



Supporting Information

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**Benign by Molecular Design: Active Polymeric Super Acid Catalysts and Highly
Conductive Polymeric Lithium Electrolytes****

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DCB – 1, 2-dichlorobenzene

TCB – 1,2,4-trichlorobenzene

THF – Tetrahydrofuran

DSC - Differential scanning calorimetry

GPC - Gel permeation chromatography

PMAO - Polymethylaluminoxane

NMR – Nuclear magnetic resonance

ICF₂CF₂OCF₂CF₂SO₂F was obtained from Shanghai Institute of Organic Chemistry,
China. Other chemicals were purchased from Aldrich.

Catalyst Synthesis

Catalysts **A – E** were prepared in a nitrogen drybox by following published literatures.^{1,2}

Monomer Synthesis

Preparation of $\text{CH}_2=\text{CH}(\text{CH}_2)_4(\text{CF}_2)_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ – Monomer 1

A mixture of 72 g of hexadiene, 127.8 g of $\text{ICF}_2\text{CF}_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$, 7.0 g of Cu powder and 180 mL of hexane was stirred at 90°C overnight. Solids were removed by filtration and washed with hexane. After removal of volatiles, residue was distilled to give 115.3 g of product (76% yield), bp $80^\circ\text{C}/1.6$ mm Hg. ^{19}F NMR: +45 (t, J = 6.0 Hz, 1F), -82.7 (m, 2F), -88.1 (dt, J = 42.5 Hz, J = 12.6 Hz, 1F), -88.7 (dt, J = 45.5 Hz, J = 12.6 Hz, 1F), -112.7 (m, 2F), -115.9 (ddd, J = 2662.2 Hz, J = 30.0 Hz, J = 8.2 Hz, 1F), -118.9 (ddd, J = 262.2 Hz, J = 26.8 Hz, J = 7.4 Hz, 1F). IR: 3082 (m), 2929 (m), 1643 (m), 1152 (s).

To a stirred solution of 100 g of $\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{CHICH}_2(\text{CF}_2)_2\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ and 200 mL of ether was added 63 g of Bu_3SnH at room temperature. After the addition was complete, the reaction mixture was refluxed for 4 hours and then cooled with ice water. Excess of Bu_3SnH was destroyed by addition of iodine. After being diluted with 200 mL of ether, the reaction mixture was treated with a solution of 25 g of KF in 200 mL of water for 30 min. The solids were removed by filtration through a funnel with silica gel and washed with ether. The ether layer was separated and washed with water, aqueous NaCl solution and dried over MgSO_4 . After removal of the ether, residue was distilled to give 54.7 g of product (73% yield), bp $72^\circ\text{C}/10$ mm Hg, and 12.2 g of starting material. ^{19}F NMR: +45 (m, 1F), -82.7 (m, 2F), -88.0 (m, 2F), -112.6 (m, 2F), -118.6 (t, J = 18.4 Hz, 2F). ^1H NMR: 5.80–5.95 (m, 1H), -5.05–5.15 (m, 2H), 2.00–2.20 (m, 4H), 1.62–1.75 (m, 2H), 1.55–1.61 (m, 2H).

Preparation of $\text{CH}_2=\text{CH}(\text{CH}_2)_4(\text{CF}_2)_4\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ – Monomer 2

A mixture of 24 g of hexadiene, 53 g of $\text{I}(\text{CF}_2)_4\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$, 3.0 g of Cu powder and 60 mL of hexane was stirred at 70°C overnight. Solids were removed by filtration and washed with hexane. After removal of volatiles, residue was distilled to give 49.5 g of adduct (81% yield), $\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{CHICH}_2(\text{CF}_2)_4\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$, bp $74^\circ\text{C}/0.07$ mm Hg. ^{19}F NMR: +45.5 (m, 1F), -82.4 (m, 2F), -83.5 (m, 2F), -112.2 (dm, J = 270 Hz, 1F), -112.6 (m, 2F), -115.2 (dm, J = 270 Hz, 1F), -124.3 (s, 2F), -125.5 (m, 2F).

To stirred solution of 47 g of $\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{CHICH}_2(\text{CF}_2)_4\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ and 150 mL of ether was added 27 g of Bu_3SnH at room temperature. After the addition was complete, the reaction mixture was stirred overnight. Excess of Bu_3SnH was destroyed by addition of iodine. After being diluted with 150 mL of ether, the reaction mixture was treated with a solution of 20 g of KF in 100 mL of water for 30 min. The solids were removed by filtration through a funnel with silica gel and washed with ether. The ether layer was separated and washed with water, aqueous NaCl solution and dried

over MgSO₄. After removal of the ether, residue was distilled to give 24.7 g of product (76% yield) with 6.8 g of the adduct recovered (88% conversion), bp 103^oC/9.8 mm Hg. ¹⁹F NMR: +45.4 (m, 1F), -82.4 (m, 2F), -83.5 (m, 2F), -112.6 (t, J = 2.6 Hz, 2F), -115.1 (t, J = 15 Hz, 2F), -124.3 (s, 2F), -125.7 (t, J = 14 Hz, 2F). HRMS: calcd for C₁₂H₁₁F₁₃SO₃: 482.0221. Found: 482.0266.

Polymer Synthesis

Procedure for Making the Ethylene/CH₂=CH₂(CH₂)₄(CF₂)_nO(CF₂)₂SO₂F (n= 2 or 4) Copolymers Using the Palladium Catalysts

Entry 1 of Table 1:

The catalyst PdCH₂CH₂CH₂C(O)OCH₃[(2,6-(CHMe₂)₂C₆H₃)₂DAB(Me₂)]SbF₆ (0.0205g, 0.024mmol) and CH₂=CH₂(CH₂)₄(CF₂)₄O(CF₂)₂SO₂F (3.50g, 7.26 mmol) were dissolved in 18 mL CH₂Cl₂ in a Schlenk flask in a drybox. The flask was connected to a Schlenk line and the flask was then briefly evacuated and refilled with ethylene from the Schlenk line. This was stirred under 1 atm of ethylene for 72 h at RT. The reaction mixture was filtered and solvent evaporated. The oil was dissolved in 10mL CH₂Cl₂, followed by addition of 100 mL methanol under stirring. The upper layer was decanted. The reverse precipitation was repeated two more time. The light yellow oil product was isolated and was dried in vacuo to afford 3.68g product. Based on ¹HNMR (CDCl₃), the polymer was highly branched (89Me/1000CH₂). Comparison of the integral of the -CH₂CF₂- with the integral of methyls (0.8-1.0 ppm) and methylenes (1.1-1.4 ppm) indicated a comonomer content of 8.5 mole%. ¹⁹F NMR (CDCl₃): δ 45.27 ppm, -SO₂F; -82.56 ppm, -83.66 ppm, -112.82 ppm, -115.34 ppm, -124.45 ppm, -125.85 ppm, CF₂ peaks. It exhibited a glass transition temperature of -57^oC by differential scanning calorimetry. Gel permeation chromatography (THF, polystyrene standard): Mw = 120,000; Mn = 78,900; Mw/Mn = 1.54.

Entry 2 of Table 1

The catalyst PdCH₂CH₂CH₂C(O)OCH₃[(2,6-(CHMe₂)₂C₆H₃)₂DAB(Me₂)]SbF₆ (0.0848g, 0.1mmol) and CH₂=CH₂(CH₂)₄(CF₂)₂O(CF₂)₂SO₂F (11.5g, 0.0300 mol) were dissolved in 25 mL CH₂Cl₂ in a Schlenk flask in a drybox. The flask was connected to a Schlenk line and the flask was then briefly evacuated and refilled with ethylene from the Schlenk line. This was stirred under 1 atm of ethylene for 74 h at RT. The reaction mixture was filtered. To the filtrate was added 350 mL methanol under stirring. The oil precipitate was isolated and was redissolved in 70 mL CH₂Cl₂, followed by addition of 350 mL methanol. The light yellow oil product was isolated and was dried in vacuo to yield 14.24g product. Based on ¹HNMR (CD₂Cl₂), the comonomer incorporation was 6.7 mole%. The polymer was highly branched (89Me/1000CH₂). It exhibited a glass transition temperature of -69^oC by differential scanning calorimetry. Gel permeation chromatography (THF, polystyrene standard): Mw = 155,000; Mn = 90,100; Mw/Mn = 1.73.

Entry 3 of Table 1

The catalyst PdCH₂CH₂CH₂C(O)OCH₃[(2,6-(CHMe₂)₂C₆H₃)₂DAB(Me₂)]SbF₆ (0.0848g, 0.1mmol) and CH₂=CH₂(CH₂)₄(CF₂)₂O(CF₂)₂SO₂F (11.5g, 0.0300 mol) were dissolved in 72 mL CH₂Cl₂ in a Schlenk flask in a drybox. The flask was connected to a Schlenk line and the flask was then briefly evacuated and refilled with ethylene from the Schlenk line. This was stirred under 1 atm of ethylene for 72 h at RT. The reaction mixture was filtered. The filtrate was concentrated to 70mL, and was added 350 mL methanol. The oil precipitate was isolated and was redissolved in 70 mL CH₂Cl₂, followed by addition of 350 mL methanol. The light yellow oil product was isolated and was dried in vacuo to yield 24.10g product. Based on ¹HNMR (CDCl₃), the polymer was highly branched (113Me/1000CH₂). Comparison of the integral of the -CH₂CF₂- with the integral of methyls (0.8-1.0 ppm) and methylenes (1.1-1.4 ppm) indicated a comonomer content of 2.9 mole%. It exhibited a glass transition temperature of -66°C by differential scanning calorimetry. Gel permeation chromatography (THF, polystyrene standard): Mw = 186,000; Mn = 90,500; Mw/Mn = 2.06.

General Procedure for Making the Ethylene/CH₂=CH₂(CH₂)₄(CF₂)_nO(CF₂)₂SO₂F (n= 2 or 4) Copolymers Using the (α-diimine)NiBr₂ Catalysts.

Polymers 3 to 10 were produced by combining in a Schlenk flask in a drybox the indicated amounts of the indicated catalyst, comonomer, and solvent. The mixture was placed under 1 atmosphere of ethylene and purged with ethylene for 15 minutes. PMAO in toluene (2.2 mL, 7.1wt%) was added to initiate the reaction which continued under agitation for the indicated time at 0°C (using a ice/water bath). Small amount of methanol(*ca.* 5 mL) was then added to the reaction mixture slowly. The mixture was then poured into 300 mL of methanol, followed addition of 5 mL conc. HCl to the mixture. The white solid polymer was filtered, washed with methanol and dried in vacuo. GPC analyses of the copolymers were done at 135°C in TCB using polystyrene as standard and was calculated as linear polyethylene. Melting points were obtained from DSC and they were reported as melt transition of the second heat (10°C/min heating rate). The % of comonomer in the polymer was determined by a combination of proton and ¹³C nuclear magnetic resonance.

Table 1: Synthesis of Polymers 4-10

Polymer	Reaction Conditions						Product				
	Catalyst		Comonomer				Yield (g)	# of Me Per 1000 CH ₂	Mole-% co-monomer	Mw/Mn x10 ³	m.p. (°C)
	Type	Amount (mmols)	n=	Amount	Quantity of Toluene (ml)	Reaction Time (min)					
4	B	0.017	4	9.8 g	30	40	3.87	77	3.9	330/141	102
5	B	0.017	2	13.75 g	30	18	2.66	49	4.4	186/72	94
6	C	0.017	2	13.75 g	30	30	2.16	6	6.9	67/25	126
7	D	0.014	2	13.75 g	30	30	2.61	4	5.3	26/9	126
8	E	0.034	2	13.75 g	70	30	7.11	20	2.6	173/36	118
9	E	0.017	2	13.75 g	30	30	3.2	11	3.7	251/49	124
10	E	0.017	2	27.50 g	20	105	2.51	8	10.8	246/44	127

* 4.4 mL 7.1% solution of PMAO in toluene was used in this case.

Hydrolysis of copolymers

Hydrolysis of Copolymer of Entry 1 of Table 1 (Catalyst **4-1**)

Copolymer made in Entry 1, containing 8.5 mol % of fluorinated comonomer (1.5 g) was dissolved in 30 mL of THF at room temperature. KOH (0.5 g) in 5 mL of ethanol and 3 mL of water was added and the resulting mixture was stirred at room temperature for 6 h. After removal of the solvent, residue was treated with diluted HCl for 70 h and then filtered to give solids which were washed with water, dilute HCl and dried under full vacuum at 70°C for two days to give 1.4 g solid.

Hydrolysis of copolymer of Entry 2 of Table 1 to make polymeric acid 4-2 (Catalyst **4-2**)

A flask was charged with copolymer (Entry 2 in table 1. 6.7 %) and 20 mL of THF, and then a solution of 2.5 g of KOH in 10 mL of ethanol and 3 mL of water was added. The resulting mixture was stirred at room temperature overnight and at 50°C for 2 hrs. After removal of volatile, the residue was treated with Conc. HCl at room temperature for 3 hrs, washed with water and dried at 60°C in a vacuum oven overnight to give 4.5 g of polymeric acid. IR indicated the absence of sulfonyl fluoride peak at 1467 cm⁻¹.

Hydrolysis of Copolymer of Entry 3 of Table 1 (Catalyst **4-3**)

A mixture of 10.6 g of copolymer (2.9 mole% fluorinated comonomer, Entry 3 of Table 1), 5.0 g of KOH, 2 mL of water, 30 mL of ethanol and 30 mL of THF was stirred at RT overnight and at 65°C for 5 h. After removal of a half of solvents, residue was treated with Conc. HCl to give rubbery material, which was poured into a blender and blended with water for 30 min. Filtration gave solids, which were washed with conc. HCl, and water and dried under vacuum at 60°C overnight to give 8.7 g of dark rubbery material. ¹⁹F NMR(THF): -82.8 (br, 2F), -88.5 (br, 2F), -118.3 (br, 2F), -118.5 (br, 2F).

THF polymerization using polymeric acids 4-x

Entry 1 of Table 2

In a dry box, the polymeric acid **4-2** (0.66 g), THF (10.0 g) and acetic anhydride (0.53 g) were placed in a 20 mL vial equipped with a stirring bar. After 20 h at RT, the vial was removed from the dry box and the polymerization terminated by the addition of THF, water and ether. The organic phase was separated, washed with water (2x), dried over anhydrous sodium sulfate, concentrated at reduced pressure and then dried under vacuum, affording 8.33 g of polymer. GPC analysis (THF, PS STD.): $M_n = 12200$, $M_w = 22000$, $PDI = 1.80$.

Entry 2 of Table 2

In a dry box, the polymeric acid **4-2** (0.57 g), THF (10.10 g) and acetic anhydride (0.65 g) were placed in a 20 mL vial equipped with a stirring bar. After 1 h at RT, the vial was removed from the dry box and the polymerization terminated by the addition of THF, water and ether. The organic phase was separated, washed with water (2x), dried over anhydrous sodium sulfate, concentrated at reduced pressure and then dried under vacuum, affording 4.44 g of polymer. GPC analysis (THF, PS STD.): $M_n = 17600$, $M_w = 26000$, $PD = 1.48$.

Entry 3 of Table 2

In a dry box, the polymeric acid **4-3** (0.37 g), THF (10.10 g) and acetic anhydride (0.56 g) were placed in a 20 mL vial equipped with a stirring bar. After 2 h at RT, the vial was removed from the dry box and the polymerization terminated by the addition of THF, water (2-3 mL) and ether, dried over anhydrous sodium sulfate, concentrated at reduced pressure and then dried under vacuum, affording 4.93 g of polymer. GPC analysis (THF, PS STD.): $M_n = 25700$, $M_w = 42300$, $PD = 1.65$.

Entry 4 of Table 2

In a dry box, the polymeric acid **4-2** (0.426 g), THF (10.08 g) and acetic anhydride (0.503 g) were placed in a 20 mL vial equipped with a stirring bar. After stirring for 2 h at room temperature, the vial was removed from the dry box and the polymerization terminated by the addition of THF, water (1.00 mL) and ether. The separated organic phase was concentrated at reduced pressure and then dried under vacuum affording 5.50 g of polymer. GPC analysis (THF, PS STD.): $M_n = 33,300$, $M_w = 52,400$, $PD = 1.57$.

Entry 5 of Table 2

In a dry box, the polymeric acid **4-2** (0.350 g), THF (4.10 g), THF/3-Me-THF (50/50 mol %, 6.05 g) and acetic anhydride (0.503 g) were placed in a 20 mL vial equipped with a stirring bar. After stirring for 18 h at room temperature, the vial was removed from the dry box and the polymerization terminated by the addition of THF, water (1.00 mL) and ether. The separated organic phase was concentrated at reduced pressure and then dried under vacuum affording 6.19 g of polymer. GPC analysis (THF, PS STD.): $M_n = 20,100$, $M_w = 35,300$, $PD = 1.76$.

THF polymerization with Nafion[®] NR50

Entry 6 of Table 2

In a dry box, Nafion[®] NR50 (0.57 g), THF (10.10 g) and acetic anhydride (0.56 g) were placed in a 20 mL vial equipped with a stirring bar. After 1 h at RT, the vial was removed from the dry box and the Nafion[®] removed via filtration [Nafion[®] washed with THF (2 x 25 mL)]. Water, THF and ether were added and the organic phase separated, concentrated at reduced pressure and then dried under vacuum affording 0.77 g of polymer. GPC analysis (THF, PS STD.): Mn = 6040, Mw = 15900, PD = 2.64.

Entry 7 of Table 2

In a dry box, Nafion[®] NR50 (0.37 g), THF (10.10 g) and acetic anhydride (0.62 g) were placed in a 20 mL vial equipped with a stirring bar. After 2 h at RT, the vial was removed from the dry box and the Nafion[®] removed via filtration (Nafion[®] washed with THF (2 x 25 mL)). Water, THF and ether were added and the organic phase separated, concentrated at reduced pressure and then dried under vacuum affording 1.41 g of polymer. GPC analysis (THF, PS STD.): Mn = 13700, Mw = 29400, PD = 2.14.

General Procedures for the Friedel-Crafts Acylation of m-Xylene with Benzoyl Chloride and the Isomerization of 1-Dodecene.

The acid catalyzed reactions were studied in 100 ml three-necked round bottom flasks with magnetic agitation. Prior to the reaction, 0.25 –1.00g solid acid catalyst **4-6** was dried in a 110°C vacuum oven for more than 3 hours. The acylation reaction was carried out with 14g benzoyl chloride and 21.2g m-xylene at 140°C. The 1-dodecene isomerization (e.g., double bond migration) was carried out with 10g 1-dodecene in 32g decane at 75°C. Product samples were taken at different time intervals and analyzed by a HP 5880GC to monitor the conversion of the reagents to products.

General procedure for preparation of films of lithium polymeric fluorosulfonates

Polymeric films were pressed between Kapton[®] film press sheets using a hydraulic press (model P218C, Pasadena Hydraulic Industries) equipped with Omron Electronics Inc. E5C5 temperature controllers. Typical press cycles consisted of preheating for two minutes, pressing for two minutes, and then cooling under pressure.

The polymers were used with thickness varying from 2 to 4 mils. The films were heated in a filtered, saturated solution of LiOH in 1:1 water/methanol (approx. 1 M) for 4-8 hours at 45-80°C followed by a 1:1 water/methanol soak and a heated methanol/water rinse. Samples were then dried under vacuum with heat.

Conductivity and Solvent Uptake Measurements

All measurements were performed in dry boxes under a nitrogen or argon environment due to the moisture sensitivity of lithium batteries and the presumed sensitivity of the membrane properties to water content. Ionic conductivity measurements on film samples are made using custom designed and fabricated four-point-probe conductivity cells. The ionic conductivity is calculated from the bulk sample impedance in the 100 Hz to 10 kHz range at zero phase angle. Electrochemical impedance measurements are performed using either a Voltech TF2000 Transfer Function Analyzer or an EG&G PAR Model 5301 Lock-in Amplifier with a Wavetek Model 166 50 MHz Pulse/Function Generator to calculate the impedance from the measured voltage induced by a small imposed AC current perturbation. The size of the membrane sample should be 1.0 cm wide by 1.2 to 2.0 cm long for conductivity measurement in these cells.

Propylene carbonate (PC) purchased from Selectipur was brought immediately into the dry environment of the glove box, and then used as received. Solvent uptake is measured by immersing a dry polymer film sample into a 25 ml glass vial containing the solvent of interest, allowing the solvent to imbibe into the film for a given amount of time, and then measuring the final weight and thickness of the film. The films are patted dry to remove surface solvent prior to all measurements. Percent solvent uptake and membrane swelling are calculated with respect to the initial dry weight and thickness of the films.

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