Supplementary material for manuscript “Very fast CO_2 response and hydrophobic properties of novel poly(ionic liquid)s”

Syntheses

[2-(methacryloyloxy)ethyl]dimethylheptylammonium bromide (M0). To 10 mL of [2-(methacryloyloxy)ethyl]dimethylamine (0.06 mol) was added, under stirring, 10 mL of 1-bromoheptane (0.06 mol). The reaction mixture was left at room temperature for 15 days. After decantation, the white solid was washed three times with petroleum ether and then dried in a rotavapor at 35 °C.

Yield: 56 %. FT-IR (KBr, nujol mull, cm^{-1}): ν_{CO}: 1718. ^1H NMR ($CDCl_3$, δ, ppm): 0.86 (m, 3H), 1.34 (m, 8H), 1.73 (m, 2H), 1.93 (s, 3H), 3.49 (s, 6H), 3.59 (m, 2H), 4.16 (m, 2H), 4.63 (m, 2H), 5.66 (d, 1H), 6.12 (d, 1H). Elemental analysis: Calcd for $C_{15}H_{30}BrNO_2$ (336.31): C, 53.57%; H, 8.99%; N, 4.16%. Found: C, 54.02%; H, 9.04%; N, 4.86%.

[2-(methacryloyloxy)ethyl]dimethylhepthylammonium bis(trifluoromethylsulfonyl)imide (**M1**)**.** Addition, at room temperature and under a nitrogen atmosphere, of 2.5 g (8 mmol) of bis(trifluoromethylsulfonyl)imide lithium salt, dissolved in 10 mL of deionized water, to a vigorously stirred solution of [2-(methacryloyloxy)ethyl]dimethylheptylammonium bromide (3 g, 8 mmol) in 10 mL of deionized water led, after a few minutes, to the formation of two liquid phases. The reaction mixture was left under stirring for four hours at room temperature. After decantation the aqueous top phase was removed and the remaining ionic liquid washed two times with water to remove unreacted materials and inorganic salts. The viscous liquid was dried in a rotavapor at 35 °C.

Yield: 98 %. FT-IR (KBr, nujol mull, cm^{-1}): ν_{CO}: 1724. ^1H NMR ($CDCl_3$ δ, ppm): 0.87 (m, 3H), 1.31 (m, 8H), 1.72 (m, 2H), 1.93 (s, 3H), 3.17 (s, 6H), 3.32 (m, 2H), 3.72 (m, 2H), 4.56 (m, 2H), 5.67 (d, 1H), 6.11 (d, 1H). Elemental analysis: Calcd for $C_{17}H_{30}F_6N_2O_6S_2$ (536.55): C, 38.05%; H, 5.64%; N, 5.22%. Found: C, 38.67%; H, 5.22%; N, 5.75%.

[2-(methacryloyloxy)ethyl]dimethylheptylammonium nonafluoro-1-butanesulfonate (**M2**). To a solution of 2.5 g (7 mmol) of [2-(methacryloyloxy)ethyl]dimethylheptylammonium bromide dissolved in 10 mL of deionized water was added, under vigorous stirring, 2.5 g (7 mmol) of nonafluoro-1-butanesulfonate potassium salt dissolved in 50 mL of deionized water at 60 °C. The mixture was left, under a nitrogen atmosphere, at room temperature for 18 hours until the formation of a white solid. After decantation, the solid was filtered and then washed three times with deionized water to ensure the removal of inorganic byproducts. The white product was then dried under vacuum at 35 °C.

Yield: 85 %. FT-IR (KBr, nujol mull, cm^{-1}): ν_{CO}: 1722. ^1H NMR ($CDCl_3$, δ, ppm): 0.86 (m, 3H), 1.24 (m, 8H), 1.72 (m, 2H), 1.93 (s, 3H), 3.24 (s, 6H), 3.38 (m, 2H), 3.83 (m, 2H), 4.58 (m, 2H), 5.67 (d, 1H), 6.11 (d, 1H). Elemental analysis: Calcd for $C_{19}H_{30}F_9NO_5S$ (555.50): C, 41.08%; H, 5.44%; N, 2.52%. Found: C, 40.87%; H, 5.13%; N, 2.67%.

[2-(methacryloyloxy)ethyl]dimethylheptylammonium dodecylbenzenesulfonate (**M3**). To a solution of 2.5 g (7 mmol) of [2-(methacryloyloxy)ethyl]dimethylheptylammonium bromide dissolved in 10 mL of deionized water was added, under stirring in a nitrogen atmosphere, 2.6 g (7 mmol) of dodecylbenzenesulfonate sodium salt dissolved in water (75 mL) at 65 °C. The mixture was left on stirring for 42 hours at room temperature. The molten salt was recovered as a white solid by extracting four times the milk-white mixture with $CHCl_3$ and by drying in a rotavapor the organic phase at 35 °C.

Yield: 66 %. FT-IR (KBr, nujol mull, cm^{-1}): ν_{CO}: 1724. ^1H NMR ($CDCl_3$, δ, ppm): 0.82 (m, 6H), 1.15 (m, 28H), 1.18 (m, 2H), 1.73 (m, 2H), 1.90 (s, 3H), 3.39 (s, 6H), 3.47 (m, 2H), 3.99 (m, 2H), 4.59 (m, 2H), 5.62 (d, 1H), 6.09 (d, 1H), 7.10 (d, 2H), 7.76 (d, 2H). Elemental analysis: Calcd for $C_{33}H_{59}NO_5S$ (581.89): C, 68.11%; H, 10.22%; N, 2.41%. Found: C, 68.85%; H, 10.02%; N, 2.32%.

[2-(methacryloyloxy)ethyl]dimethylheptylammonium heptadecafluorooctanesulfonate (**M4**). The product **M4** was prepared by adding, under stirring in a nitrogen atmosphere, a solution containing 4 g (7 mmol) of potassium heptadecafluorooctanesulfonate dissolved in 350 mL of deionized water to a solution of 2.5 g (7 mmol) of [2-(methacryloyloxy)ethyl]dimethylheptylammonium bromide in 10 mL of deionized water. The cloudy reaction mixture was left under stirring at room temperature for 17 hours. The white solid was filtered, washed five times with deionized water and then dried under vacuum at 35 °C.

Yield: 67 %. FT-IR (KBr, nujol mull, cm^{-1}): ν_{CO}: 1726. ^1H NMR ($CDCl_3$, δ, ppm): 0.85 (m, 3H), 1.28 (m, 8H), 1.70 (m, 2H), 1.92 (s, 3H), 3.24 (s, 6H), 3.39 (m, 2H), 3.82 (m, 2H), 4.58 (m, 2H), 5.65 (d, 1H), 6.10 (d, 1H). Elemental analysis: Calcd for $C_{23}H_{30}F_{17}NO_5S$ (755.53): C, 36.56%; H, 4.00%; N, 1.85%. Found: C, 36.86%; H, 4.53%; N, 1.78%.

[2-(methacryloyloxy)ethyl]dimethylheptylammonium 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecanoate (**M5**). To a stirring solution of 1 g (2 mmol) of [2-(methacryloyloxy)ethyl]dimethylheptylammonium bromide in 10 mL of deionized water was added, under nitrogen, 1.58 g (2 mmol) of potassium 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecanoate dissolved in 50 mL of deionized water. The mixture was left on standing at room temperature for 22 hours. The viscous liquid product was recovered by extracting five times the milky mixture with $CHCl_3$ and by drying in a rotavapor the organic phase at 35 °C.

Yield: 46 %. FT-IR (KBr, nujol mull, cm^{-1}): ν_{CO}: 1720. ^1H NMR ($CDCl_3$, δ, ppm): 0.83 (m, 3H), 1.24 (m, 8H), 1.71 (m, 2H), 1.88 (s, 3H), 2.42 (m, 2H), 2.62 (m, 2H), 3.25 (s, 6H), 3.31 (m, 2H), 3.83 (m, 2H), 4.60 (m, 2H), 5.59 (d, 1H), 6.07 (d, 1H). Elemental analysis: Calcd for $C_{26}H_{34}F_{17}NO_4$ (747.53): C, 41.77%; H, 4.58%; N, 1.87%. Found: C, 41.65%; H, 4.56%; N, 1.78%.

Poly[2-(methacryloyloxy)ethyl]dimethylheptylammonium bis(trifluoromethylsulfonyl)imide (**P1**). A mixture of 3 g of **M1** (6.6 mmol) and 0.044 g (0.13 mmol) of AIBN was heated, under nitrogen, to 60 °C with vigorous stirring. Suddenly the formation of a white material occurred. Then the reaction was stopped by pouring the mixture on an ice-bath. The product was washed several times with methanol to remove the monomer, purified three times from an acetone/petroleum ether mixture and then dried at 80 °C for 24 h. Yield: 78 %. FT-IR (KBr, nujol mull, cm^{-1}): ν_{CO}: 1732. ^{1}H NMR (acetone-d_6, δ, ppm): 1.90 (br, 3H), 2.81 (br, 6H), 3.54 (br, 2H), 3.84 (br, 2H), 4.54 (br, 2H). Elemental analysis: Calcd for $C_{17}H_{32}F_6N_2O_6S_2$ (538.57): C, 37.91%; H, 5.99%; F, 21.17%; N, 5.20%; S, 11.91%. Found: C, 38.17%; H, 5.64%; F, 18.05%; N, 5.14%; S, 12.02%. Contact angle: θ_{adv} = 97.31°; θ_{rec} = 47.57°.

Poly[2-(methacryloyloxy)ethyl]dimethylheptylammonium nonafluoro-1-butanesulfonate (**P2**). To a solution of **M2** (3 g, 5.4 mmol) dissolved in chloroform (20 mL) was added, under vigorous stirring in nitrogen, 0.022 g (0.13 mmol) of AIBN and the mixture heated to 65 °C. After one hour the reaction was stopped by pouring the mixture on an ice-bath. Treatment with petroleum ether (40-60 °C) led to the formation of a white solid that was washed three times with dioxane to remove unreacted **M2** and then dried under vacuum at 80 °C.

Yield: 75 %. FT-IR (KBr, nujol mull, cm^{-1}): ν_{CO}: 1727. ^{1}H NMR (acetone-d_6, δ, ppm): 1.96 (br, 3H), 2.90 (br, 6H), 3.65 (br, 2H), 3.71 (br, 2H), 4.53 (br, 2H). Elemental analysis: Calcd for $C_{19}H_{32}F_9NO_5S$ (557.51): C, 40.93%; H, 5.79%; F, 30.67%; N, 2.51%; S, 5.75%. Found: C, 40.39%; H, 5.39%; F, 28.07%; N, 2.45%; S, 5.82%. Contact angle: θ_{adv} = 108.76°; θ_{rec} = 48.97°.

Poly[2-(methacryloyloxy)ethyl]dimethylheptylammonium dodecylbenzenesulfonate (**P3**). **P3** was obtained as a white solid using the same procedure as for **P2**.

Yield: 80 %. FT-IR (KBr, nujol mull, cm^{-1}): ν_{CO}: 1725. ^{1}H NMR (acetone-d_6, δ, ppm): 2.91 (br, 6H), 3.64 (br, 2H), 3.88 (br, 2H), 4.54 (br, 2H), 7.08 (d, 2H), 7.70 (d, 2H). Elemental analysis: Calcd for $C_{33}H_{61}NO_5S$ (583.91): C, 67.88%; H, 10.53%; N, 2.40%; S, 5.49%. Found: C, 66.43%; H, 10.07%; N, 2.44%; S, 5.65%. Contact angle: θ_{adv} = 99.96°; θ_{rec} = 53.98°.

Poly[2-(methacryloyloxy)ethyl]dimethylheptylammonium bis(trifluoromethylsulfonyl)imide-*co*-[2-(methacryloyloxy)ethyl]dimethylheptylammonium heptadecafluorooctanesulfonate (**C1-4**). Copolymer **C1-4** was synthesized according to the previous procedure, by employing an equimolecular amount of **M1** and **M4** as starting material.

Yield: 70 %. FT-IR (KBr, nujol mull, cm^{-1}): ν_{CO}: 1728. ^{1}H NMR (acetone-d$_6$, δ, ppm): 2.04 (br, 3H), 2.80 (br, 6H), 3.57 (br, 2H), 3.91 (br, 2H), 4.55 (br, 2H). Elemental analysis: Calcd for $C_{40}H_{64}F_{23}N_3O_{11}S_3$ (1296.11): C, 37.07%; H, 4.98%; F, 33.71%; N, 3.24%; S, 7.42%. Found: C, 37.16%; H, 4.68%; F, 32.90%; N, 3.18%; S, 7.56%. Contact angle: $\theta_{adv} = 113.24°$; $\theta_{rec} = 41.99°$.

Poly[2-(methacryloyloxy)ethyl]dimethylheptylammonium bis(trifluoromethylsulfonyl)imide-*co*-[2-(methacryloyloxy)ethyl]dimethylheptylammonium 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecanoate (**C1-5).** To a solution of 1.21 g (2.3 mmol) of **M1** and 1.76 g (2.3 mmol) of **M5**, dissolved in 20 mL of $CHCl_3$, was added 0.018 g (0.11 mmol) of AIBN and the mixture heated, under nitrogen, to 60 °C under stirring. After three hours the polymerization was stopped by pouring the mixture on an ice-bath. Treatment with hexane led to the precipitation of a white solid that was washed three times with ether and then dried in a rotavapor at 80 °C.

Yield: 80 %. FT-IR (KBr, nujol mull, cm^{-1}): ν_{CO}: 1722. ^{1}H NMR (acetone-d$_6$, δ, ppm): 2.04 (br, 3H), 2.46 (br, 2H), 3.16 (br, 2H), 3.45 (br, 6H), 3.71 (br, 2H), 4.13 (br, 2H), 4.60 (br, 2H). Elemental analysis: Calcd for $C_{43}H_{68}F_{23}N_3O_{10}S_2$ (1288.11): C, 40.09%; H, 5.32%; F, 33.92%; N, 3.26%; S, 4.98%. Found: C, 38.83%; H, 5.21%; F, 31.03%; N, 3.14%; S, 7.00%. Contact angle: $\theta_{adv} = 78.32°$; $\theta_{rec} = 22.22°$.

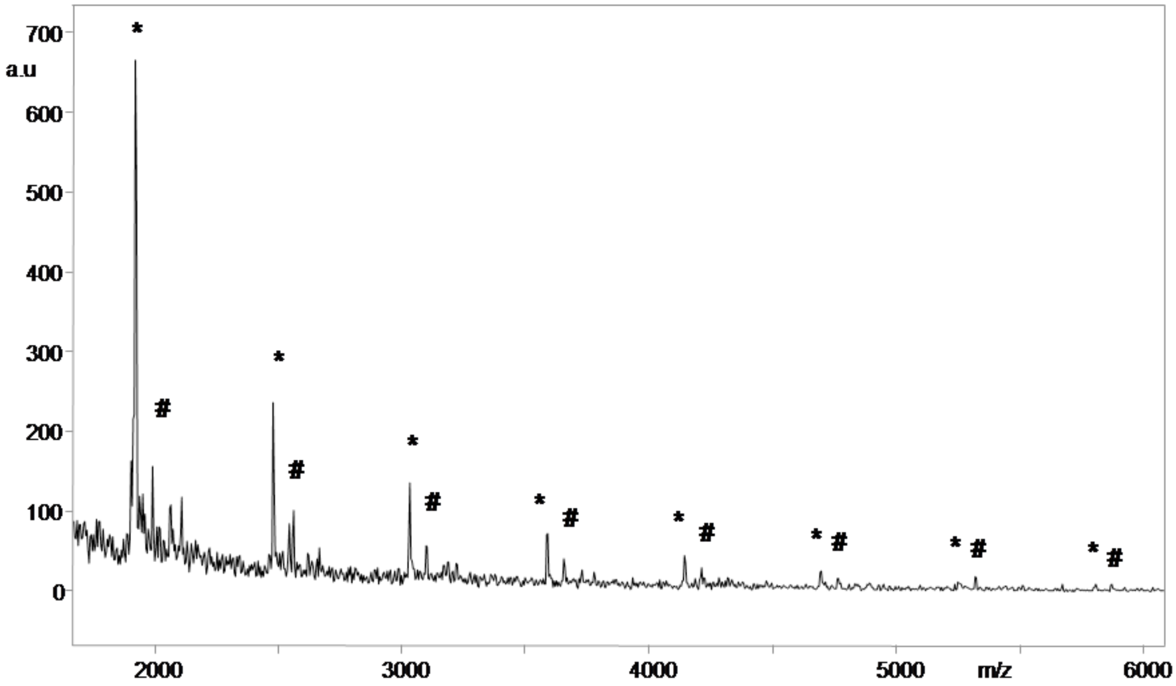

Figure ESI 1 - MALDI-TOF mass spectrum of **P2**

The mass spectrum of **P2** consists essentially of two series of peaks, detected as M^+, at m/z values 1921+*n* 555 (*) with n=0-6 and 1989+*n* 555 (#) with n = 0-6, respectively. Both the ions of (*) and (#) are detected as M^+ species due to loss of a $[C_4F_9SO_3]^-$ fragment from the corresponding oligomeric species. It is worth to notice that the first series of peaks (*) corresponds to structures relative to oligomers (from tetramers to decamers) having hydrogen and/or vinyl as end groups, while the latter (#) corresponds to chains (from tetramers to decamers) having an isobutyronitrile and hydrogen as endgroups. Little signals due to oligomers having isobutyronitrile fragments as end-groups (deriving from chain coupling phenomena) are also present.