Supporting Information

Nitrogen-Containing Polymers as Potent Ionogens for Aqueous Solutions of Switchable Ionic Strength: Application to Separation of Organic Liquids and Clay Particles from Water

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1. Experimental Methods

1.1 Materials

Polyethyleneimines ("PEIs", M_W= 600, 1,800, 10,000), polymethyl methacrylate (M_W = 120,000), and 3-dimethylamino-1-propylamine (Alfa Aesar); iodoethane, iodopropane, iodobutane, polyacrylic acid (M_W = 1,800 and 450,000), and polystyrene-co-polymethyl methacrylate (40 mol% styrene, Sigma Aldrich); poly(diallylmethylamine) hydrochloride M_W = 5,000 (25 wt% solids in water) and polyacrylic acid (M_W = 50,000, 25% solution in water, Polysciences Inc.); polymethyl methacrylate (M_W = 15,000 and M_W = 35,000, Acros Organics); and polystyrene-co-polymethyl methacrylate (1.4, 10, 20, and 31 mol% styrene, Polymer Source) were purchased and used as received.

Kaolinite samples (obtained from Edgar, Florida) were purchased from Ward's Natural Science and used as received. The particle size (720 nm) and PDI (0.313) were measured using a Nano-ZS90 Zetasizer instrument (Malvern). Montmorillonite samples (obtained from Panther Creek, Colorado) were purchased from Ward's Natural Science and used as received. Due to the swelling character of montmorillonite, the particle size (20 µm) was estimated for a dry, rather than a wet sample, using a calibrated Nikon Eclipse E600-POL microscope. Oil sand tailing samples were obtained from the Northern Alberta Institute of Technology and had a solid content of 46%. The particle size was measured on a Malvern Mastersizer 2000 (size range from 0.05 to 2000 µm) equipped with a Hydro2000S optical unit, showing a broad range in particle size with two maxima at 1-60 µm and 160-2000 µm. The mineralogical composition of the tailings was studied by XRD analysis showing that the solids in the tailings mainly consist of quartz and kaolinite, with minor amounts of montmorillonite and illite. A sample of oil sand process water was obtained from Albion (Shell, Athabasca, Alberta). Deionized water with a resistivity of 18.2 MΩ·cm (Synergy® UV, Millipore) was used throughout this study. CO_2 (Supercritical Chromatographic Grade, 99.998%, Praxair) was used as received. 100 mL graduated cylinders (Kimble Kimax, single metric scale, 26 mm i.d., 20025H 50) were used for all settling tests. Consistency in cylinder dimensions is particularly important, as it has been reported that container height can influence settling rate.[1,2] ζ-potential measurements were taken on a Nano-ZS90 Zetasizer instrument (Malvern) using a dip cell.

2. Polymer synthesis

2.1 Methylated polyethyleneimines (MPEI, **1**)

In a 250 mL round bottom flask, 1.8 g (41.9 mmol, 1 eq) of the polyethyleneimine was dissolved in 9.73 mL (120 mmol, 2.9 eq) formaldehyde solution and 4.53 mL (120 mmol, 2.9 eq) formic acid. The flask was equipped with a condenser and the reaction mixture was heated to 60 °C for 16 h with an oil bath. The mixture was allowed to cool to room temperature and the solvents were removed under reduced pressure. Then, the crude product was dissolved in 20 mL EtOH (anhydrous) and 4 g of Amberlite resin was added to the solution. The resulting mixture was stirred for 16 h at room temperature before the resin was filtered and the EtOH was removed under reduced pressure. The methylated polymers were obtained as dark yellow oils.

2.1.1 Methylated polyethyleneimine (M_W: 600 g/mol before methylation)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.18-2.91 (m), no NH signal appears in the spectra;
^{13}C NMR ($CDCl_3$, 100.7 MHz): δ = 42.2, 44.1, 44.4, 50.5-56.0 (m).

2.1.2 Methylated polyethyleneimine (M_W: 1,800 g/mol before methylation)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.16 (s, CH_3), 2.23 (bs, CH_3), 2.44-2.64 (m), no NH signal appear in the spectra;
^{13}C NMR ($CDCl_3$, 100.7 MHz): δ = 41.5, 44.0, 50.8-51.1 (m), 53.7, 55.0.

2.1.3 Methylated polyethyleneimine (M_W: 10,000 g/mol before methylation)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.18 (s, CH_3), 2.21 (s, CH_3), 2.28-2.62 (m), no NH signal appear in the spectra;

^{13}C NMR ($CDCl_3$, 100.7 MHz): δ = 42.9, 43.0, 45.9, 46.0, 52.8-54.0 (m), 55.8-56.9 (m), 57.2-57.8 (m).

2.1.4 Methylated polyethyleneimine (M_W: 70,000 g/mol before methylation)

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.22 (bs, CH_3), 2.31-2.64 (m), no NH signal appear in the spectra;

^{13}C NMR ($CDCl_3$, 100.7 MHz): δ = 43.0, 43.1, 53.0, 53.1, 56.0, 56.1, 57.4.

2.2 Ethylated, *n*-propylated and n-butylated polyethylenimines (EPEI, PPEI, BPEI)

General procedure I (**GP I**): The iodoalkane (1.15 eq) was dissolved in absolute EtOH. To this, a solution of PEI (1.0 eq) in EtOH and solid K_2CO_3 (3.72 eq) was added. The round bottom flask was then equipped with a reflux condenser and the reaction mixture was heated to reflux (80 °C) for 3 days. After cooling to room temperature, another portion of K_2CO_3 (3.72 eq) was added and the mixture was refluxed again for 3 days. After cooling to room temperature, the K_2CO_3 was filtered off and the EtOH was removed under reduced pressure. The crude product was then dissolved in a mixture of 20 mL EtOAc and 20 mL 15% (w/v) NaOH solution in water. The phases were separated and the organic layer was washed twice with 10 mL 15% (w/v) NaOH solution in water. The organic layer was then dried with $MgSO_4$ and the solvent was removed under reduced pressure to yield yellow oils.

2.2.1 Ethylated Polyethyleneimines (EPEI, **2**)

2.2.1.1 Ethylated Polyethyleneimine (M_W: 600 g/mol before alkylation)

According to **GP I**, 3.1 mL (6.1 g, 39.0 mmol) iodoethane in 10 mL EtOH was reacted with 1.8 g (41.9 mmol) polyethyleneimine (MW= 600) in 10 mL EtOH in the presence of 8.3 g (60.0 mmol) K_2CO_3. Work-up with NaOH (3 x 10 mL) and EtOAc (10 mL) yielded 1.84 g (65%) of a light yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.969 (bt, 3H, CH_3), 2.39-2.56 (m, 6H, CH_2);

^{13}C NMR ($CDCl_3$, 100.7 MHz): δ = 11.8 (CH_3), 47.4 (CH_2 ethyl), 48.6 (CH_2 ethylene), 50.9-54.0 (CH_2 ethylene), NMR spectrum shows 9% quaternized nitrogens in the polymer;

IR (film) : $\tilde{\upsilon}$ [cm^{-1}] = 2967 (s), 2934 (m), 2808 (s), 1653 (w), 1457 (m), 1382 (w), 1292 (w), 1097 (w), 1062 (m).

2.2.1.2 Ethylated Polyethyleneimine (M_W: 1,800 g/mol before alkylation)

According to **GP I**, 3.1 mL (6.1 g, 39.0 mmol) iodoethane in 10 mL EtOH was reacted with 1.8 g (41.9 mmol) polyethyleneimine (MW= 1,800) in 10 mL EtOH in the presence of 8.3 g (60.0 mmol) K_2CO_3. Work-up with NaOH (3 x 10 mL) and EtOAc (10 mL) yielded 2.38 g (84%) of a light brown oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.91 (bt, 3H, CH_3), 2.38-2.54 (m, 6H, CH_2);

^{13}C NMR ($CDCl_3$, 100.7 MHz): δ = 11.8 (CH_3), 47.5 (CH_2 ethyl), 50.8-54.1 (CH_2 backbone);

IR (film): $\tilde{\upsilon}$ [cm^{-1}] = 2966 (s), 2933 (m), 2807 (s), 1456 (m), 1382 (w), 1292 (w), 1097 (w), 1061 (m).

2.2.1.3 Ethylated Polyethyleneimine (M_W: 10,000 g/mol before alkylation)

According to **GP I**, 3.1 mL (6.1 g, 39.0 mmol) iodoethane in 10 mL EtOH was reacted with 1.8 g (41.9 mmol) polyethyleneimine (MW= 10,000) in 10 mL EtOH in the presence of 8.3 g (60.0 mmol) K_2CO_3. Work-up with NaOH (3 x 10 mL) and EtOAc (10 mL) yielded 2.23 g (78%) of a light yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.98 (bt, 3H, CH_3), 1.40 (bs, remaining free NH), 2.42-2.62 (m, 6H, CH_2), NMR spectrum shows 7% quaternized nitrogens in the polymer;

^{13}C NMR ($CDCl_3$, 100.7 MHz): δ = 11.7 (CH_3), 47.4 (CH_2 ethyl), 47.8-54.0 (CH_2 backbone);

IR (film): $\tilde{\upsilon}$ [cm^{-1}] = 2973 (s), 2809 (s), 1643 (w), 1562 (w), 1471 (m), 1100 (w), 1055 (w).

2.2.2 *n*-Propylated polyethyleneimines (PPEI, **3**)

2.2.2.1 Propylated Polyethyleneimine (M_W: 600 g/mol before alkylation)

According to **GP I**, 4.7 mL (8.2 g, 48.0 mmol) iodopropane in 10 mL EtOH was reacted with 1.8 g (41.9 mmol) polyethyleneimine (MW= 600) in 10 mL EtOH in the presence of 21.6 g (156.0 mmol) K_2CO_3 (over two equal additions). Work-up with NaOH (3 x 10 mL) and EtOAc (10 mL) yielded 2.54 g (71%) of a yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.84 (bt, 3H, CH_3), 1,41 (bq, 2H, CH_2, propyl), 2.30-2.39 (m, 2H, CH_2, propyl), 2.43-2.57 (m, 4H, CH_2, backbone), NMR spectrum shows 6% quaternized nitrogens in the polymer;

^{13}C NMR ($CDCl_3$, 100.7 MHz): δ = 11.4 (CH_3), 20.4 (CH_2, propyl), 52.2-53.9 (CH_2 backbone) 56.9 (CH_2, propyl);

IR (film): $\tilde{\upsilon}$ [cm^{-1}] = 2957 (s), 2933 (m), 2807 (s), 1458 (m), 1378 (w), 1261 (w), 1076 (w), 800 (m).

2.2.2.2 Propylated Polyethyleneimine (M_W: 1,800 g/mol before alkylation)

According to **GP I**, 4.7 mL (8.2 g, 48.0 mmol) iodopropane in 10 mL EtOH was reacted with 1.8 g (41.9 mmol) polyethyleneimine (MW= 1,800) in 10 mL EtOH in the presence of 21.6 g (156.0 mmol) K_2CO_3 (over two equal additions). Work-up with NaOH (3 x 10 mL) and EtOAc (10 mL) yielded 2.3 g (65%) of a yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.83 (bt, 3H, CH_3), 1.41 (bq, 2H, CH_2, propyl), 1.76 (bs, remaining free NH), 2.35 (bq, 2H, CH_2, propyl), 2.42-2.58 (m, 4H, CH_2, backbone), NMR spectrum shows 12% quaternized nitrogens in the polymer;

^{13}C NMR ($CDCl_3$, 100.7 MHz): δ = 12.1 (CH_3), 20.3 (CH_2, propyl), 52.3-53.9 (CH_2 backbone) 56.8 (CH_2, propyl);

IR (film): $\tilde{\upsilon}$ [cm^{-1}] = 3421 (s), 2958 (s), 2872 (m), 2809 (s), 1653 (m), 2559 (m), 1464 (m), 1379 (w), 1076 (w), 800 (m).

2.2.2.3 Propylated Polyethyleneimine (M_W: 10,000 g/mol before alkylation)

According to **GP I,** 5.7 mL (10.0 g, 5870 mmol) iodopropane in 12 mL EtOH was reacted with 1.8 g (41.9 mmol) polyethyleneimine (MW= 10,000) in 12 mL EtOH in the presence of 26.2 g (190.0 mmol) K_2CO_3 (over two equal additions). Work-up with NaOH (3 x 12 mL) and EtOAc (12 mL) yielded 4.2 g (99%) of a yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.82 (bt, 3H, CH_3), 1.40 (bq, 2H, CH_2, propyl), 1.76 (bs, remaining free NH), 2.34 (bq, 2H, CH_2, propyl), 2.42-2.58 (m, 4H, CH_2, backbone), NMR spectrum shows 15% quaternized nitrogens in the polymer;

^{13}C NMR ($CDCl_3$, 100.7 MHz): δ = 11.8 (CH_3), 20.4 (CH_2, propyl), 52.2-53.9 (CH_2 backbone) 56.8 (CH_2, propyl);

IR (film): $\tilde{\upsilon}$ [cm^{-1}] = 3439 (m), 2958 (s), 2933 (m), 2872 (s), 2808 (s), 1463 (m), 1379 (w), 1075 (w).

2.2.3 Synthesis of *n*-butylated polyethyleneimines (BPEI, **4**)

2.2.3.1 Butylated polyethyleneimine (M_W: 600 g/mol before alkylation)

According to **GP I**, 5.46 mL (8.83 g, 48.0 mmol) iodobutane in 10 mL EtOH was reacted with 1.8 g (41.9 mmol) polyethyleneimine (MW= 600) in 10 mL EtOH in the presence of 21.6 g (156.0 mmol) K_2CO_3 (over two equal additions). Work-up with NaOH (3 x 10 mL) and EtOAc (10 mL) yielded 3.95 g (98%) of a yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.86 (bt, 3H, CH_3), 1.19-1.30 (m, 2H, CH_2 butyl), 1.31-1.42 (m, 2H, CH_2 butyl), 2.32-2.42 (m, 2H, CH_2 butyl), 2.44- 2.54 (m, CH_2 ethylene);

^{13}C NMR ($CDCl_3$, 100.7 MHz): δ = 14.1 (CH_3), 20.7 (CH_2 butyl), 29.4 (CH_2 butyl), 52.4-54.1 (CH_2, ethylene) 54.5 (CH_2 butyl), 54.8-55.1 (CH_2 ethylene);

IR (film): $\tilde{\upsilon}$ [cm^{-1}] = 2956 (s), 2931 (s), 2861 (m), 2805 (s), 1458 (m), 1376 (w), 1083 (m).

2.2.3.2 Butylated polyethyleneimine (M_W: 1,800 g/mol before alkylation)

According to **GP I**, 5.46 mL (8.83 g, 48.0 mmol) iodobutane in 10 mL EtOH was reacted with 1.8 g (41.9 mmol) polyethyleneimine (MW= 1,800) in 10 mL EtOH in the presence of 21.6 g (156.0 mmol) K_2CO_3 (over two equal additions). Work-up with NaOH (3 x 10 mL) and EtOAc (10 mL) yielded 2.50 g (62%) of a yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.86 (bt, 3H, CH_3), 1.24 (bq, 2H, CH_2 butyl), 1.31-1.44 (m, 2H, CH_2 butyl), 1.64 (bs, remaining NH), 2.37 (q, 2H, CH_2 butyl), 2.42-2.54 (m, CH_2 ethylene), NMR spectrum shows 14% quaternized nitrogens in the polymer;

^{13}C NMR ($CDCl_3$, 100.7 MHz): δ = 14.1 (CH_3), 20.7 (CH_2 butyl), 29.4 (CH_2 butyl), 52.1-53.8 (CH_2, ethylene) 54.5 (CH_2 butyl), 58.0-59.2 (CH_2 ethylene);

IR (film): $\tilde{\upsilon}$ [cm^{-1}] = 3424, (s), 2957 (s), 2871 (m), 2810 (s), 1647 (s), 1558 (w), 1458 (m).

2.2.3.3 Butylated polyethyleneimine (M_W: 10,000 g/mol before alkylation)

According to **GP I**, 5.46 mL (8.83 g, 48.0 mmol) iodobutane in 10 mL EtOH was reacted with 2.0 g (46.5 mmol) polyethyleneimine (MW= 10,000) in 10 mL EtOH in the presence of 21.2 g (154.0 mmol) K_2CO_3 (over two equal additions). Work-up with NaOH (3 x 10 mL) and EtOAc (10 mL) yielded 2.47 g (55%) of a yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.88 (bt, 3H, CH_3), 1.27 (bq, 2H, CH_2 butyl), 1.33-1.44 (m, 2H, CH_2 butyl), 2.32-2.43 (m, 2H, CH_2 butyl), 2.44- 2.56 (m, CH_2 ethylene), NMR spectrum shows 3% quaternized nitrogens in the polymer;

^{13}C NMR ($CDCl_3$, 100.7 MHz): δ = 14.1 (CH_3), 20.7 (CH_2 butyl), 29.5 (CH_2 butyl), 52.0-53.5 (CH_2, ethylene) 54.5 (CH_2 butyl), 54.8-55.1 (CH_2 ethylene);

IR (film): $\tilde{\upsilon}$ [cm^{-1}] = 2955 (s), 2930 (s), 2861 (m), 2805 (s), 1467 (m), 1378 (w), 1080 (m).

2.3 Polydiallylmethylamine **5** (M_W: 5,000)

Polydiallylmethylamine hydrochloride (M_W= 5000, 16.0 g of a 25 wt% suspension in water) was placed into a 50 mL round bottom flask. Dichloromethane (10 ml) was added and the mixture was stirred. Then 10 mL of 15% (w/v) NaOH solution was slowly added and the stirring was continued for 1 h after the addition was complete. The phases were separated. The organic layer was then washed twice with 5 mL of 15% (w/v) NaOH solution, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The polydiallylmethylamine was obtained as a yellow solid (0.5 g, 69% yield).

2.4 Amine-functionalized polyacrylic acids (AFPAA, **6**)

General Procedure II (**GP II**): Polyacrylic acid (1 eq) was weighed under nitrogen into a 2-neck round bottom flask equipped with a reflux condenser. 3-(Dimethylamino)-1-propylamine (1.1 eq) was added via syringe to the polymer. The mixture was heated to 160 °C for 2.5 days under nitrogen. After that time, the reaction mixture was a slightly cloudy colourless solution and was allowed to cool to 100 °C, causing it to become more cloudy and making stirring difficult. The mixture was dried at 100 °C for 6 h under high vacuum followed by removal of the solid, which was ground with a mortar and pestle giving a sticky white solid. The solid was further dried in a flask at 80 °C under high vacuum for 16 h. The flask was cooled and the polymers were obtained as powders.

2.4.1 Amine-functionalized polyacrylic acid (M_W: 50,000 before functionalization)

According to **GP II**, 1.0 g, polyacrylic acid (13.9 mmol) was reacted with 1.57 mL 3-(dimethylamino)-1-propylamine (12.5 mmol) to obtain 1.42 g of the functionalized polymer.

^{1}H NMR (400 MHz, D_2O) δ 3.18 (m, 2H, $NHCH_2$), 2.42 (m, 2H, Me_2NCH_2), 2.29 (s, 6H, $N(CH_3)_2$), 2.20-1.95 (b, 1H, backbone CH), 1.73 (m, 2H, $CH_2CH_2CH_2$), 1.80-1.25 (b, 2H, backbone CH_2).

2.4.2 Amine-functionalized polyacrylic acid (M_W: 450,000 before functionalization)

According to **GP II**, 1.0 g, polyacrylic acid (13.9 mmol) was reacted with 1.57 mL 3-(dimethylamino)-1-propylamine (12.5 mmol) to obtain 0.36 g of the functionalized polymer.

^{1}H NMR (400 MHz, D_2O) δ 3.18 (m, 2H, $NHCH_2$), 2.41 (m, 2H, Me_2NCH_2), 2.27 (s, 6H, $N(CH_3)_2$), 2.20-1.90 (b, 1H, backbone CH), 1.72 (m, 2H, $CH_2CH_2CH_2$), 1.85-1.25 (b, 2H, backbone CH_2).

2.5 Amine-functionalized polymethyl methacrylates (AFPMMA, **7**)

General Procedure III (**GP III**): Polymethyl methacrylate (1 eq) was weighed under nitrogen into a 2-neck round bottom flask equipped with a reflux condenser. 3-(Dimethylamino)-1-propylamine (8.1 eq) was added via syringe to the polymer. The mixture was heated to 150 °C for 16 h under nitrogen. After this time, the reaction mixture was a clear and colorless solution and was allowed to cool to room temperature causing a white precipitate to form. The liquid was decanted and the remaining solid was washed with 2 x 25 mL of isopropanol. It was then dried at 80°C under high vacuum for 5 h. The solid was then broken up with a spatula until more of a powder formed and then re-dried using the same conditions for 16 h. The polymers were obtained as white powders with approximately 50% of the methacrylate sites functionalized, as determined by integration of the appropriate resonances in the ^{1}H NMR spectrum in D_2O.

2.5.1 Amine-functionalized polymethyl methacrylate (M_W: 15,000 g/mol)

According to **GP III**, 1.47 g polymethyl methacrylate (14.7 mmol) was reacted with 15 mL 3-(dimethylamino)-1-propylamine (119 mmol). 1.02 g of white powder was obtained and approximately 80% of the methacrylate sites were functionalized.

^{1}H NMR (400 MHz, D_2O) δ 3.64 (bs, 3H, OCH_3), 2.86 (t, J = 8.0 Hz, 2H, $NHCH_2$), 2.58 (t, J = 8.0 Hz, 2H, Me_2NCH_2), 2.35 (s, 6H, $N(CH_3)_2$), 2.0-1.6 (b, 2H, backbone CH_2), 1.80 (m, 2H, $CH_2CH_2CH_2$), 1.2-0.7 (b, 3H, CH_3).

2.5.2 Amine-functionalized polymethyl methacrylate (M_W: 35,000 g/mol)

According to **GP III**, 0.62 g polymethyl methacrylate (6.2 mmol) was reacted with 4 mL 3-(dimethylamino)-1-propylamine (31.7 mmol). 0.7 g of white powder was obtained and approximately 50% of the methacrylate sites were functionalized.

^{1}H NMR (400 MHz, D_2O) δ 3.64 (bs, 3H, OCH_3), 2.82 (t, *J* = 8.0 Hz, 2H, $NHCH_2$), 2.53 (b, 2H, Me_2NCH_2), 2.31 (s, 6H, $N(CH_3)_2$), 2.0-1.6 (b, 2H, backbone CH_2), 1.76 (m, 2H, $CH_2CH_2CH_2$), 1.3-0.7 (b, 3H, CH_3).

2.5.3 Amine-functionalized polymethyl methacrylate (M_W: 120,000 g/mol)

According to **GP III**, 1.7 g polymethyl methacrylate (17.0 mmol) was reacted with 10 mL 3-(dimethylamino)-1-propylamine (79.0 mmol). 2.07 g of white powder was obtained and approximately 50% of the methacrylate sites were functionalized.

^{1}H NMR (400 MHz, D_2O) δ 3.65 (bs, 3H, OCH_3), 2.81 (b, 2H, $NHCH_2$), 2.52 (m, 2H, Me_2NCH_2), 2.31 (s, 6H, $N(CH_3)_2$), 2.0-1.6 (b, 2H, backbone CH_2), 1.75 (m, 2H, $CH_2CH_2CH_2$), 1.3-0.7 (b, 3H, CH_3).

2.5.4 Amine-functionalized polymethyl methacrylate (M_W: 350,000 g/mol)

According to **GP III**, 1.47 g polymethyl methacrylate (14.7 mmol) was reacted with 15 mL 3-(dimethylamino)-1-propylamine (119.0 mmol). 0.8 g of white powder was obtained and approximately 80% of the methacrylate sites were functionalized.

^{1}H NMR (400 MHz, D_2O) δ 3.65 (bs, 3H, OCH_3), 2.84 (b, 2H, $NHCH_2$), 2.57 (b, 2H, Me_2NCH_2), 2.35 (bs, 6H, $N(CH_3)_2$), 1.95-1.55 (b, 2H, backbone CH_2), 1.79 (b, 2H, $CH_2CH_2CH_2$), 1.5-0.7 (b, 3H, CH_3).

2.6 Amine-functionalized polymethyl methacrylate polystyrene copolymers (AFPMMA-co-PS, **8**)

General procedure IV (**GP IV**): Polystyrene-co-methyl methacrylate (1 eq) was added under nitrogen to a 2 neck round bottom flask equipped with a reflux condenser. 3-(Dimethylamino)-1-propylamine (8.1 eq) was added via syringe. The mixture was heated to 150 °C overnight under nitrogen. The resulting yellow solution was cooled to only 80 °C so that its viscosity didn't increase significantly; the solution was decanted slowly into 900 mL of rapidly stirred isopropanol giving a white-yellow precipitate that was filtered through a Buchner funnel. The polymer was dried at 80 °C under high vacuum for several hours giving a solid chunk, which was broken up with a mortar and pestle giving a light yellow solid. This was dried overnight at 80 °C under high vacuum. The polymers were obtained as white-yellow powders.

2.6.1 PMMA/PS (10 mol% styrene, M_W: 10,600-15,900 g/mol)

According to **GP IV**, 1.15 g polystyrene-co-methyl methacrylate was reacted with 15 mL 3-(dimethylamino)-1-propylamine (119.0 mmol). 1.07 g of white powder was obtained.

^{1}H NMR (400 MHz, D_2O) δ 7.45-7.0 (b, 5H, aromatic CH), 3.65 (bs, 3H, OCH_3), 2.85 (t, J = 8.0 Hz, 2H, $NHCH_2$), 2.56 (b, 2H, Me_2NCH_2), 2.34 (s, 6H, $N(CH_3)_2$), 2.1-1.6 (b, backbone CH_2 and CH), 1.79 (m, 2H, $CH_2CH_2CH_2$), 1.6-0.6 (b, backbone CH and CH_3).

2.6.2 PMMA/PS (31 mol% styrene, M_W: 117,000-192,000 g/mol)

According to **GP IV**, 1.13 g polystyrene-co-methyl methacrylate was reacted with 15 mL 3-(dimethylamino)-1-propylamine (119.0 mmol). 1.09 g of white powder was obtained.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.3-6.8 (b, 5H, aromatic CH), 3.55 (bs, 3H, OCH_3), 2.83 (b, 2H, $NHCH_2$), 2.42 (b, 2H, Me_2NCH_2), 2.26 (s, 6H, $N(CH_3)_2$), 2.0-1.5 (b, backbone CH_2 and CH), 1.71 (b, 2H, $CH_2CH_2CH_2$), 1.2-0.4 (b, backbone CH and CH_3).

3. Clay Settling experiments

Clay suspensions were prepared by adding 1 to 7.5 g of clay fines to 100 mL of aqueous solution containing various concentrations of the polymers. The concentrations of the polymers are given in ppm (500 ppm = 0.05% (w/v, polymer/water)). The mixtures were stirred with a magnetic stirrer for 30 min at 600 rpm in a 250 mL round bottom flask. CO_2 was bubbled through the mixture in the graduated cylinder using a gas dispersion tube for 1 h at a flow rate of 100-150 mL/min as measured by a Varian Intelligent Digital Flowmeter. Settling was monitored over 2 h. Supernatant from each settling experiment was sampled and its turbidity was measured using a turbidimeter (TB200, Orbeco-Hellige).

3.1 Settling profiles kaolinite

All settling experiments shown in this section were conducted using 2 g of kaolinite and 100 mL of water containing 500 ppm of the polymer indicated in the presence of CO_2. Only the profiles of the polymers that induced settling are shown.

3.1.1 Amine-functionalized polymethyl methacrylate (M_W: 120,000 g/mol before functionalization)

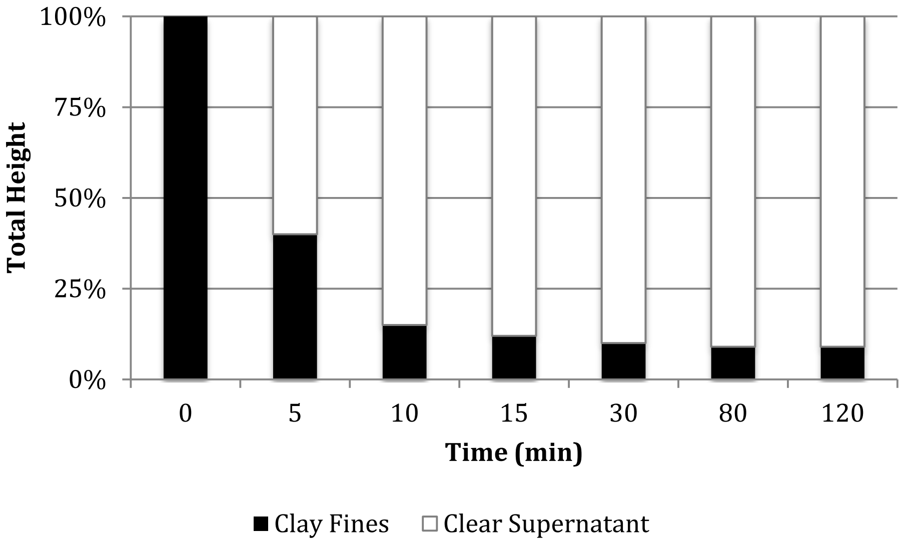

Figure 1: Time dependence of the height of the settled clay (the mud line) as a percentage of the total height of a 2 w% kaolinite/water mixture, in the presence of 500 ppm of amine-functionalized polymethyl methacrylate (M_W: 120,000 g/mol).

3.1.2 Amine-functionalized polymethyl methacrylate (MW: 350,000 g/mol before functionalization)

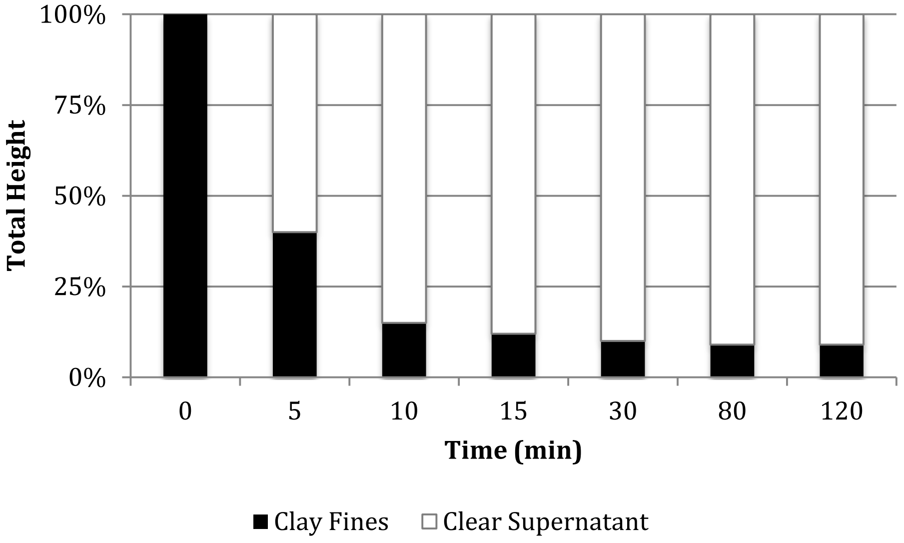

Figure 2: Time dependence of the height of the settled clay (the mud line) as a percentage of the total height of a 2 wt% kaolinite/water mixture, in the presence of 500 ppm of amine-functionalized polymethyl methacrylate (M_W: 350,000 g/mol).

3.1.3 Amine-functionalized polymethyl methacrylate polystyrene copolymers (10% polystyrene, M_W: 10,000-15,000 g/mol)

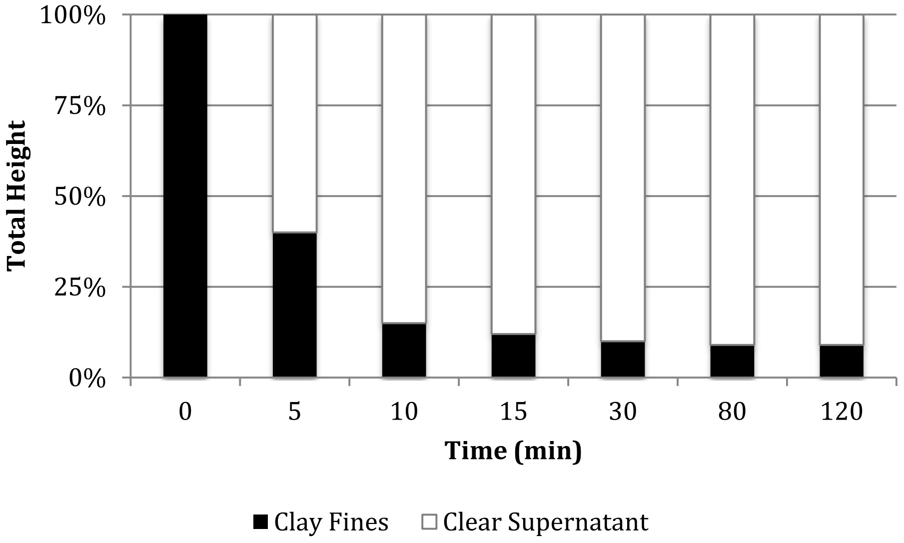

Figure 3: Time dependence of the height of the settled clay (the mud line) as a percentage of the total height of a 2 wt% kaolinite/water mixture, in the presence of 500 ppm of amine-functionalized polymethyl methacrylate polystyrene copolymers (10% polystyrene, M_W: 10,000-15,000 g/mol).

3.1.4 Amine-functionalized polymethyl methacrylate polystyrene copolymers (10% polystyrene, M_W: 117,000-192,000 g/mol)

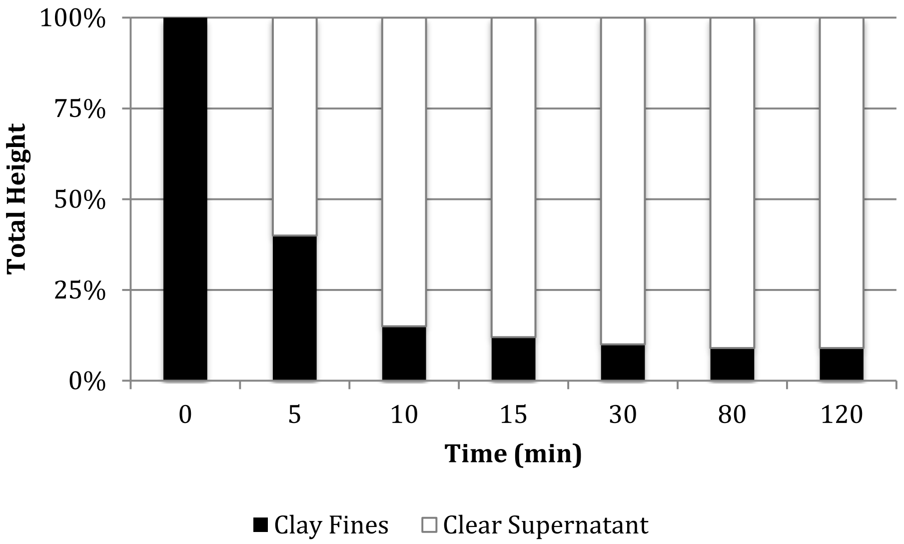

Figure 4: Time dependence of the height of the settled clay (the mud line) as a percentage of the total height of a 2 wt% kaolinite/water mixture, in the presence of 500 ppm of amine-functionalized polymethyl methacrylate polystyrene copolymers (10% polystyrene, M_W: 117,000-192,000 g/mol).

3.2 Settling profiles montmorillonite

All settling experiments were conducted using 1 g of montmorillonite in 100 mL of water containing 500 ppm of the polymer in the presence of CO_2.

3.2.1 Propylated polyethyleneimine (M_W: 600 g/mol before alkylation)

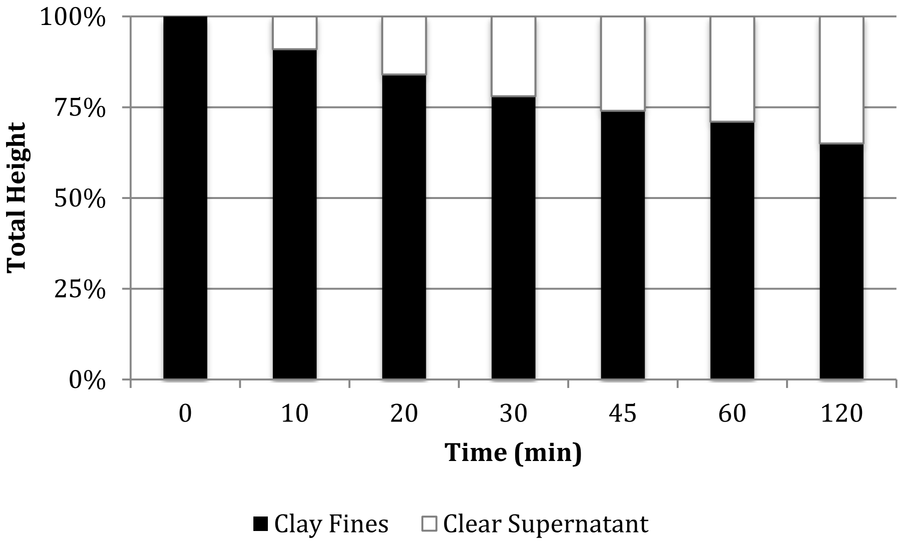

Figure 5: Time dependence of the height of the settled clay (the mud line) as a percentage of the total height of a 1 wt% montmorillonite/water mixture, in the presence of 500 ppm of propylated polyethyleneimine (M_W: 600 g/mol).

3.2.2 Propylated polyethyleneimine (M_W: 10,000 g/mol before alkylation)

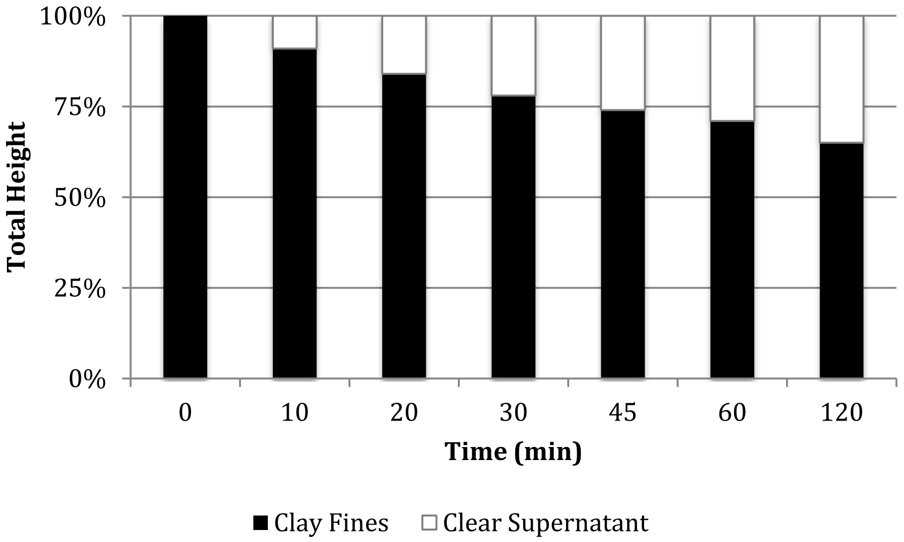

Figure 6: Time dependence of the height of the settled clay (the mud line) as a percentage of the total height of a 1 wt% montmorillonite/water mixture, in the presence of 500 ppm of propylated polyethyleneimine (M_W: 10,000 g/mol).

3.2.3 Butylated polyethyleneimine (M_W:10,000 g/mol before alkylation)

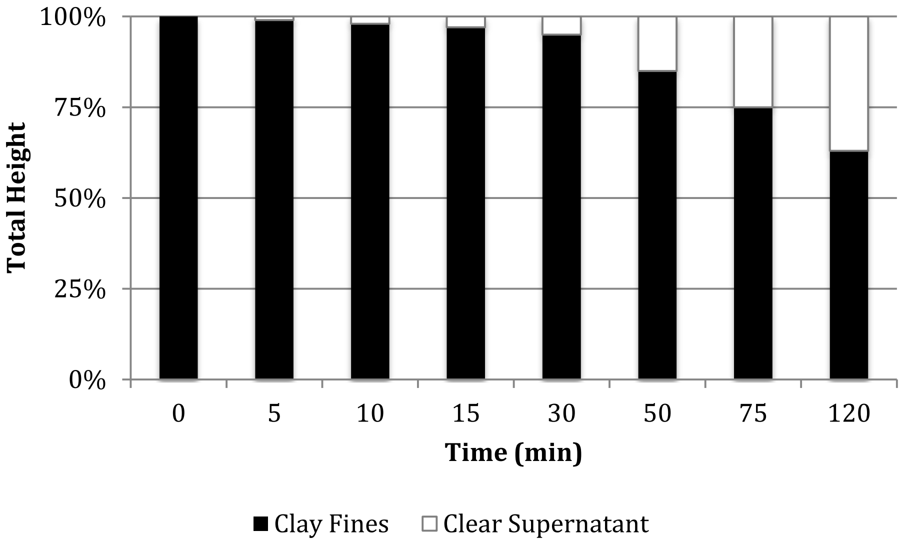

Figure 7: Time dependence of the height of the settled clay (the mud line) as a percentage of the total height of a 1 wt% montmorillonite/water mixture, in the presence of 500 ppm of butylated polyethyleneimine (M_W: 10,000 g/mol).

3.2.4 Amine-functionalized polyacrylic acid (M_W: 50,000 g/mol before functionalization)

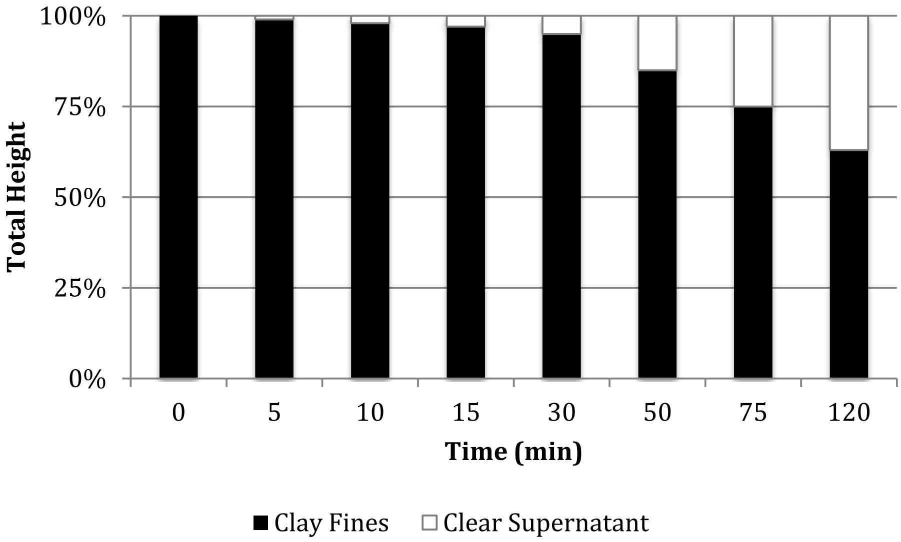

Figure 8: Time dependence of the height of the settled clay (the mud line) as a percentage of the total height of a 1 wt% montmorillonite/water mixture, in the presence of 500 ppm of amine-functionalized polyacrylic acid (M_W: 50,000 g/mol).

3.2.5 Amine-functionalized polyacrylic acid (M_W: 450,000 g/mol before functionalization)

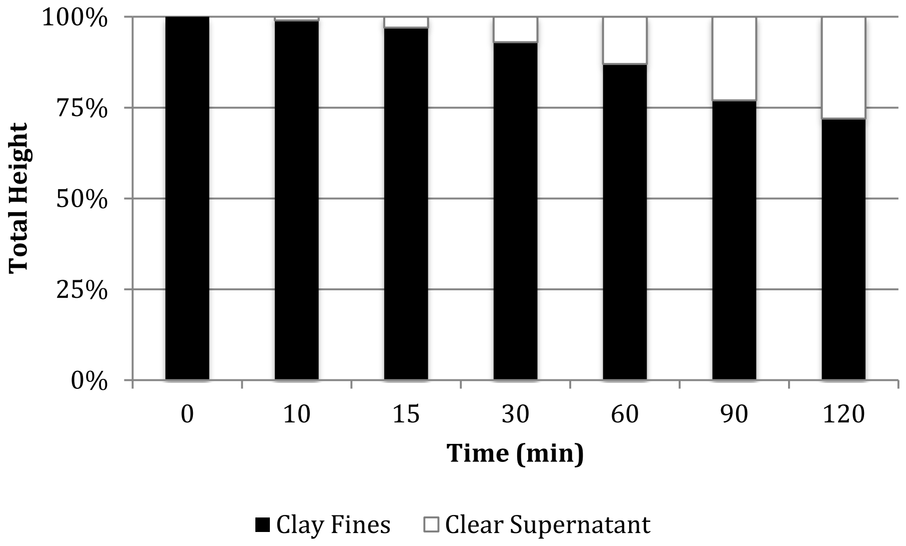

Figure 9: Time dependence of the height of the settled clay (the mud line) as a percentage of the total height of a 1 wt% montmorillonite/water mixture, in the presence of 500 ppm of amine-functionalized polyacrylic acid (M_W: 450,000 g/mol).

3.2.6 Amine-functionalized polymethyl methacrylate (M_W: 120,000 g/mol before functionalization)

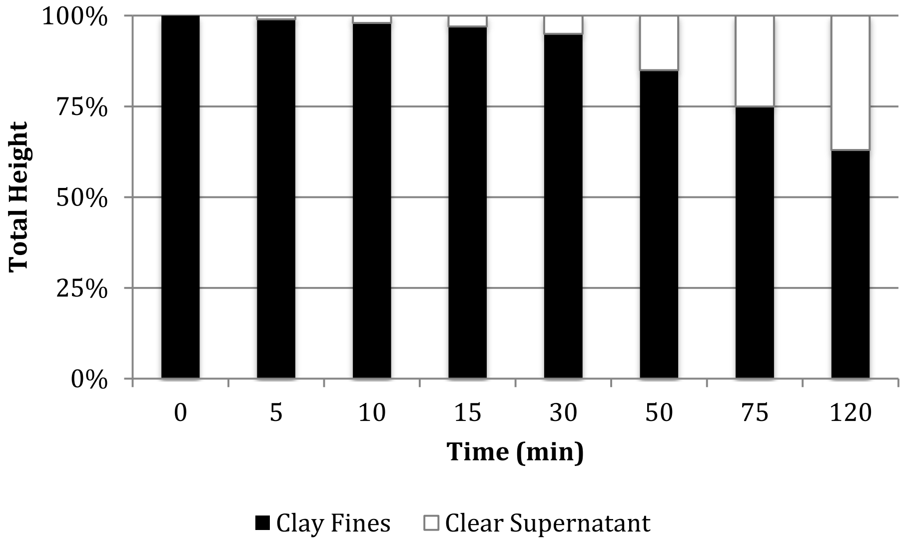

Figure 10: Time dependence of the height of the settled clay (the mud line) as a percentage of the total height of a 1 wt% montmorillonite/water mixture, in the presence of 500 ppm of amine-functionalized polymethyl methacrylate (M_W: 120,000 g/mol).

3.2.7 Amine-functionalized polymethyl methacrylate polystyrene copolymers (10% polystyrene, M_W: 10,000-15,000 g/mol)

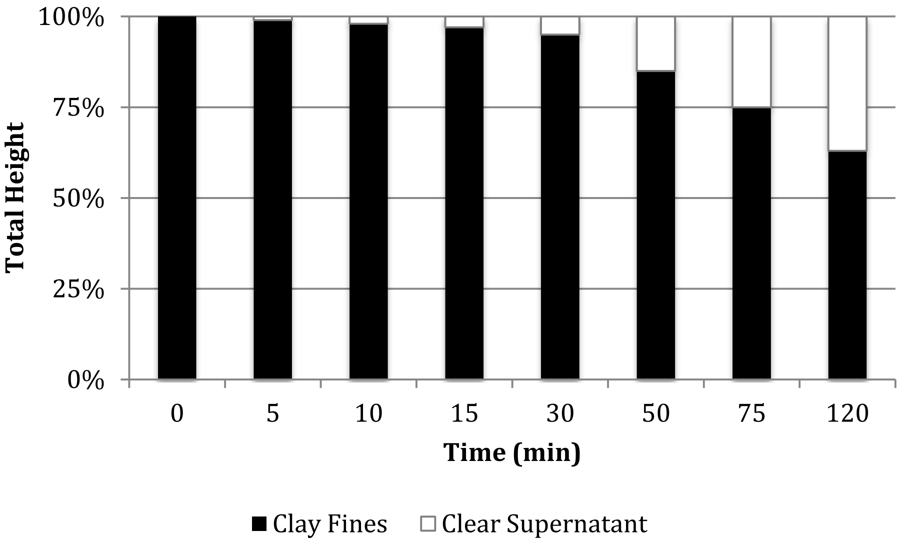

Figure 11: Time dependence of the height of the settled clay (the mud line) as a percentage of the total height of a 1 wt% montmorillonite/water mixture, in the presence of 500 ppm of amine-functionalized polymethyl methacrylate polystyrene copolymers (10% polystyrene, M_W: 10,000-15,000 g/mol).

3.2.8 Amine-functionalized polymethyl methacrylate polystyrene copolymers (10% polystyrene, M_W: 117,000-192,000 g/mol)

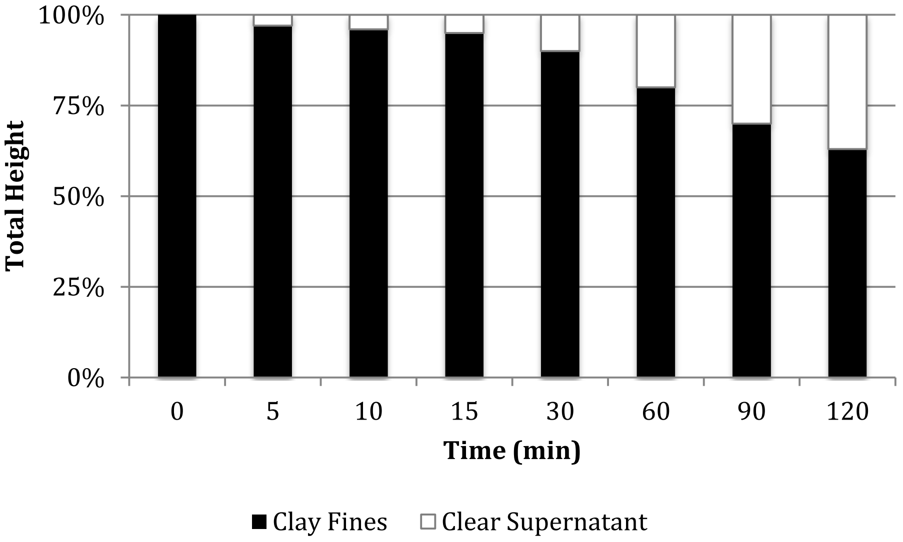

Figure 12: Time dependence of the height of the settled clay (the mud line) as a percentage of the total height of a 1 wt% montmorillonite/water mixture, in the presence of 500 ppm of amine-functionalized polymethyl methacrylate polystyrene copolymers (10% polystyrene, M_W: 117,000-192,000 g/mol).

4. XRD data

The XRD measurements were conducted on a Philips X'Pert 4 Circle Diffractometer with a copper anode.

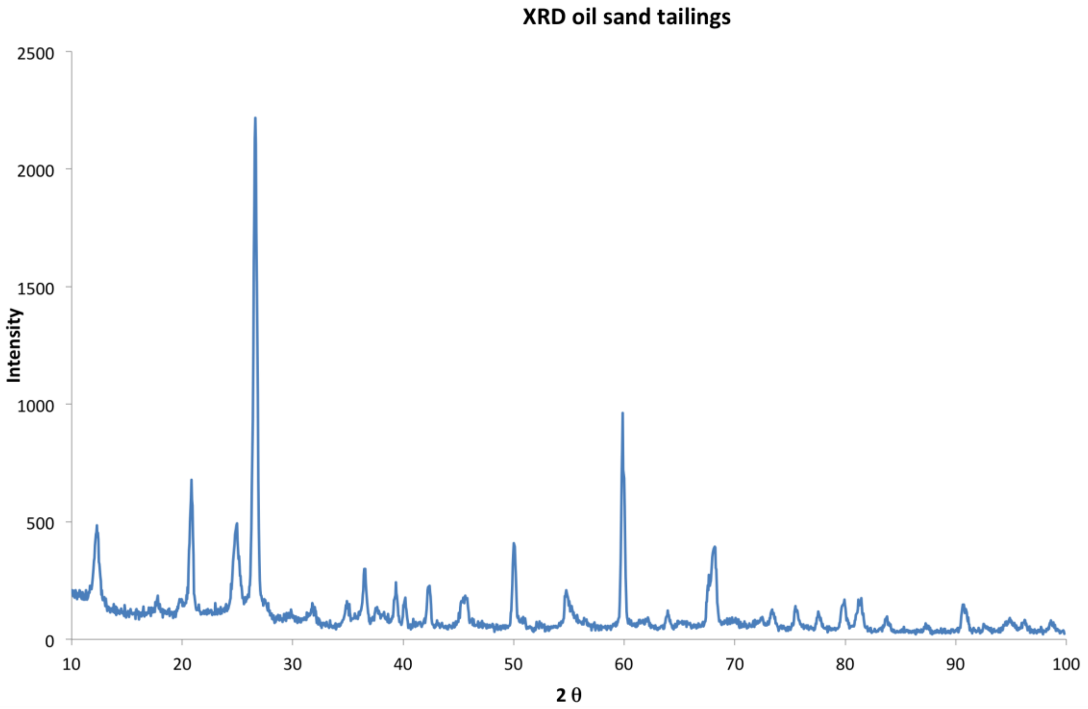

Figure 13: XRD spectra of oil sand tailings sample.

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[1] Gaudin, A.M.; Fuerstenau, M.C.; Mitchell, S.R., *Mining Eng.* **1959**, *11*, 613-616.

[2] Michaels, A.S.; Bolger, J. C. Settling rates and sediment volumes of flocculated kaolin suspensions. *Ind. Eng. Chem. Fundam.* **1962**, *1*, 24-33.