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Supporting Information

Grafting of Chain-End-Functionalized Perfluorocyclobutyl (PFCB) Aryl Ether Ionomers onto Mesoporous Carbon Supports

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Experimental Details

1. Materials

Chlorosulfonic acid (CSA) and 4-bromopheonol were purchased from Alfa Aesar. Commercially available monomer 4,4'-bis(4-trifluorovinyloxy)biphenyl was generously donated by Tetramer Technologies, LLC and is also available through Oakwood Chemicals, Inc. Anhydrous sodium sulfate (Na_2SO_4, 99%) was purchased from Mallinckrodt. Sodium hydroxide (NaOH, 0.01N) and hydrochloric acid (HCl, 0.0lN) were obtained from Fisher Scientific. Dimethylformamide (DMF) (Sigma-Aldrich) was vacuum distilled prior to use. All other starting chemicals and solvents were purchased from Sigma-Aldrich and used as received.

2. General Methods

^{1}H, ^{19}F, and ^{31}P NMR spectra were recorded in $CDCl_3$, acetone- d_6 or DMSO-d_6 using a JEOL Eclipse + 300. Gel permeation chromatography (GPC) data were collected in $CHCl_3$ from a Waters 2690 Alliance System with photodiode array detection and molecular weights were obtained using polystyrene as a standard. Thermal gravimetric analysis (TGA) was carried out on a Mettler-Toledo 851 instrument in nitrogen and air at a heating rate of 10 °C/min up to 800 °C. Differential scanning calorimetry (DSC) analysis was performed on a TA Q1000 instrument in nitrogen at a heating rate of 10 °C/min up to 210 °C. The glass transition temperature (T_g) of polymers was obtained from a second heating cycle using TA Universal Analysis 2000 software suite. Energy-dispersive X-ray spectroscopy (EDX) was performed on a field emission scanning electron microscope (FESEM-Hitachi S4800) equipped with an Oxford INCA energy 200 EDX system. Elemental microanalysis (EA) data for sulfur, carbon, hydrogen and fluorine were obtained from Atlantic Microlab, Inc. (Norcross, GA). Ion-exchange capacity

(IEC) of ionomer samples was determined via a direct neutralization titration method using standard 0.01 N NaOH. The relative sizes of the ionomer solutes were investigated by dynamic light scattering (DLS) using a scattering angle of 90° at room temperature with a Coulter N4 Plus particle size analyzer equipped with a laser source of 10 mV helium-neon at 632.8 nm.

3. Preparation and characterization of polymers

3.1. Synthesis of diethyl(4-hydroxyphenyl)phosphonate **1**[1]

Diethyl(4-hydroxyphenyl)phosphonate was synthesized as described in literature.[1] A 4-bromophenol (1 g, 5.8 mmol), nickel(II) bromide (0.1 g, 0.46 mmol), and mesitylene (3 mL) were charged into a round-bottom flask equipped with a reflux condenser and stirred at 170 °C under nitrogen. Triethylphosphite (1.44 g, 8.7 mmol) was added drop wise to the mixture and stirred at 170 °C for 2 h under nitrogen. The mixture was then allowed to cool to room temperature and filtered through Celite. The crude mixture was dissolved in ether and extracted with a 10% sodium hydroxide solution. The aqueous phase was washed with ether, acidified by concentrated hydrochloric acid and extracted with diethyl ether several times. The collected organic phase was then dried using anhydrous magnesium sulfate and solvent was removed by rotary evaporation. Diethyl(4-hydroxyphenyl)phosphonate was obtained as a white solid. (0.96 g, 72% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.30 (t, *J* = 7.1 Hz, CH_3–), 3.94–4.21 (m,–CH_2–), 6.99 (dd, *J* = 8.7, 3.7 Hz, Ar-H), 7.63 (dd, *J* = 13.0, 8.7 Hz, Ar-H), 9.47 (s, –OH) ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.32 (d, *J* = 7.3 Hz, CH_3–), 62.44 (d, *J* = 5.8 Hz, –CH_2–), 116.12 (d, *J* = 15.9 Hz, $\underline{C}$=C–OH), 116.54 (d, *J* = 197 Hz, C=$\underline{C}$–P), 133.87 (d, *J* = 12.3Hz, $\underline{C}$=C–P), 162.05 (s, C=$\underline{C}$–OH); ^{31}P NMR (121 MHz, $CDCl_3$): δ 21.82 (s).

3.2. Synthesis of PFCB aryl ether polymer **2**

4,4'-bis(4-trifluorovinyloxy)biphenyl monomer (10 g, 28.88 mmol) was added into a three-neck round-bottom flask equipped with a mechanical stirrer, condenser, and argon gas inlet. The monomer was heated to 80 °C and the molten monomer system was sparged with argon gas for 30 min. Thermal step-growth cyclopolymerization was then conducted at 160 °C for 12 h under argon blanket. After cooling to room temperature, the viscous product was dissolved in tetrahydrofuran (THF) and precipitated in a large excess of methanol. The white precipitate was filtered, washed with methanol in a Soxhlet extractor for 24 h, and dried in a vacuum oven at 60 °C for 24 h. PFCB aryl ether polymer 2 was obtained as a white power (8.02 g, 80% yield). ^{1}H NMR (300 MHz $CDCl_3$): δ 7.28 (s, Ar-$\underline{H}$), 7.66 (s, Ar-$\underline{H}$); ^{19}F NMR (283 MHz, $CDCl_3$): δ –133.86 (dd, *J* = 110, 58.3 Hz, $-C\underline{F}=CF_2$), –127.7-(–131.23) (m, cyclobutyl-F_6), –126.30 (dd, *J* = 110, 14.4 Hz, *trans*–$CF=C\underline{F}_2$), –119.3 (dd, *J* = 96.4, 58.3 Hz, *cis*–$CF=C\underline{F}_2$); M_n 7,300 (^{19}F NMR)

3.3. Synthesis of polymer **3**

Sodium hydride (28.80 mg, 1.20 mmol) and DMF (3 mL) were charged into a two-neck round-bottom flask equipped with a reflux condenser under nitrogen. Diethyl(4-hydroxyphenyl) phosphonate (0.23 g, 1 mmol) was added drop wise into a stirred suspension of NaH/DMF and polymer-2 (3.64 g, 0.50 mmol) dissolved in DMF (10 mL) was added into the solution at room temperature. The flask was then placed in a preheated oil bath at 80 °C and stirred for 5 hr. The mixture was allowed to cool to room temperature and treated with DI H_2O. The white precipitate was filtered, washed with methanol and hexane, and dried under a vacuum at 60 °C. Polymer 3 was obtained as a white powder (3.43 g, 89% yield). ^{1}H-NMR (300 MHz, Acetone-*d6*): δ 1.19-1.29 (m, CH_3–), 3.96–4.10 (m, –CH_2–), 6.42-6.61 (d, *J* = 58.6 Hz, $-C\underline{H}F-$), 7.29 (s, Ar–H), 7.39–7.47 (m, Ar–H), 7.67 (s, Ar–H), 7.80–7.91 (m, Ar–H); ^{19}F-NMR (283 MHz, Acetone-*d6*): δ –141.36 (d, *J* = 59.4 Hz, –CHF–CF$_2$–), –127.7-(–131.23) (m, overlap of *trans*–CF=CF and cyclobutyl-F$_6$), –123.6 and –122.0 (d, *J* = 41.5, *cis*–CF=CF), –86.54 (dd, *J* = 2460, 144.2 Hz, –CHF–CF$_2$–); ^{31}P NMR (121 MHz, Acetone-*d6*): δ 17.04 (s); M$_n$ 7,700 (^{19}F NMR); PDI = 2.08 (GPC, M_w/M_n = 11,603 /5,581)

3.4. Synthesis of polymer **4**

In a two-neck round-bottom flask equipped with a reflux condenser, polymer 3 (3 g, 0.321 mmol) was dissolved in dichloromethane (DCM, 25mL) and then chlorosulfonic acid (6.60 mL, 32.1 mmol) was added in a single portion at 36 °C internal temperature. After stirring vigorously for 1 h, gel-like precipitates were observed as a dark-brown color in the flask. After cooling to room temperature, distilled water (100 ml) was gradually added into the flask placed on the ice bath to quench excess chlorosulfonic acid. A small amount of ethyl acetate was added as a co-solvent and the solvents were removed slowly by rotary evaporation. The crude product, a pale brown powder, was washed with DCM, filtered under vacuum and dried at 60 °C under vacuum. The sulfonated polymer was then refluxed in concentrated hydrochloric acid (37%) at 70 °C for 10 days to de-protect the phosphonic acid groups. The resulting phosphonic acid polymer 4 was filtered under vacuum and washed with DCM several times. The final products were dried under vacuum at 60 °C for 24h. Polymer 4 was obtained as a pale brown powder (3.09 g, 92% yield). ^{1}H-NMR (300 MHz, Acetone-*d6*): δ 6.63-6.87 (m, –CHF–), 7.08–7.9 (m, Ar–H), 8.03 (s, Ar–H adjacent to -SO$_3$H); ^{19}F-NMR (283 MHz, DMSO-*d6*): δ –141.2 (d, *J* = 55.9 Hz, –CHF–CF$_2$–), –124.0-(–133.4) (m, cyclobutyl-F$_6$), –84.5 (d, J_{ab} = 148.0 Hz, –CHF–CF$_2$–), –83.1 (d, J_{ab} = 148.0 Hz, –CHF–CF$_2$–), –79.54 (d, *J* = 112.4 Hz, –CHF–CClF–); ^{31}P NMR (121 MHz, DMSO-*d6*): δ

12.19 (s); M_n 10,500 (^{1}H NMR); Elemental Analysis-Found: C, 36.15; H, 2.15; F, 20.59; S, 9.97.

3.5. Solubility of phosphonated polymers

The solubility of polymers was determined in the common organic solvents as shown in Table S1. The phosphonate diester polymer 3 was soluble in nonpolar organic solvents. On the other hand, the sulfonated polymers were found be soluble in water as well as in polar organic solvents.

Table S1. Solubility of the polymers in common organic solvents at room temperature

Polymer	DCM	THF	$CHCl_3$	MeOH	DMAc	DMSO	H_2O
3	++	++	++	–	–	–	–
4	–	+	+	++	++	++	++

++ soluble; + partially soluble; - insoluble

3.6. Preparation of aqueous ionomer solutions

Four salt-added ionomer aqueous solutions were prepared by adding a fixed amount (0.05 g) of ionomer into sodium sulfate (Na_2SO_4) aqueous solutions, which contained 0, 2.5, 5.0, and 50 mmol Na_2SO_4, respectively. The final solution volumes were then fixed at 50 mL.

4. Carbon/zirconia nanocomposite materials

4.1. Preparation of Mesoporous carbon/zirconia nanocomposites

Mesoporous carbon/zirconia nanocomposites (ca. 16 wt.% ZrO_2) were prepared as described in literature.[2] The composite sample used in this work had a total BET surface area of 778 $m^2 \cdot g^{-1}$, a total pore volume of 2.22 $cm^3 \cdot g^{-1}$, and a porosity of 84.6 %. The pore size distribution calculated by the BJH method revealed that the specific pore volume of the composite was mostly composed of pores in the range of 10 to 30 nm with the most probable pore size at ~15 nm.

4.2. Preparation of SF-Ionomer-C/ZrO_2 and SA-Ionomer-C/ZrO_2 materials

Attachment of the ionomer onto C/ZrO_2 was performed by immersing 0.2 g of the C/ZrO_2 powder sample in the aqueous ionomer solution (50 mL) with salt (0.05 M Na_2SO_4) or without salt (0 M Na_2SO_4) at 100 °C for 5 h. To remove physically adsorbed ionomer, the treated samples were heated in DI water at 80 °C under continuous stirring for 2 h. The hot suspension was then centrifuged and the supernatant solution was removed by decantation. The C/ZrO_2 sample was then dispersed again in hot DI water (e.g., 80 °C). These successive washing steps were repeated seven times. The washed sample was dried overnight at 80 °C under vacuum. The dried sample was then immersed in a 0.2 M HCl solution for 5 h under stirring to ensure that all acid groups are in the protonated form. Finally, the HCl-treated sample was centrifuged, rinsed with 10 mL DI water, and vacuum-dried at 120 °C for 24 h. The resulting samples prepared in the salt-free (SF) and salt-added (SA) ionomer solutions were designated as SF-Ionomer-C/ZrO_2 and SA-Ionomer-C/ZrO_2, respectively. As a control experiment, the identical treatment with a 0.05 M salt solution (no ionomer) was also applied to C/ZrO_2.

4.3. Ion exchange capacity of carbon/zirconia nanocomposite materials

A 0.1 g quantity of dried SF-Ionomer-C/ZrO_2 and SA-Ionomer-C/ZrO_2 was placed in 10 mL of a 2.0 M NaCl solution and mechanically stirred at room temperature for 72 h to allow for complete exchange of Na^+ ions with H^+ ions. Only the solution was retrieved by filtration. A 5 mL quantity of the retrieved solution was then mixed with 5 mL of a standard 0.01 N HCl solution so that a total 10 mL volume of titration solution was prepared. The resulting solution was titrated with a standard 0.01 N NaOH solution under a nitrogen blanket. The pH change was monitored to identify the endpoint using a pH meter (Accumet AB15, Fisher) with a double-junction pH electrode (Ag/AgCl reference, Accumet). EA (S, wt.%): SF-Ionomer- C/ZrO_2: 1.58, SA-Ionomer-C/ZrO_2: 1.89. EDX (S, wt%): SF-Ionomer- C/ZrO_2: 1.52, SF-Ionomer- C/ZrO_2: 1.95.

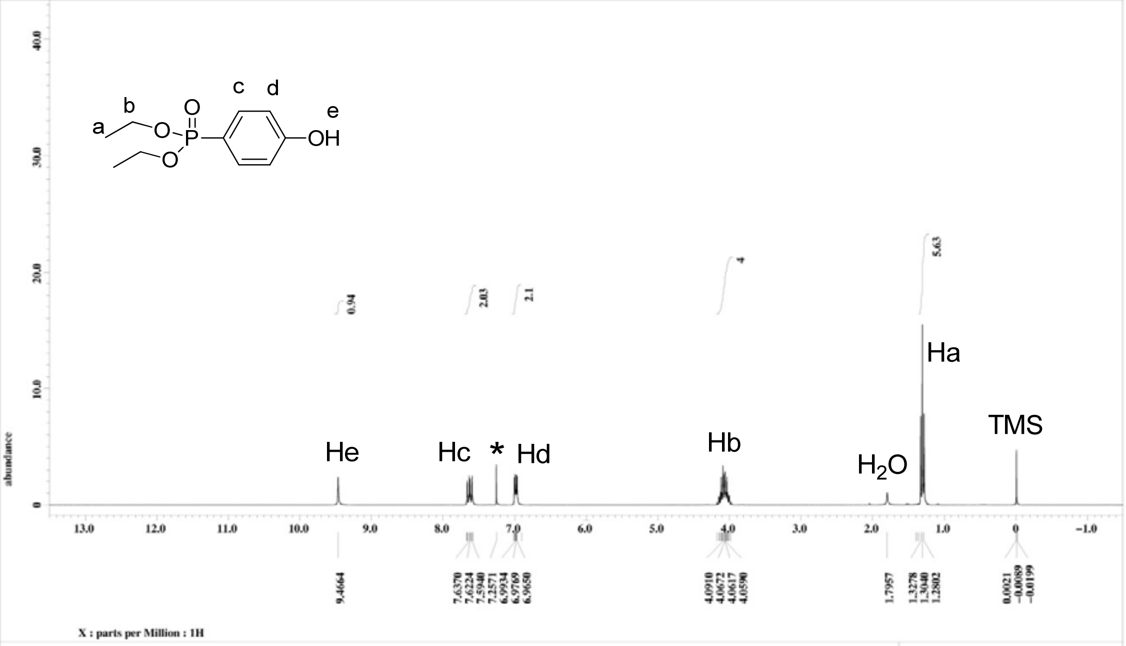

Figure S1. ^{1}H NMR (in $CDCl_3$*) spectrum of diethyl(4-hydroxyphenyl) phosphonate **1**.

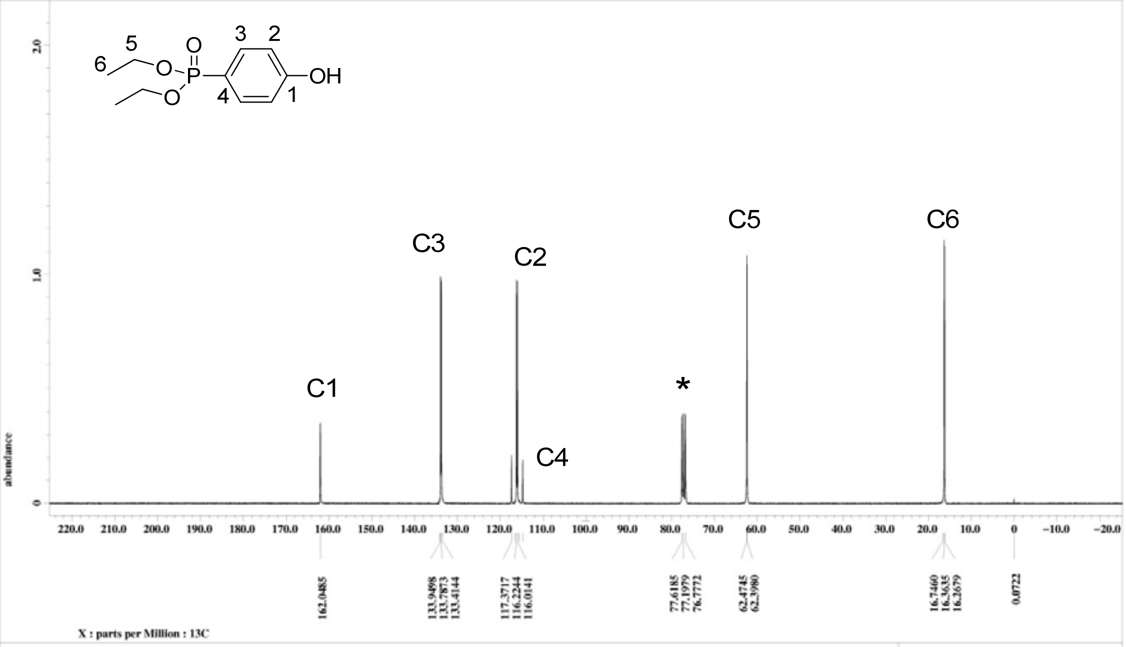

Figure S2. ^{13}C NMR (in $CDCl_3$*) spectrum of diethyl(4-hydroxyphenyl) phosphonate **1**

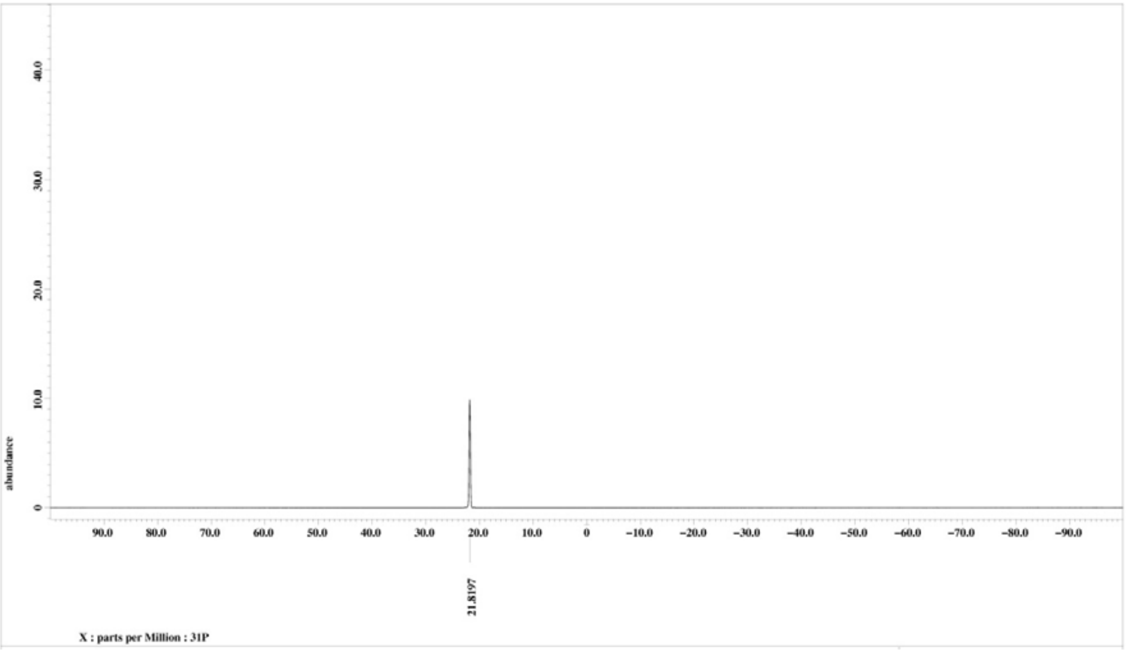

Figure S3. ^{31}P NMR (in $CDCl_3$*) spectrum of diethyl(4-hydroxyphenyl) phosphonate **1**.

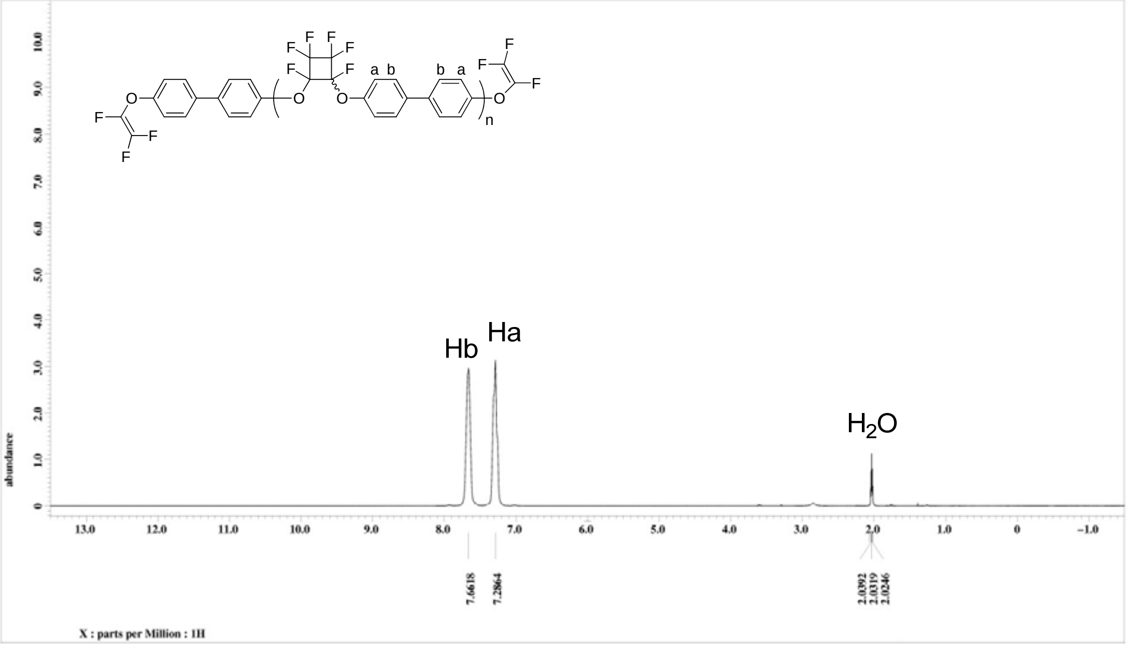

Figure S4. ^{1}H NMR (in Acetone-d6) spectrum of PFCB aryl ether polymer **2**.

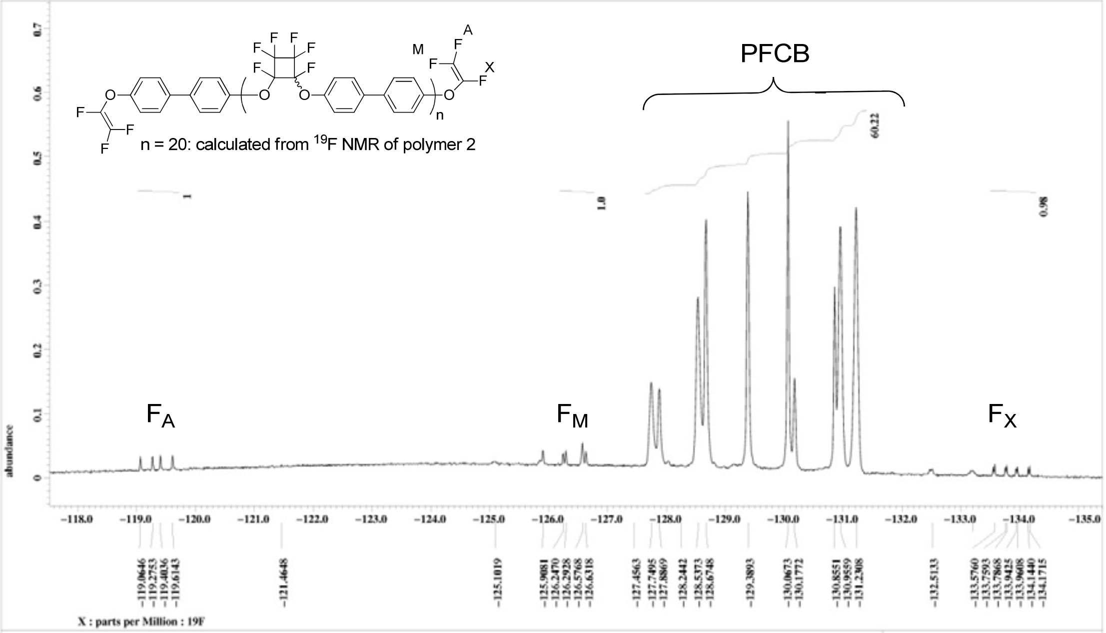

Figure S5. ^{19}F NMR (in Acetone-d6) spectrum of PFCB aryl ether polymer **2**.

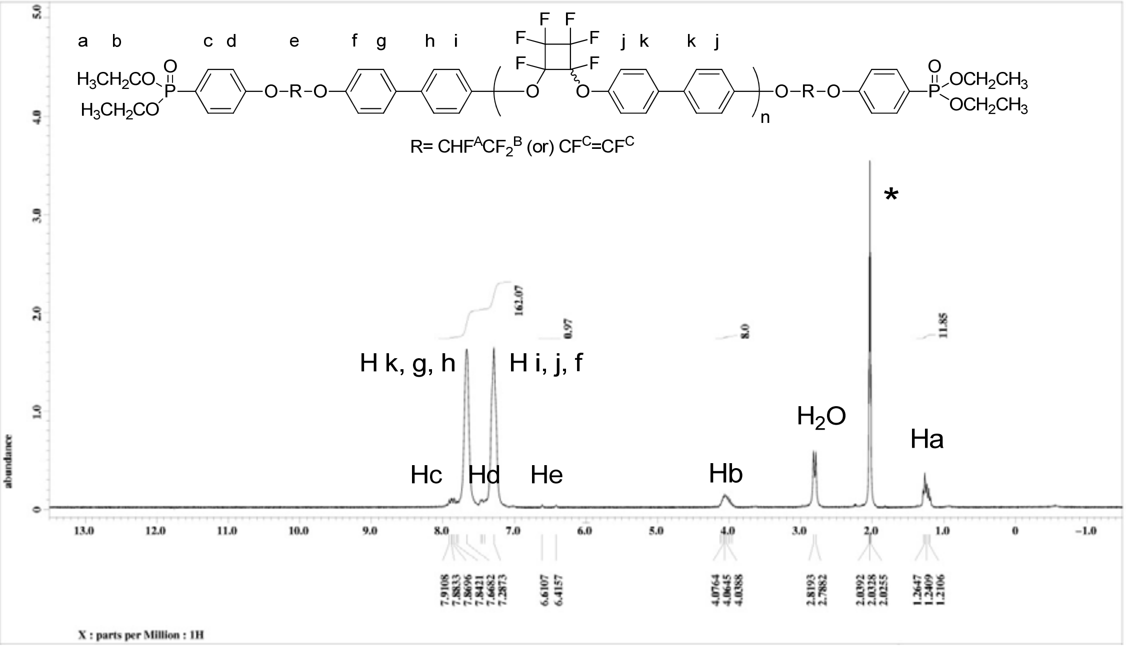

Figure S6. ^{1}H NMR (in Acetone-d6*) spectrum of polymer **3**.

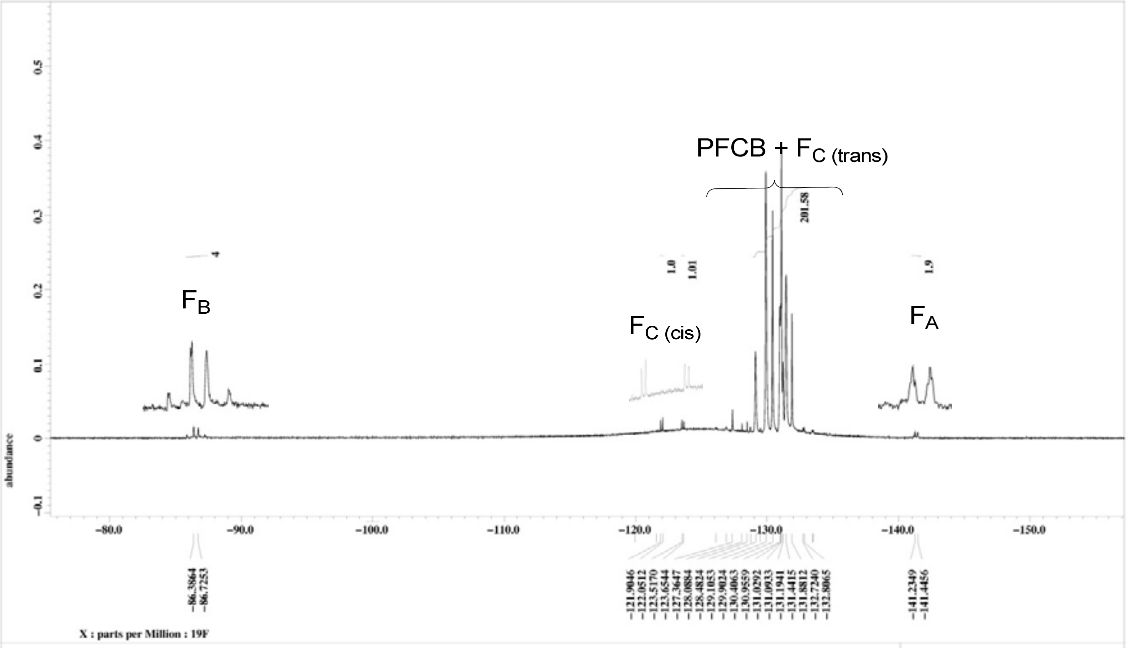

Figure S7. ^{19}F NMR (in Acetone-d6) spectrum of polymer **3**.

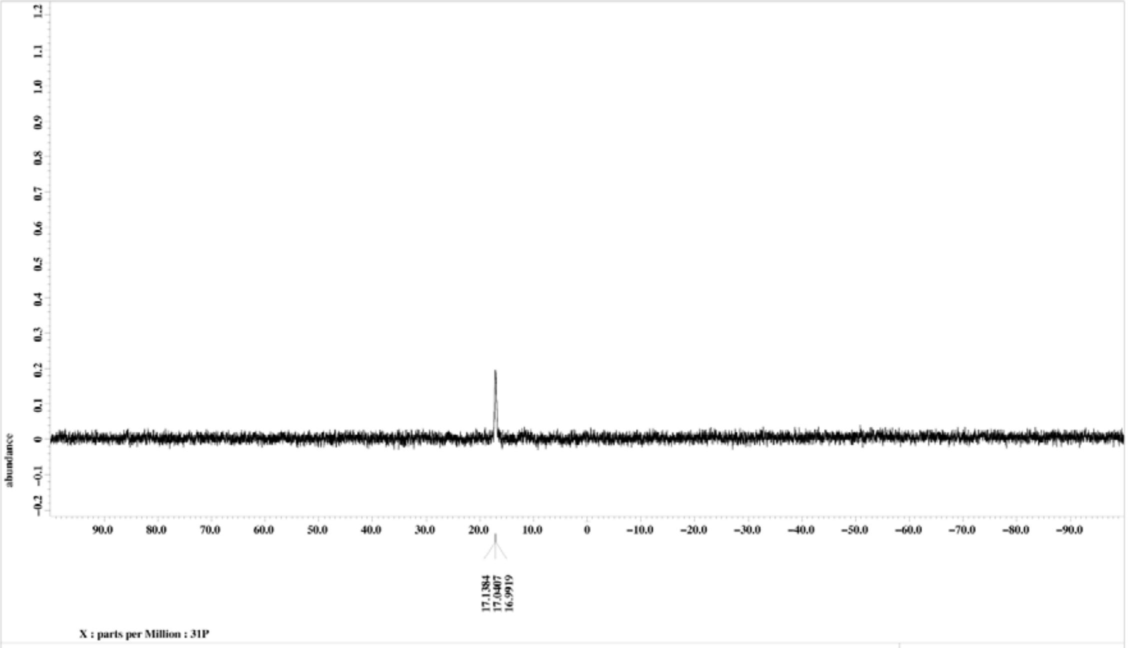

Figure S8. ^{31}P NMR (in Acetone-d6) spectrum of polymer **3**.

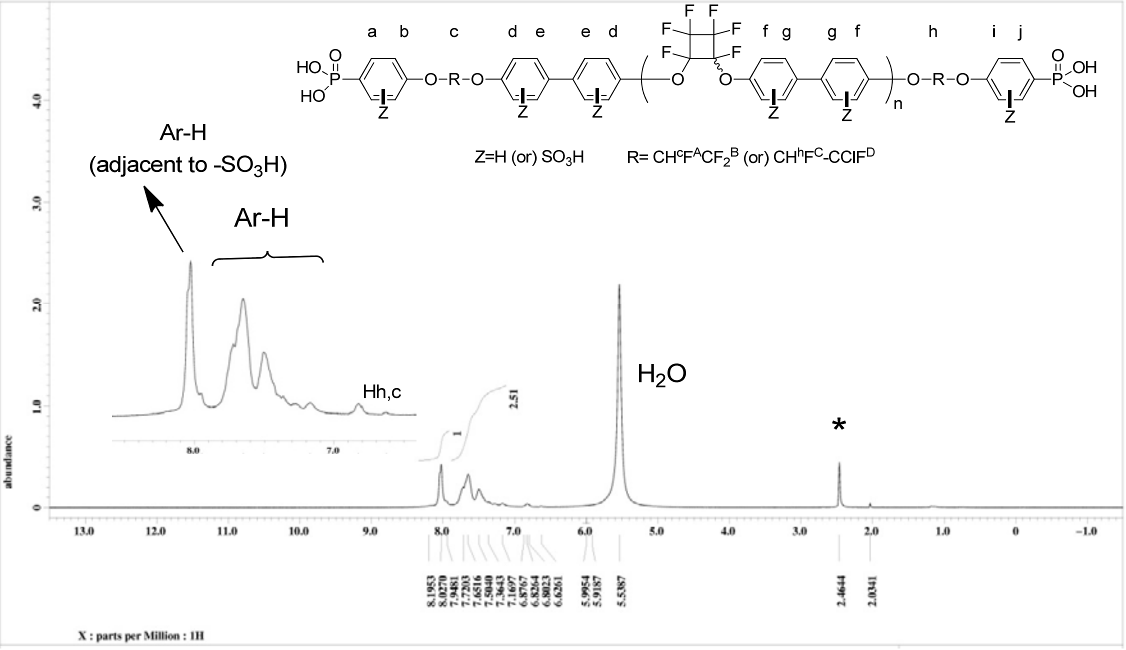

Figure S9. ^{1}H NMR (in DMSO-*d6**) spectrum of polymer **4**

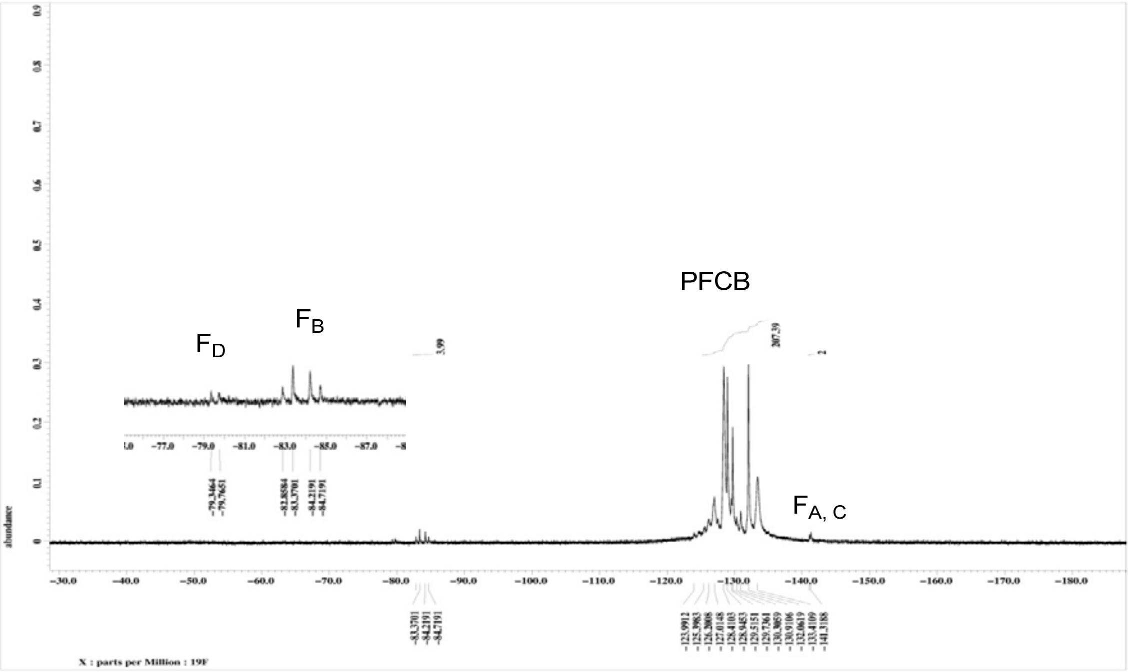

Figure S10. ^{19}F NMR (in DMSO-*d6*) spectrum of polymer **4**.

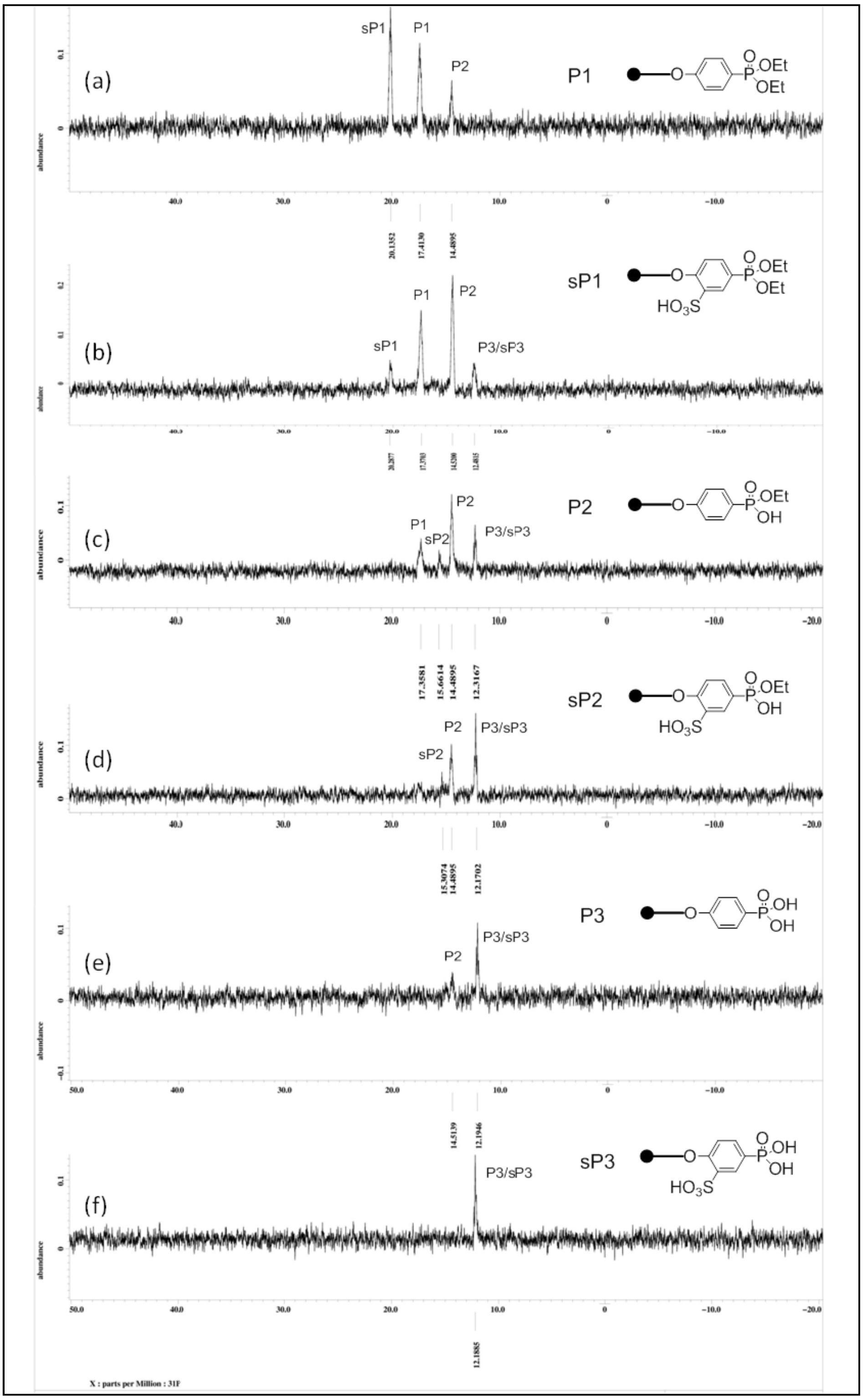

Figure S11. ^{31}P NMR (in DMSO-*d6*) spectra of (a) after sulfonation and (b-f) hydrolysis as a function of time.

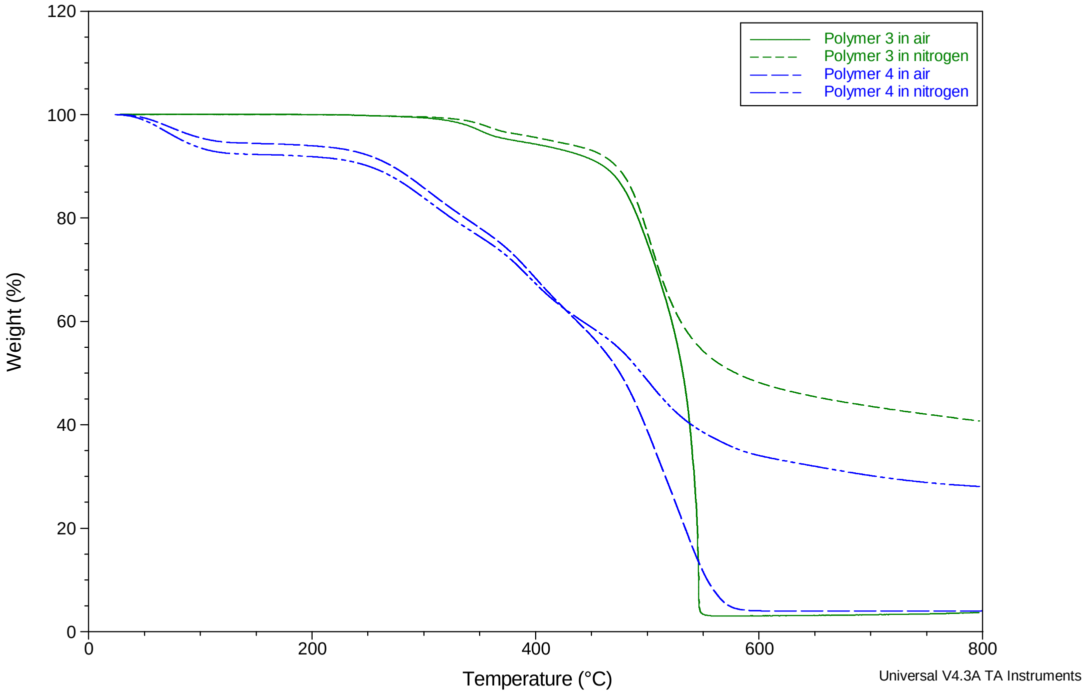

Figure S12. TGA curves of polymers 3 and 4

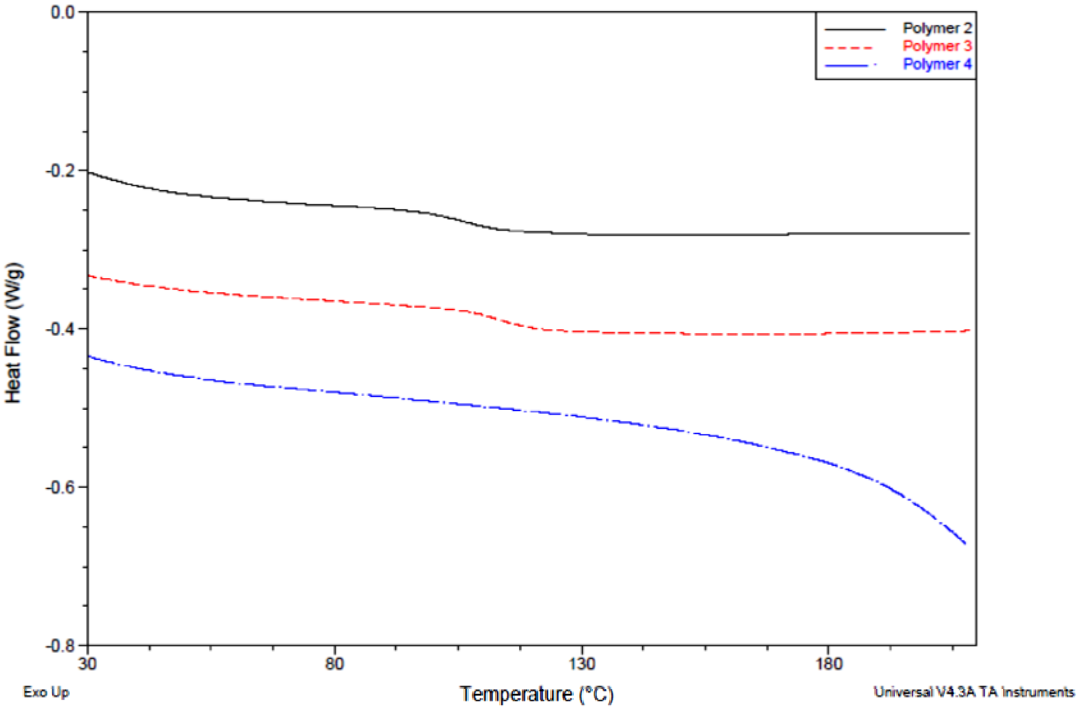

Figure S13. DSC of polymers 2, 3, and 4

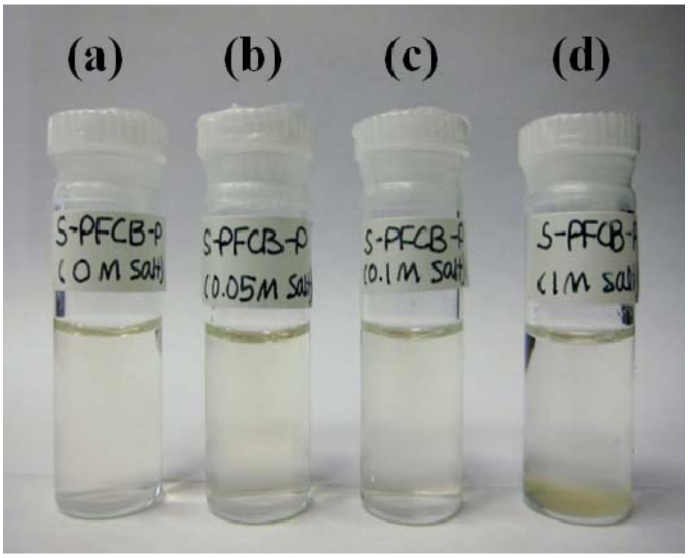

Figure S14. A photo image of the aqueous ionomer solutions containing different Na_2SO_4 salt concentrations; (a) 0.00, (b) 0.05, (c) 0.10, and (d) 1.00 M. (Note the yellow precipitate in the 1.0 M ionomer solution.)

References

1. N. Lejeune, I. Dez, P.-A. Jaffrès, J.-F. Lohier, P.-J. Madec and J. Sopkova-de Oliveira Santos, *Eur. J. Inorg. Chem.*, 2008, **2008**, 138.
2. J.-M. Oh, A. S. Kumbhar, O. Geiculescu and S. E. Creager, *Langmuir*, 2012, **28**, 3259.