration; 1415 cm^{-1} , C–H CH₂ deformation vibration; 1149 cm^{-1} C–N stretching vibration; 1110 cm^{-1} asymmetric stretching vibration of SO₃; 1041 cm^{-1} symmetric stretching vibration of SO₃. ¹H NMR (300 MHz, D₂O + KCl, 298 K) δ ppm 0.76 - 1.52 (m, 7 H) 1.72 - 2.36 (m, 6 H) 2.37 - 2.57 (m, 2 H) 2.77 - 2.99 (m, 2 H) 3.05 - 3.26 (m, 2 H) 3.42 (br. s., 6 H) 3.60 - 3.85 (m, 2 H) 3.88 - 4.16 (m, 2 H) 4.18 - 4.45 (m, 2 H) 4.54

- 4.70 (m, 1 H). EA experiment (calculated): C 36.2% (52.8%), H 6.9% (7.5%), N 9.2% (6.5%), S 11.9% (7.4%). Value dn/dc = 0.144 mL/g.

A2^{CN}. FTIR (ATR, 298 K): 3046 cm⁻¹, C–N stretching vibration; 2252 cm⁻¹, CN stretching vibration; 1724 cm⁻¹ and 1646 cm⁻¹, C=O stretching vibration; 1415 cm⁻¹, C–H CH₂ deformation vibration; 1149 cm⁻¹ C–N stretching vibration; 1110 cm⁻¹ asymmetric stretching vibration of SO₃; 1041 cm⁻¹ symmetric stretching vibration of SO₃. ¹H NMR (300 MHz, D₂O + KCl, 298 K) δ ppm 0.49 - 1.44 (m, 7 H) 1.57 - 2.49 (m, 8 H) 2.65 - 2.87 (m, 2 H) 2.89 - 3.14 (m, 2 H) 3.30 (br. s., 6 H) 3.51 - 3.75 (m, 3 H) 3.78 - 4.02 (m, 2 H) 4.06 - 4.35 (m, 2 H) 4.41 - 4.67 (m, 1 H). EA experiment (calculated): C 29.4% (52.8%), H 6.0% (7.5%), N 9.4% (6.5%), S 11.9% (7.4%). Value dn/dc = 0.146 mL/g. M_n(¹H NMR) = 179.1 kg/mol.

A3^{CN}. FTIR (ATR, 298 K): 3046 cm⁻¹, C–N stretching vibration; 2252 cm⁻¹, CN stretching vibration; 1724 cm⁻¹ and 1646 cm⁻¹, C=O stretching vibration; 1415 cm⁻¹, C–H CH₂ deformation vibration; 1149 cm⁻¹ C–N stretching vibration; 1110 cm⁻¹ asymmetric stretching vibration of SO₃; 1041 cm⁻¹ symmetric stretching vibration of SO₃. ¹H NMR (300 MHz, D₂O + KCl, 298 K) δ ppm 0.50 - 1.46 (m, 8 H) 1.60 - 2.47 (m, 9 H) 2.63 - 2.85 (m, 2 H) 2.91 - 3.13 (m, 3 H) 3.17 - 3.45 (m, 6 H) 3.50 - 3.69 (m, 2 H) 3.70 - 3.78 (m, 2 H) 3.79 - 3.99 (m, 2 H) 4.06 - 4.32 (m, 2 H) 4.37 - 4.65 (m, 2 H). EA experiment (calculated): C 35.6% (52.8%), H 7.0% (7.5%), N 9.3% (6.5%), S 10.7% (7.4%). Value dn/dc = 0.146 mL/g. M_n(¹H NMR) = 123.6 kg/mol.

A4^{CN}. FTIR (ATR, 298 K): 3046 cm⁻¹, C–N stretching vibration; 2252 cm⁻¹, CN stretching vibration; 1724 cm⁻¹ and 1646 cm⁻¹, C=O stretching vibration; 1465 cm⁻¹ C–H scissor vibration; 1415 cm⁻¹, C–H CH₂ deformation vibration; 1149 cm⁻¹ C–N stretching vibration; 1110 cm⁻¹ asymmetric stretching vibration of SO₃; 1041 cm⁻¹ symmetric stretching vibration of SO₃. ¹H NMR (300 MHz, D₂O + KCl, 298 K) δ ppm 0.80 - 1.53 (m, 13 H) 1.68 - 2.61 (m, 17 H) 2.79 -

2.97 (m, 4 H) 3.06 - 3.22 (m, 5 H) 3.41 (br. s., 12 H) 3.64 - 3.90 (m, 38 H) 3.92 - 4.12 (m, 4 H) 4.17 - 4.40 (m, 4 H). EA experiment (calculated): C 39.0% (52.8%), H 7.0% (7.5%), N 7.1% (6.5%), S 7.9% (7.4%). Value $dn/dc = 0.152$ mL/g. $M_n(^1H\text{ NMR}) = 397.2$ kg/mol.

B1. FTIR (ATR, 298 K): 2981 cm^{-1} , C–H stretching vibration of R–CH₃; 1731 cm^{-1} and 1650 cm^{-1} , C=O stretching vibration; 1484 cm^{-1} , CH scissor vibration; 1184 cm^{-1} , C–N stretching vibration, 1041 cm^{-1} , symmetric stretching of SO₃; 962 cm^{-1} , S–O–C asymmetric stretching; 929 cm^{-1} , S–O–C symmetric stretching. ¹H NMR (300 MHz, D₂O + KCl, 298 K) δ ppm 0.66 - 1.59 (m, 3 H) 1.63 - 2.57 (m, 5 H) 2.89 - 3.15 (m, 4 H) 3.39 (s, 10 H) 3.75 (s, 7 H) 3.81 - 4.03 (m, 3 H) 4.38 - 4.65 (m, 3 H). EA experiment (calculated): C 42.6% (47.3%), H 10.1% (7.6%), N 4.6% (5.0%), S 10.0% (11.5%). Value $dn/dc = 0.143$ mL/g. $M_n(\text{AF4}) = 1053.0$ kg/mol, PDI = 1.80.

B2. FTIR (ATR, 298 K): 2981 cm^{-1} , C–H stretching vibration of R–CH₃; 1731 cm^{-1} and 1650 cm^{-1} , C=O stretching vibration; 1484 cm^{-1} , CH scissor vibration; 1184 cm^{-1} , C–N stretching vibration, 1041 cm^{-1} , symmetric stretching of SO₃; 962 cm^{-1} , S–O–C asymmetric stretching; 929 cm^{-1} , S–O–C symmetric stretching. ¹H NMR (300 MHz, D₂O + KCl, 298 K) δ ppm 0.52 - 1.40 (m, 4 H) 1.55 - 2.50 (m, 5 H) 3.05 (br. s., 2 H) 3.30 (br. s., 6 H) 3.52 - 3.76 (m, 2 H) 3.78 - 4.04 (m, 2 H) 4.32 - 4.63 (m, 2 H). EA experiment (calculated): C 42.3% (47.3%), H 10.2% (7.6%), N 4.6% (5.0%), S 10.1% (11.5%). Value $dn/dc = 0.085$ mL/g. $M_n(^1H\text{ NMR}) = 630.8$ kg/mol, $M_n(\text{AF4}) = 1746.0$ kg/mol, PDI = 1.52.

B3. FTIR (ATR, 298 K): 2981 cm^{-1} , C–H stretching vibration of R–CH₃; 1731 cm^{-1} and 1650 cm^{-1} , C=O stretching vibration; 1484 cm^{-1} , CH scissor vibration; 1184 cm^{-1} , C–N stretching vibration, 1041 cm^{-1} , symmetric stretching of SO₃; 962 cm^{-1} , S–O–C asymmetric stretching; 929 cm^{-1} , S–O–C symmetric stretching. ¹H NMR (300 MHz, D₂O + KCl, 298 K) δ ppm 0.53 - 1.52 (m, 3 H) 1.60 - 2.53 (m, 4 H) 3.02 (br. s., 2 H) 3.27 (br. s., 6 H) 3.51 - 3.72 (m, 2 H) 3.85 (br. s.,

2 H) 4.26 - 4.64 (m, 2 H). EA experiment (calculated): C 42.9% (47.3%), H 10.1% (7.6%), N 4.6% (5.0%), S 10.3% (11.5%). Value $dn/dc = 0.144$ mL/g. $M_n(^1H\text{ NMR}) = 555.9$ kg/mol.

B4. FTIR (KBr, 298 K): 2981 cm^{-1} , C–H stretching vibration of R–CH₃; 1731 cm^{-1} and 1650 cm^{-1} , C=O stretching vibration; 1484 cm^{-1} , CH scissor vibration; 1184 cm^{-1} , C–N stretching vibration, 1041 cm^{-1} , symmetric stretching of SO₃; 962 cm^{-1} , S–O–C asymmetric stretching; 929 cm^{-1} , S–O–C symmetric stretching. ¹H NMR (300 MHz, D₂O + KCl, 298 K) δ ppm 0.71 - 1.49 (m, 4 H) 1.61 - 2.54 (m, 5 H) 3.03 - 3.21 (m, 2 H) 3.38 (br. s., 6 H) 3.59 - 3.83 (m, 2 H) 3.84 - 4.16 (m, 2 H) 4.43 - 4.66 (m, 2 H). EA experiment (calculated): C 42.1% (47.3%), H 10.2% (7.6%), N 4.5% (5.0%), S 10.6% (11.5%). Value $dn/dc = 0.138$ mL/g. $M_n(^1H\text{ NMR}) = 11760.4$ kg/mol, $M_n(\text{AF4}) = 1133.0$ kg/mol, PDI = 1.28.

S1: Polymerization conditions and nomenclature of the polymers used in the current study. For chemical structures see Figure 2. TMAEMA is 2-(Trimethylamino)ethyl methacrylate, CPDMAEMA is 2-((3-Cyanopropyl)-dimethylammonium)ethyl methacrylate chloride, SPM is 3-Sulfopropyl methacrylate potassium salt, MEDSAH is [2-(Methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl)ammonium hydroxide. Ampholytic polymers are labeled “A” followed by a number. Betaines are labeled “B” followed by a number. Cationic polymers are labeled “C” followed by a number. An additional superscript “CN” in the label denotes samples quaternized with the cyanopropyl group instead of the methyl group. RT is room temperature.

Polymer composition	Polymer Monomer abbreviation	Initiator Type and mg	Solvent [mL]	Reaction time [min]	Reaction temperature [°C]	Purification	Yield mass / %
P(TMAEMA)	C1 TMAEMA 4.7 mL	KPDS 31.8 mg	19.3	90	60	reduce volume to 50% and precipitate in 500 mL acetonitrile dissolve in 5 mL water and precipitate in 500 mL acetonitrile	4.01 g, 97%

Polymer composition	Polymer abbreviation	Monomer	Initiator Type and mg	Solvent [mL]	Reaction time [min]	Reaction temperature [°C]	Purification	Yield mass / %
MPEO5000-b-P(TMAEMA)	C2	TMAEMA 5.86 mL	MI1 256 mg, 19 mg CuCl, 18 µL TMEDA	10	150	RT	precipitate in 300 mL isopropylalcohol	3.00 g, 50%
P(TMAEMA)-b-PEO4600-b-P(TMAEMA)	C3	TMAEMA 5.86 mL	MI4 195 mg, 38 mg CuCl, 36 µL TMEDA	10	150	RT	dissolve in 5 mL water, precipitate in isopropylalcohol and wash with MTBE	1.1 g, 21%

Polymer composition	Polymer abbreviation	Monomer	Initiator Type and mg	Solvent [mL]	Reaction time [min]	Reaction temperature [°C]	Purification	Yield mass / %
P(CPDMAEMA)	C1 ^{CN}	CPDMAEMA 2.6 g	KPDS 16 mg	10	90	60	precipitate in 200 mL acetonitrile and wash with 81% MTBE dissolve in 5 mL water, precipitate in acetonitrile and wash with MTBE	2.1 g
MPEO5000-b-P(CPDMAEMA)	C2 ^{CN}	CPDMAEMA 5.22 g	MI1 205 mg, 19 mg CuCl, 18 µL TMEDA	20	100	RT	add 36 µL TMEDA and precipitate in 450 mL isopropylalcohol	4.5 g, 83%

Polymer composition	Polymer abbreviation	Monomer	Initiator Type and mg	Solvent [mL]	Reaction time [min]	Reaction temperature [°C]	Purification	Yield mass / %
P(CPDMAEMA)-b-PEO4600-b-P(CPDMAEMA)	C3 ^{CN}	CPDMAEMA 5.22 g	MI4 195 mg, 38 mg CuCl, 36 µL TMEDA	20	100	RT	dissolve in 10 mL water and precipitate in isopropylalcohol dissolve in 10 mL water and filtrate through 0.2 µm syringe filter	4.8 g, 90%
P(CPDMAEMA)-b-PEO100k-b-P(CPDMAEMA)	C4 ^{CN}	CPDMAEMA 5.22 g	MI5 406 mg, 38 mg CuCl, 36 µL TMEDA	20	100	RT	filtrate through 0.2 µm syringe filter	0.5 g, 9%

Polymer composition	Polymer abbreviation	Monomer	Initiator Type and mg	Solvent [mL]	Reaction time [min]	Reaction temperature [°C]	Purification	Yield mass / %
P(TMAEMA-co-SPM)	A1	TMAEMA 2.35 mL SPM 2.46 g	KPDS 32 mg	17.65	90	60	reduce volume to 50% and precipitate in 400mL acetonitrile dissolve in 20 mL pure water ($\rho=18.2 \text{ M}\Omega\cdot\text{cm}$) and add saturated $(\text{NH}_4)_2\text{SO}_4$ dissolve in 20 mL pure water and precipitate in 400 mL methanol	3.6 g, 79%

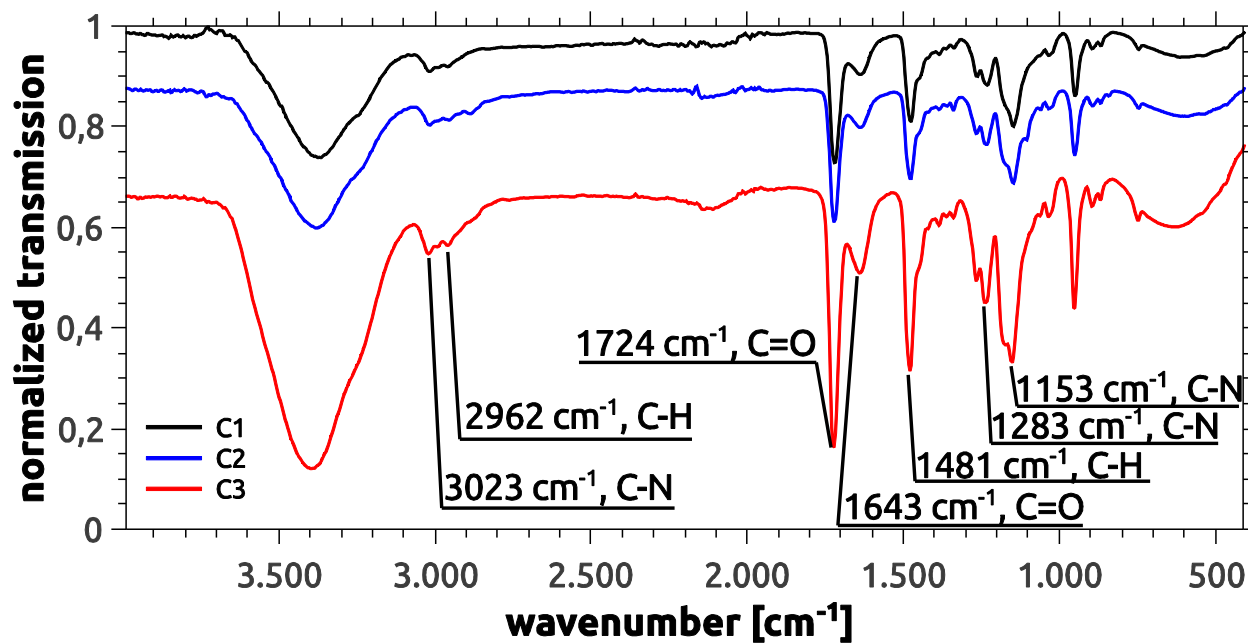
Polymer composition	Polymer abbreviation	Monomer	Initiator Type and mg	Solvent [mL]	Reaction time [min]	Reaction temperature [°C]	Purification	Yield mass / %
MPEO5000-b-	A2	TMAEMA	MI1 512 mg, 38 mg	20	150	RT		5.3 g,
P(TMAEMA-co-SPM)		5.86 mL SPM 6.16	CuCl, TMEDA	36 μL			precipitate in 400 mL methanol and wash with MTBE	50%
P(TMAEMA-co-SPM)-b-	A3	TMAEMA	MI4 242 mg, 38 mg	10	150	RT	2×dissolve in 100 mL water and add saturated (NH ₄) ₂ SO ₄	3.3 g, 60%
PEO4600-b- P(TMAEMA-co-SPM)		2.93 mL SPM 3.08 g	CuCl, TMEDA	36 μL			dissolve in 20 mL water and precipitate in 400 mL methanol	

Polymer composition	Polymer abbreviation	Monomer	Initiator Type and mg	Solvent [mL]	Reaction time [min]	Reaction temperature [°C]	Purification	Yield mass / %
P(TMAEMA-co-SPM)-b-PEO100k-b-P(TMAEMA-co-SPM)	A4	TMAEMA 2.93 mL SPM 3.08 g	MI5 500 mg, CuCl, TMEDA 38 mg 36 µL	20	150	RT		1.4 g, 34%
P(CPDMAEMA-co-SPM)	A1 ^{CN}	CPDMAEMA 2.46 g SPM 2.61 g	KPDS 32 mg	17.65	90	60		4.3 g 84%
P(CPDMAEMA-co-SPM)	A2 ^{CN}	CPDMAEMA 2.61 g SPM 2.46 g	MI1 204 mg, CuCl, TMEDA 19 mg 18 µL	15	120	RT	add saturated (NH ₄) ₂ SO ₄ 3×dissolve in 20 mL aq. KCl and add saturated (NH ₄) ₂ SO ₄	4.9 g, 93%

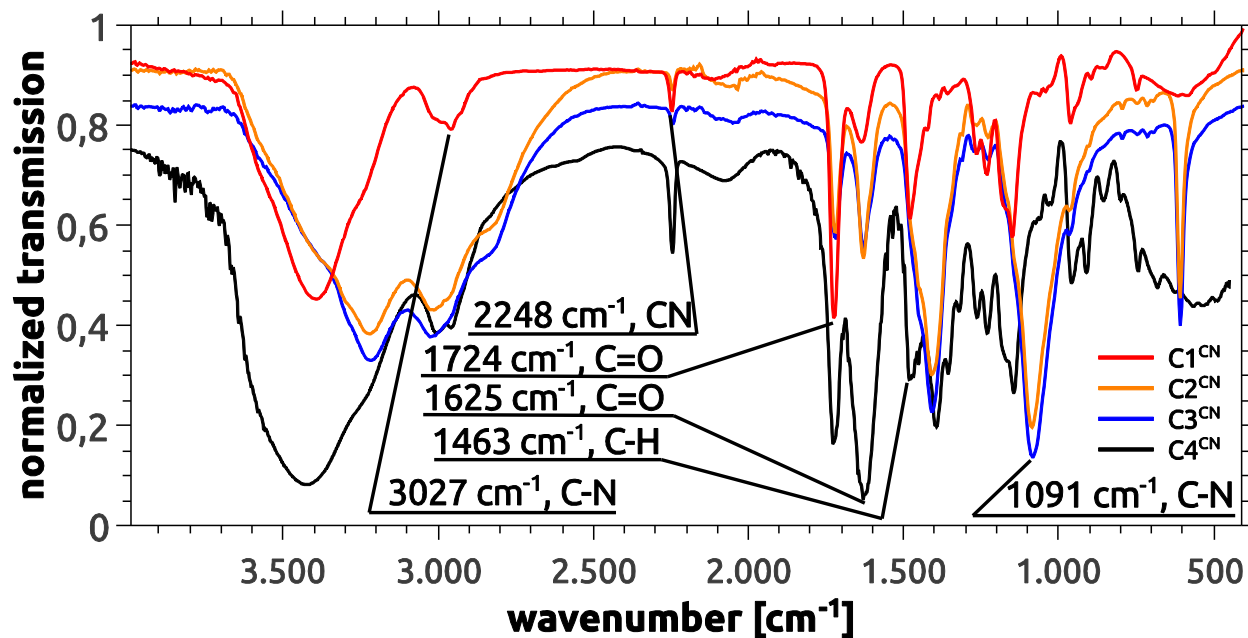
Polymer composition	Polymer abbreviation	Monomer	Initiator Type and mg	Solvent [mL]	Reaction time [min]	Reaction temperature [°C]	Purification	Yield mass / %
MPEO5000-b-P(CPDMAEMA-co-SPM)	A3 ^{CN}	CPDMAEMA 2.61 g SPM 2.46 g	MI4 195 mg, 38 mg CuCl, 36 µL TMEDA	15	120	RT		3.9 g, 74%
P(CPDMAEMA-co-SPM)-b-PEO4600-b-P(CPDMAEMA-co-SPM)	A4 ^{CN}	CPDMAEMA 2.61 g SPM 2.46 g	MI5 406 mg, 38 mg CuCl, 36 µL TMEDA			RT		2.1 g, 40%
P(MEDSAH)	B1	MEDSAH 5.0 g	KPDS 24.3 mg	18	90	60	add 60 mL water and wash with 200 mL methanol	4.48 g, 90%

Polymer composition	Polymer abbreviation	Monomer	Initiator Type and mg	Solvent [mL]	Reaction time [min]	Reaction temperature [°C]	Purification	Yield mass / %
MPEO5000-b-P(MEDSAH)	B2	MEDSAH 6.98 g	MI1 256 mg, 10 mg CuCl, 10 µL TMEDA	10	40	RT	add 60 mL water, separate by centrifugation suspend in 30 mL pure water	3.6 g, 51%
P(MEDSAH)-b-PEO4600-b-P(MEDSAH)	B3	MEDSAH 6.98 g	MI4 242 mg, 19 mg CuCl, 18 µL TMEDA	10	40	RT	and separate by centrifugation 2×dissolve in 15 mL aq. KCl and add saturated (NH ₄) ₂ SO ₄	3.8 g, 54%
P(MEDSAH)-b-PEO100k-b-P(MEDSAH)	B4	MEDSAH 6.98 g	MI5 507 mg, 19 mg CuCl, 18 µL TMEDA	20	40	RT	dissolve in water cool to 0°C 5×suspend in 25 mL pure water, separate by centrifugation	1.6 g, 22%

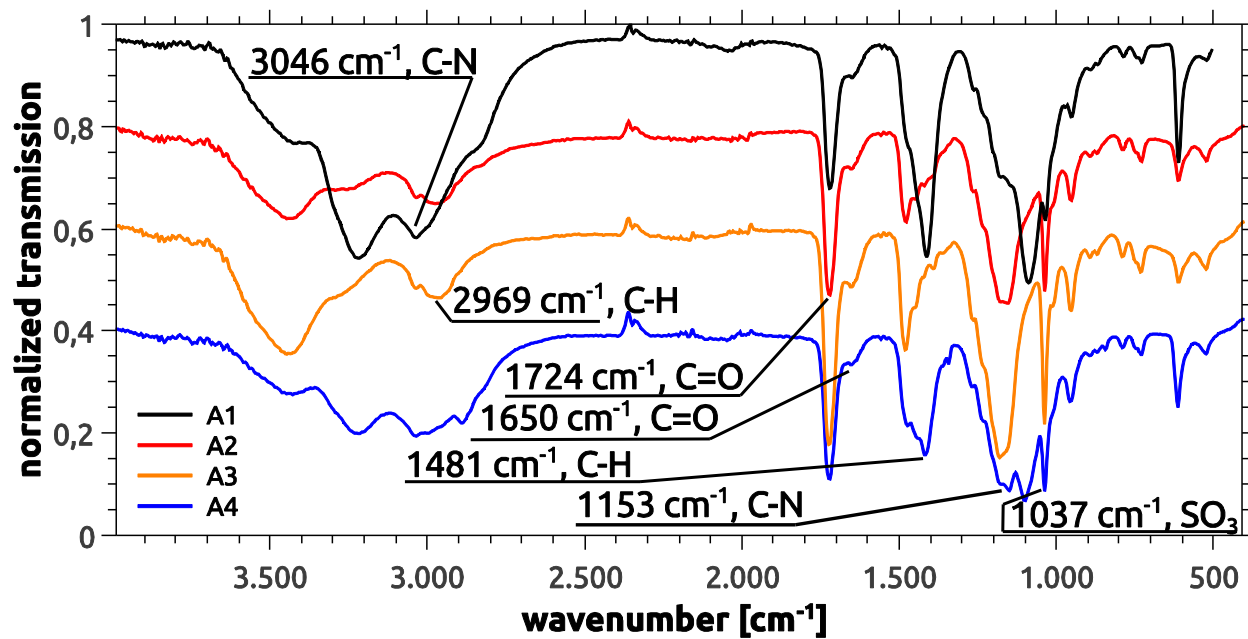
Infrared spectra



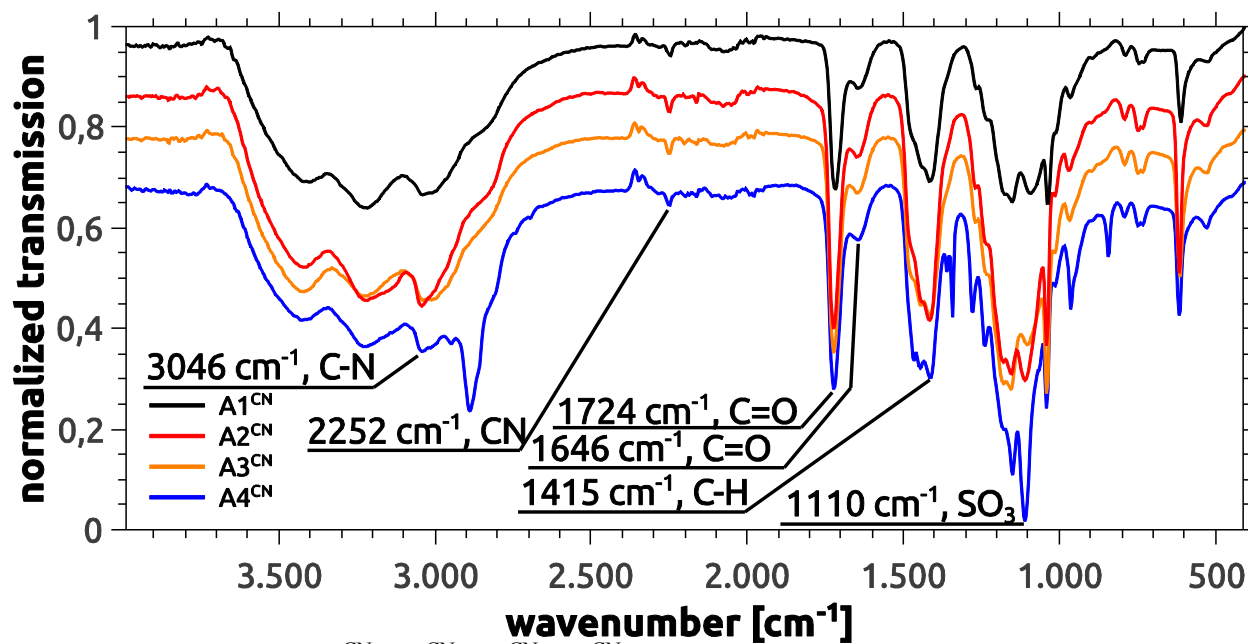
S2. Infrared spectra of C1, C2, C3



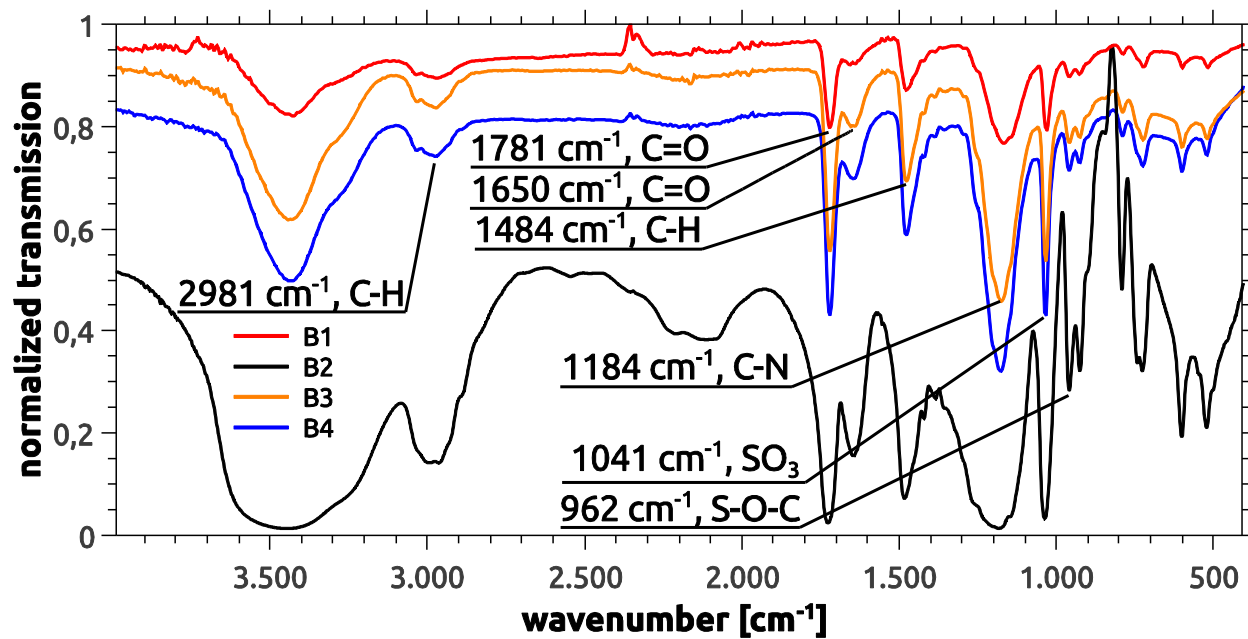
S3. Infrared spectra of C1^{CN}, C2^{CN}, C3^{CN}, C4^{CN}



S4. Infrared spectra of A1, A2, A3, A4

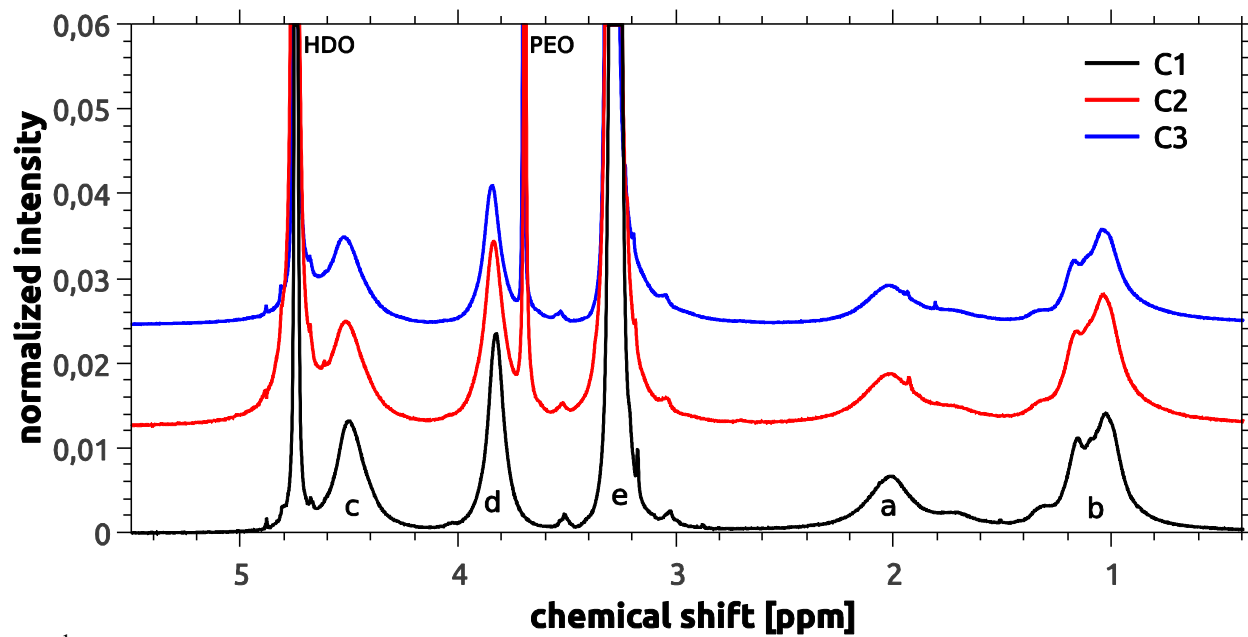


S5. Infrared spectra of A1^{CN}, A2^{CN}, A3^{CN}, A4^{CN}

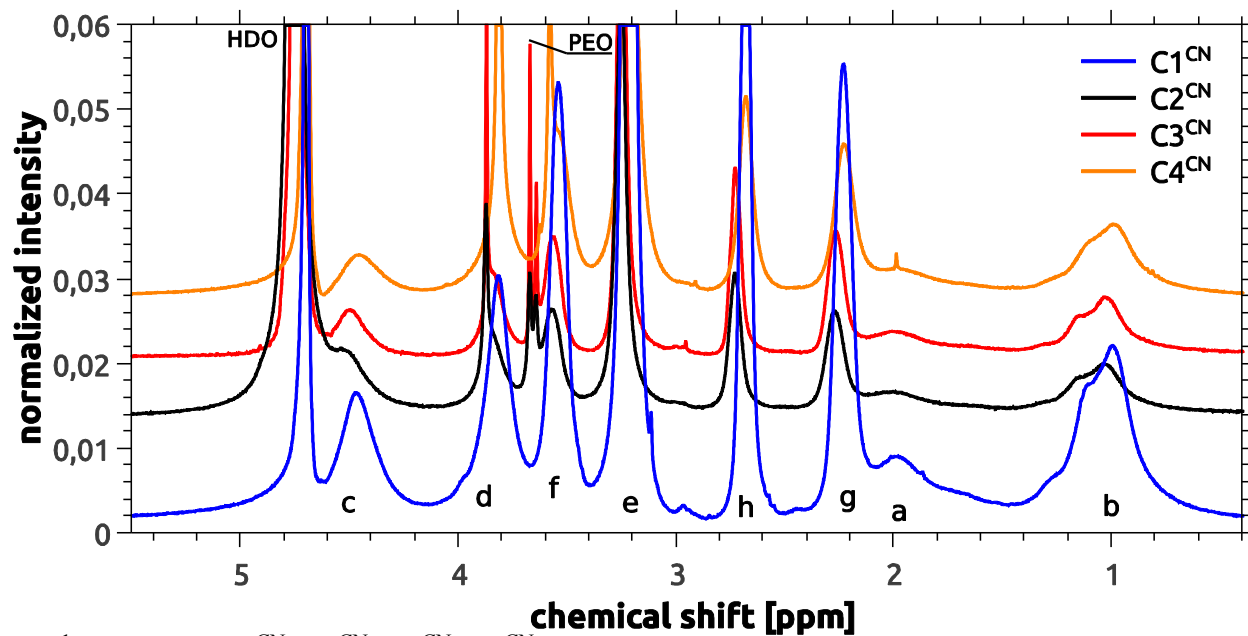


S6. ATR Infrared spectra of B1, B2, B3 and KBr infrared spectra of, B4.

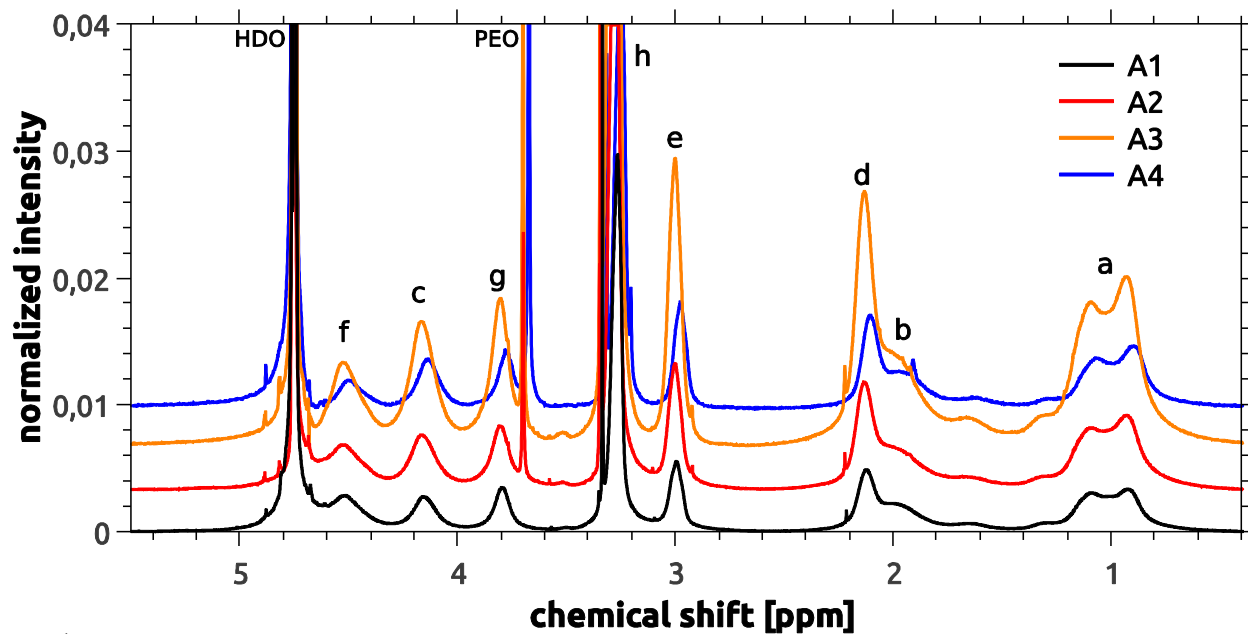
^1H NMR spectra



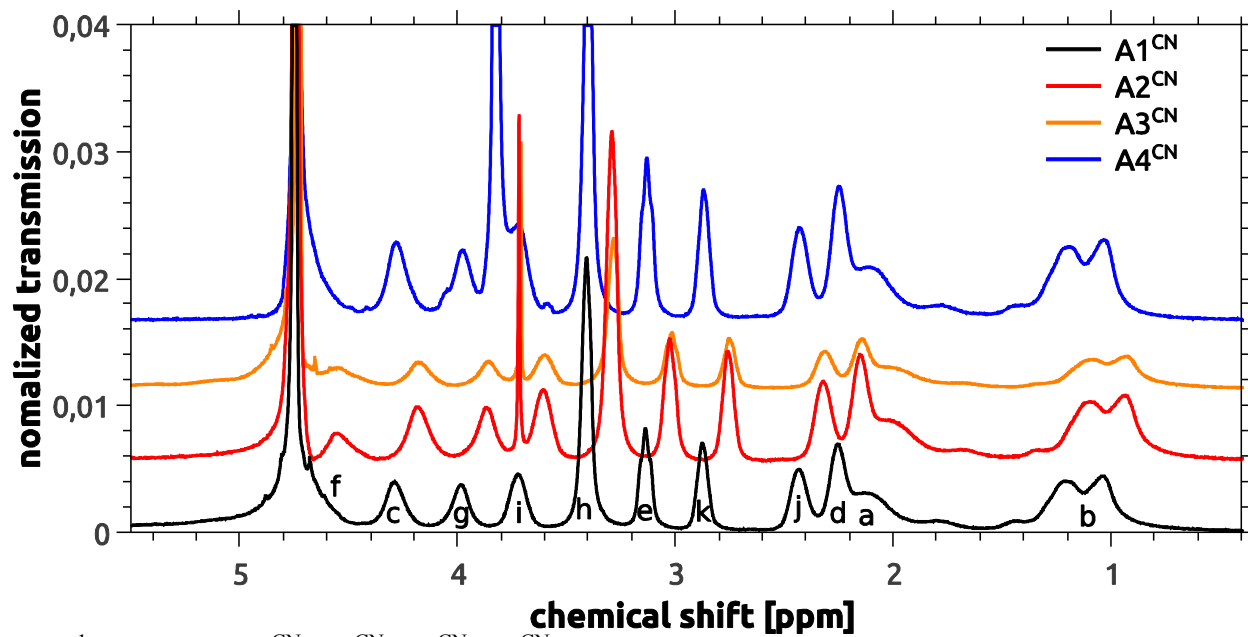
S7. ^1H NMR of C1, C2, C3



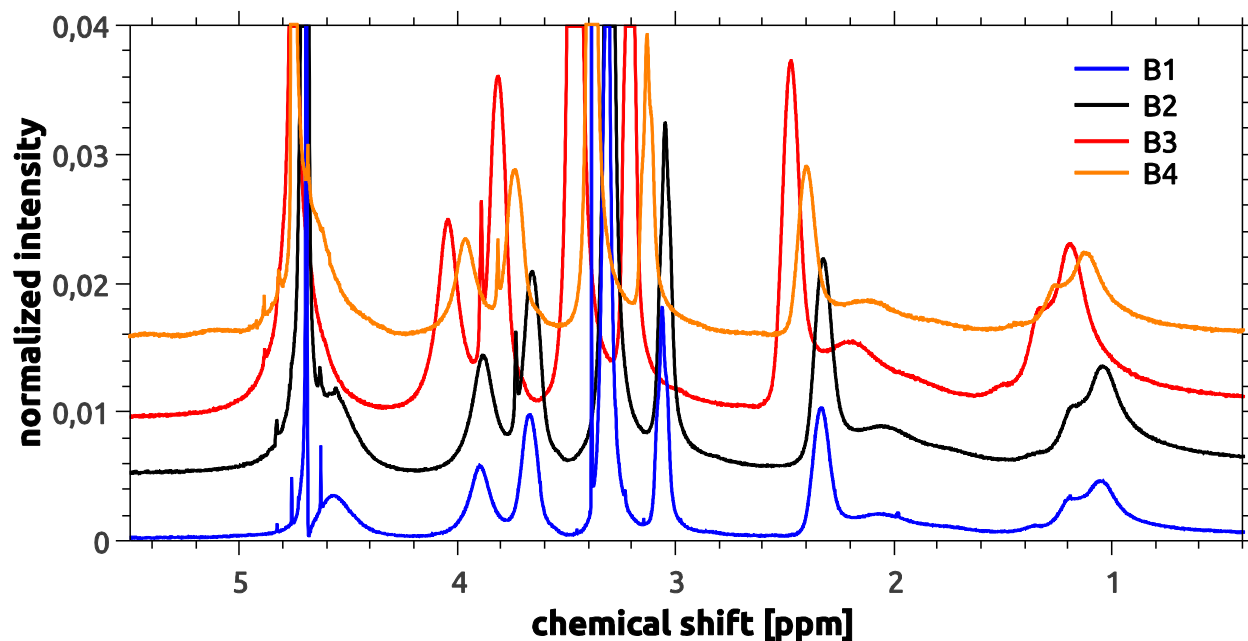
S8. ^1H NMR of C1^{CN}, C2^{CN}, C3^{CN}, C4^{CN}



S9. ^1H NMR of A1, A2, A3, A4



S10. ^1H NMR of A1^{CN}, A2^{CN}, A3^{CN}, A4^{CN}



S11. ^1H NMR of B1, B2, B3, B4

S12. Copper and potassium content of polymers measured by ICP-OES. A * means that the value is below the lower detection limit and < 0.05 means that the values are below the limit of quantification.

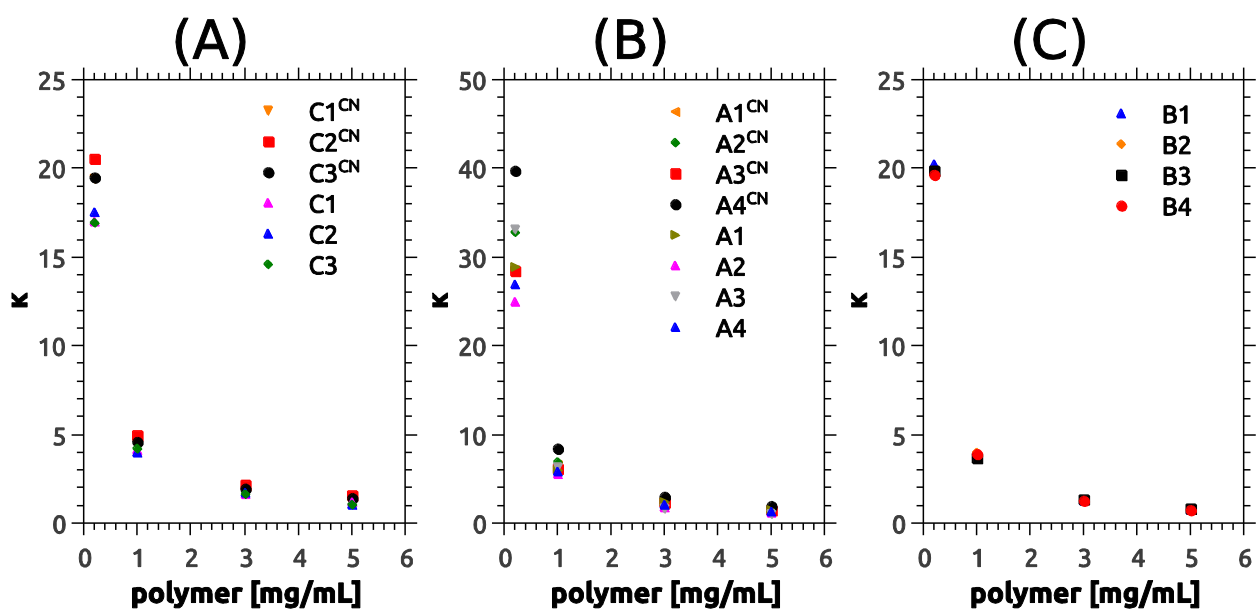
Polymer	$[\text{Cu}^{2+}]$ [mg/kg]	$\omega(\text{Cu}^{2+})$ [%]	$[\text{K}^+]$ [mg/kg]	$\omega(\text{K}^+)$ [%]
C1	*		*	
C2	1024	0.1	*	
C3	623	0.1	*	
C1 ^{CN}	< 0.05		629	0.1
C2 ^{CN}	97	0.0	28	0.0
C3 ^{CN}	85	0.0	24	0.0
C4 ^{CN}	2975	0.3	9	0.0
A1	*		742	0.1

Polymer	[Cu ²⁺] [mg/kg]	$\omega(\text{Cu}^{2+})$ [%]	[K ⁺] [mg/kg]	$\omega(\text{K}^+)$ [%]
A2	*		*	
A3	*		15	0.0
A4	*		5868	0.6
A1 ^{CN}	7.1	0.0	10950	1.1
A2 ^{CN}	13	0.0	47198	4.7
A3 ^{CN}	< 0.05	0.0	15829	1.6
A4 ^{CN}	68	0.0	17696	1.8
B1	*		757	0.1
B2	*		82	0.0
B3	*		29	0.0
B4	*		105	0.0

S13. Absolute data for calcium precipitation concentration Ca^P. Here Ca^P is the average of 3 measurements and SD the standard deviation.

Polymer	Ca ^P [mg/mL]	SD [mg/mL]	Polymer	Ca ^P [mg/mL]	SD [mg/mL]
C1	0.656	0.009	A4	0.765	0.009
C2	0.677	0.076	A1 ^{CN}	0.729	0.022
C3	0.707	0.041	A2 ^{CN}	0.716	0.034
C1 ^{CN}	0.696	0.012	A3 ^{CN}	0.698	0.007
C2 ^{CN}	0.950	0.071	A4 ^{CN}	0.717	0.013

Polymer	Ca ^P [mg/mL]	SD [mg/mL]	Polymer	Ca ^P [mg/mL]	SD [mg/mL]
C3 ^{CN}	0.963	0.079	B1	0.649	0.029
A1	0.743	0.005	B2	0.629	0.004
A2	0.691	0.009	B3	0.682	0.008
A3	0.718	0.011	B4	0.667	0.005



S14. κ of A) cationic polymers, B) ampholytic polymers and C) Betainic polymers

S15. Absolute calcium concentration after treatment of HAP powder with cationic, ampholytic and betainic homo- and block-copolymers and relative calcium dissolution per mL, κ .

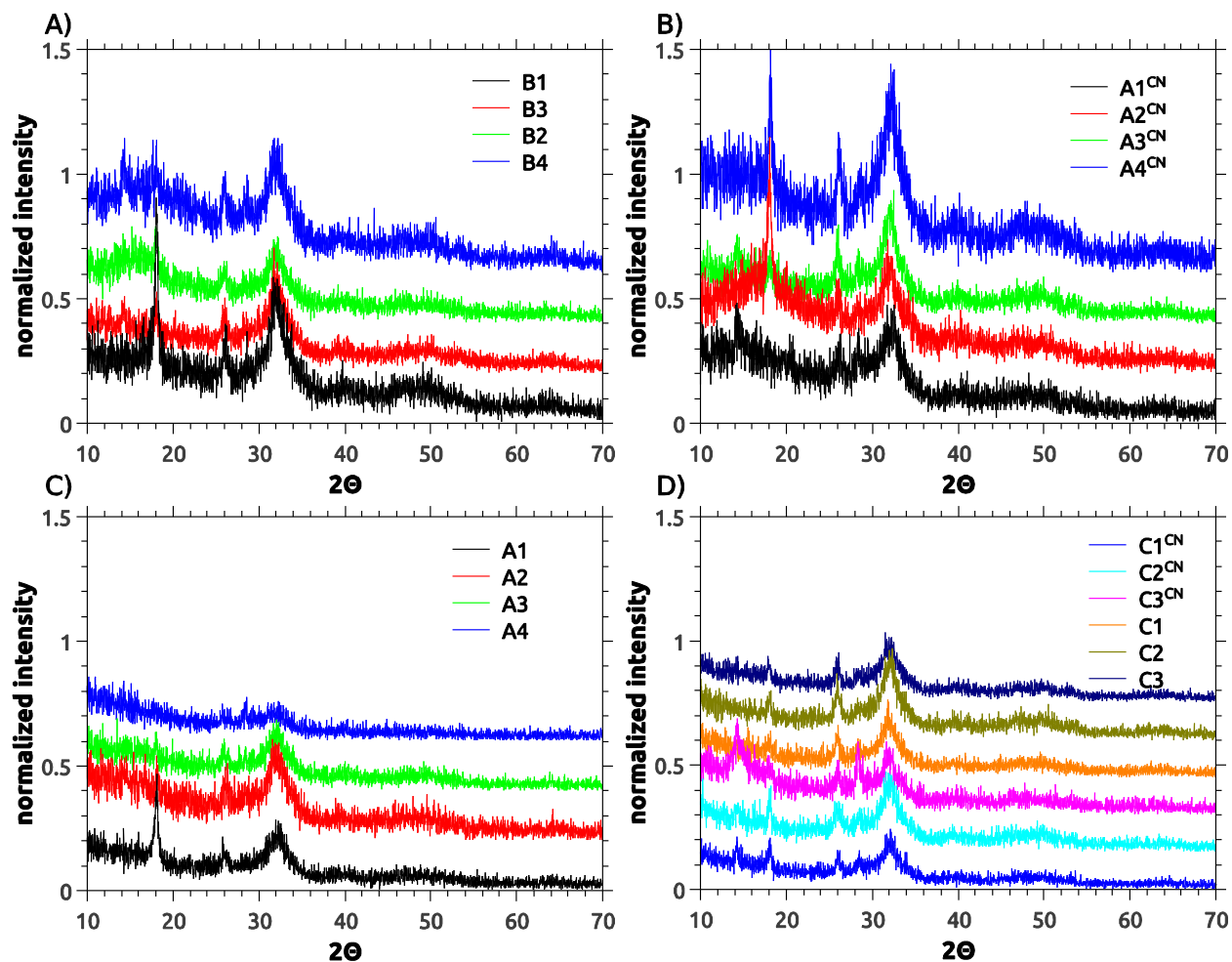
Polymer	0.2 mg/mL		1.0 mg/mL		3.0 mg/mL		5.0 mg/mL	
	[Ca ²⁺]	κ	[Ca ²⁺]	κ	[Ca ²⁺]	κ	[Ca ²⁺]	κ
C1	0.7093 ± 0.0559	17.03	0.8457 ± 0.0296	4.11	1.0270 ± 0.0160	1.68	1.2457 ± 0.0502	1.24
C2	0.6960 ± 0.0099	17.56	0.7857 ± 0.0896	4.00	0.9920 ± 0.0192	1.71	1.0023 ± 0.0127	1.04
C3	0.6960 ± 0.0107	16.95	0.8537 ± 0.0143	4.22	1.0163 ± 0.0078	1.69	1.0700 ± .0166	1.07
C1 ^{CN}	0.6493 ± 0.0046	19.43	0.7473 ± 0.0776	4.52	0.9323 ± 0.0120	1.91	0.9733 ± 0.0135	1.20
C2 ^{CN}	0.6370 ± 0.0102	20.55	0.7630 ± 0.0029	5.00	0.9683 ± 0.0070	2.15	1.1890 ± 0.0255	1.60
C3 ^{CN}	0.6180 ± 0.0107	19.48	0.7250 ± 0.0073	4.63	0.9147 ± 0.0196	1.98	1.1010 ± 0.0171	1.44
A1	0.6620 ± 0.0106	28.88	0.6903 ± 0.0058	6.04	0.8183 ± 0.0005	2.42	0.8340 ± 0.0926	1.48
A2	0.5767 ± 0.0715	25.00	0.6440 ± 0.0241	5.64	0.6203 ± 0.0567	1.81	0.7107 ± 0.0266	1.26
A3	0.7440 ± 0.0804	33.10	0.7160 ± 0.0857	6.35	0.5847 ± 0.0127	1.70	0.5787 ± 0.0007	1.01
A4	0.5937 ± 0.0630	26.94	0.6427 ± 0.0090	5.88	0.6847 ± 0.0026	2.10	0.7393 ± 0.0012	1.37
A1 ^{CN}	0.5777 ± 0.0735	28.36	0.6593 ± 0.0446	6.55	0.6523 ± 0.0338	2.16	0.7430 ± 0.0140	1.49

Polymer	0.2 mg/mL		1.0 mg/mL		3.0 mg/mL		5.0 mg/mL	
	[Ca ²⁺]	κ	[Ca ²⁺]	κ	[Ca ²⁺]	κ	[Ca ²⁺]	κ
A2 ^{CN}	0.6440 ± 0.0735	32.82	0.6803 ± 0.0446	6.97	0.7370 ± 0.0338	2.53	0.7430 ± 0.0140	1.53
A3 ^{CN}	0.5607 ± 0.0466	28.52	0.6087 ± 0.0029	6.24	0.6947 ± 0.0063	2.40	0.7353 ± 0.0790	1.53
A4 ^{CN}	0.5727 ± 0.0135	39.81	0.6043 ± 0.0154	8.45	0.6333 ± 0.0057	2.96	0.6743 ± 0.0090	1.90
B1	0.6333 ± 0.0101	20.26	0.6190 ± 0.0071	3.95	0.5983 ± 0.0012	1.27	0.5673 ± 0.0637	0.72
B2	0.6187 ± 0.110	19.91	0.6203 ± 0.0071	3.99	0.6050 ± 0.0180	1.30	0.5873 ± 0.0618	0.75
B3	0.6180 ± 0.0057	19.89	0.5817 ± 0.0582	3.72	0.6453 ± 0.0195	1.39	0.6153 ± 0.0110	0.79
B4	0.6110 ± 0.0135	19.68	0.6067 ± 0.0009	3.90	0.6077 ± 0.0029	1.30	0.5777 ± 0.0656	0.74

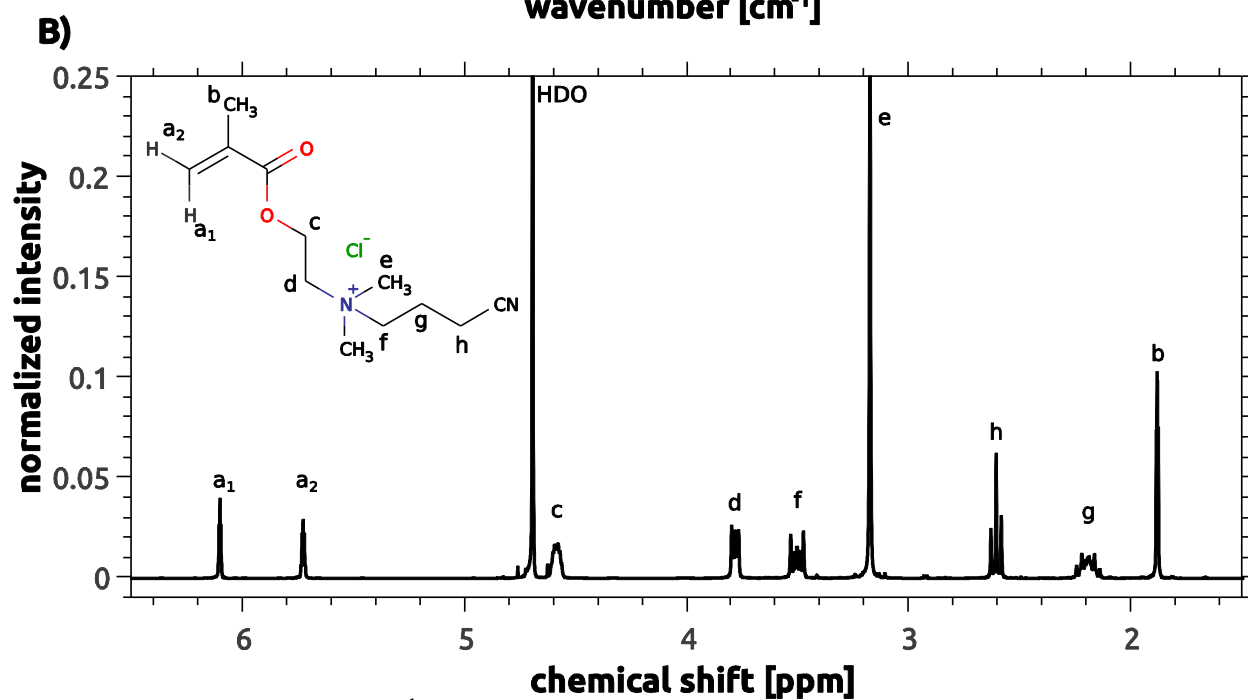
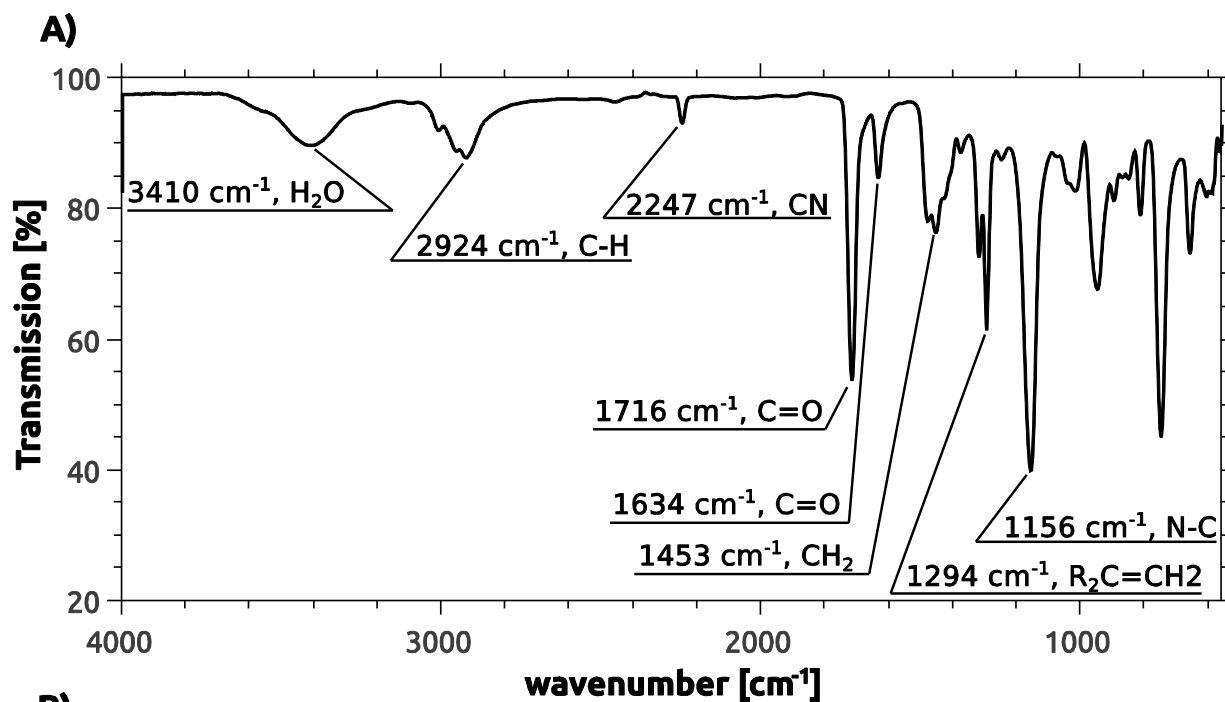
S16. EDX data of precipitates obtained in presence of polymers.

Polymer	Ca [Atom%]	P [Atom%]	S [Atom%]	Na [Atom%]	Cl [Atom%]	O [Atom%]
C1	20,9±0,2	15,0±0,1	1,0±0,1	1,2±0,1		61,9±0,2
C2	21,2±0,2	14,7±0,1	1,0±0,1	1,2±0,1		61,8±0,2
C3	21,1±0,2	14,9±0,1	0,96±0,1	1,2±0,1		61,9±0,3
C1 ^{CN}	19,2±0,2	16,8±0,2	0,3±0,1	0,6±0,1	0,5±0,1	62,5±0,3
C2 ^{CN}	20,2±0,2	15,2±0,2	1,1±0,1	1,4±0,1		62,1±0,3
C3 ^{CN}	19,9±0,2	15,2±0,2	1,2±0,1	1,4±0,1		62,3±0,3
A1	18,4±0,2	13,6±0,1	3,0±0,1	2,2±0,1	0,3±0,1	62,5±0,3
A2	20,5±0,3	13,6±0,1	2,6±0,1	0,7±0,1	0,2±0,1	62,5±0,2
A3	19,6±0,3	13,4±0,1	3,4±0,1	0,3±0,1		63,9±0,2
A4	20,0±0,3	13,5±0,2	3,0±0,1	0,5±0,1		63,0±0,3
A1 ^{CN}	15,8±0,3	10,6±0,2	7,6±0,2	0,7±0,1		65,4±0,4
A2 ^{CN}	19,8±0,2	13,9±0,2	2,8±0,1		0,3±0,1	63,2±0,3
A3 ^{CN}	19,8±0,2	13,9±0,2	3,0±0,1			63,4±0,3
A4 ^{CN}	16,4±0,2	10,9±0,2	7,0±0,2	0,8±0,1		64,9±0,3
B1	18,5±0,2	13,0±0,1	4,2±0,1	0,4±0,1		63,9±0,3
B2	19,0±0,2	13,6±0,1	3,4±0,1	0,5±0,1		63,5±0,3
B3	18,6±0,2	13,4±0,1	3,7±0,1	0,7±0,1		63,6±0,3
B4	19,0±0,2	13,1±0,1	3,7±0,1	0,7±0,1	0,2±0,1	63,3±0,3

S17. SEM recordings of the precipitates gained in presence of polymers. A) C1; B) C2; C) C3; D) C1^{CN}; E) C2^{CN}; F) C3^{CN}; G) A1; H) A2; I) A3; J) A4; K) A1^{CN}; L) A2^{CN}; M) A3^{CN}; N) A4^{CN}; O) B1; P) B2; Q) B3; R) B4.



S18. XRD recordings of precipitates from 2SBF gained in presence of polymer additives A) betainic polymers, B) amphiphilic polymers containing CPDMAEMA, C) amphiphilic polymers containing TMAEMA and D) cationic polymers.



S19. ATR Infrared spectra and ^1H NMR of CPDMAEMA/Cl