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

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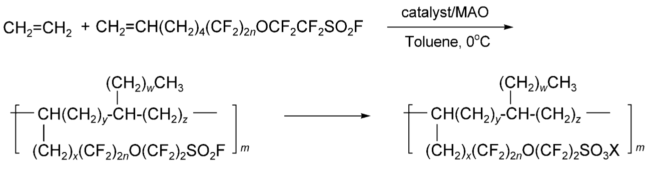
The development of polymeric strong acids as benign catalysts, and their lithium salts as electrolytes for lithium batteries, to replace very hazardous, corrosive, difficult-to-recover materials such as HF, H_2SO_4, and $LiPF_6$, has received growing attention for environmental reasons. Although perfluorinated sulfonic acid ionomers such as the Nafion resins are superior to polystyrene-based sulfonic acids such as Dowex and Amberlite in terms of acidity, they have a high equivalent weight (low-acid capacity), a high cost, and relatively low catalytic activity in nonpolar media.[1] The lithium-salt form of the Nafion membrane does not absorb enough quantities of organic solvents as is necessary for high ion conductivity. The polymeric lithium salts can offer significant advantages over conventional electrolytes, which includes fast cation transport, anion exclusion, and the absence of added thermally and hydrolytically unstable lithium salts such as $LiPF_6$ in addition to their environmental benefits.[2–3] We anticipate the catalytic activity, the ionic conductivity, and ease of process of these materials could be improved by proper architectural design of their microstructure, molecular topology, and chemical composition. The synthesis of polymers with new structures generally requires exotically designed monomers, which direct new architectures of the polymers.[4] It is highly desirable to directly polymerize existing commodity monomers to give controllable architectures that can exhibit unique properties.[5–8] Herein we report active polymeric acid catalysts and highly conductive polymeric lithium electrolytes by carefully designing molecular architectures by using metal catalyzed copolymerization of ethylene with an α-olefin that contains fluorosulfonyl fluorides.

The activities of polymeric acid catalysts are generally determined by the acid strength, surface area, or accessibility of the catalysts.[9] Homogeneous catalysts usually exhibit high activity, whereas heterogeneous catalysts also could exhibit excellent properties if they have high a surface area or swell in the reaction media.[10] The ability of polymeric lithium electrolytes to swell in selected organic solvents is particularly important for high ionic conductivity. Lithium electrolytes suitable for commercial applications also require that the electrolytes have sufficient mechanical integrity to fabricate a functional multilayered laminate that does not dissolve in battery solvents in addition to having good electrochemical stability and low cost.[3,11] To meet these diverse criteria, it is critical to synthesize polymeric materials with new architectures from low-cost monomers. Branched structures may be desirable as they could lower the crystallinity, increase the ability of the polymer to swell in organic solvents, and improve the processing of the system while maintaining excellent mechanical properties. A practical method for introducing the branched structure is to use a catalyst that can chain walk to control the position of monomer insertion during propagation, thus avoiding the use of costly monomers. The catalysts used for ethylene polymerization that chain walk are late transition metal complexes such as those recently discovered by Brookhart, Johnson, and co-workers.[12–14] Unlike Ziegler-Natta and metallocene catalysts that are readily poisoned by most functional olefins because of their high oxophilicity, the late-transition-metal catalysts such as nickel and palladium complexes not only catalyze the homo- or copolymerization of ethylene with functionalized olefins such as acrylates but are also able control the polymer topology when the right catalysts and the polymerization conditions are chosen.

We copolymerized ethylene and α-olefins that contain fluorinated sulfonyl fluoride by using α-diimine-palladium and nickel catalysts. For the palladium catalyst, the polymerization reactions were conducted under one atmosphere of ethylene in methylene chloride at room temperature. For Ni catalysts, the polymerization reactions were conducted with a cocatalyst, methylalumoxane (MAO), under one atmosphere of ethylene in toluene at 0 °C (Scheme 1).

During polymerization, the Pd catalyst does extensive chain walking to generate highly branched polymers, whereas the nickel catalysts undergo moderate chain walking to afford moderately branched polymers as determined by ^{13}C NMR



3

4-X

X = H, Li

Scheme 1. Synthesis of the copolymers **3**, which can be transformed into superacids and their Li derivatives, **4**.

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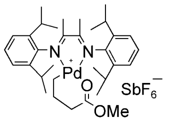
analysis. The Pd catalyst **A** produced high molecular weight oil copolymers with glass transition temperatures (T_gs) below



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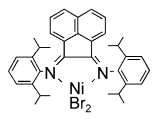

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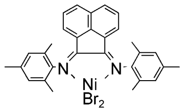

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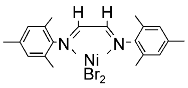

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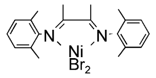

E

$CH_2{=}CH(CH_2)_4(CF_2)_2OCF_2CF_2SO_2F$, **1**

$CH_2{=}CH(CH_2)_4(CF_2)_4OCF_2CF_2SO_2F$, **2**

−55 °C (Table 1, entries 1–3); Ni catalysts gave semi-crystalline copolymers with melting points (T_ms) ranging from 94 °C to 126 °C (Table 1, entries 4–10). These semi-crystalline polymers can be thermally fabricated into strong and tough thin films or other shaped articles. The precise polymer structures can be controlled by tailoring the α-diimine backbone and the *ortho* substituents on the phenyl rings of the catalysts and the polymerization conditions. The less bulky catalysts, **C, D, E**, gave less branched and more crystalline copolymers under similar conditions (Table 1, entries 6 to 10). In addition, the comonomer content increased in the polymer as the concentration of the comonomer increased in the polymerization mixture (Table 1, entries 8 to 10). When catalyst **E** was used, under the same conditions, 0.51 M of **1** in the precharged mixture gave polymer containing 2.6 mol% of **1**. When the concentration of **1** was increased to 1.20 M and 3.60 M, polymers containing 3.7 mol% of **1** and 10.8 mol% of **1**, respectively, were obtained. More interestingly, the number of methyl groups in the polymers decreased as the mole% of **1** increased, and the melting points of the polymers were similar. Under low-pressure conditions, highly branched copolymers with more incorporated comonomer **2** were obtained because of the increase in the rate of chain walking relative to that of ethylene insertion.[6]

Table 1: High value copolymers of ethylene with $CH_2{=}CH(CH_2)_4(CF_2)_nO(CF_2)_2SO_2F$.

Entry	Catalyst	Monomer (M)	Comonomer in **3** (mol%)	No. of Me per 1000 CH_2	T_g or T_m [°C]	$\bar{M}_w \times 10^{-4}$ (PDI)
1	**A**	**2** (0.40)	**2** (8.5)	89	T_g −57	7.89 (1.5)
2	**A**	**1** (1.20)	**1** (6.7)	89	T_g −69	9.0 (1.7)
3	**A**	**1** (0.42)	**1** (2.9)	113	T_g −66	9.05 (2.1)
4	**B**	**2** (0.67)	**2** (3.9)	77	T_m 102	33 (2.3)
5	**B**	**1** (1.18)	**1** (4.4)	49	T_m 94	18.6 (2.6)
6	**C**	**1** (1.18)	**1** (6.9)	6	T_m 126	6.66 (2.7)
7	**D**	**1** (1.18)	**1** (5.3)	4	T_m 126	2.55 (3.0)
8	**E**	**1** (0.51)	**1** (2.6)	20	T_m 118	17.3(4.8)
9	**E**	**1** (1.20)	**1** (3.7)	11	T_m 124	25.1(5.1)
10	**E**	**1** (3.60)	**1** (10.8)	8	T_m 127	24.6(5.6)

These copolymers were readily hydrolyzed with KOH or LiOH in aqueous MeOH to give polymeric fluorosulfonates, which underwent ion exchange with concentrated HCl to give various polymeric acids. Because of the strong electron-withdrawing effect of the fluorinated group, these polyethylene based copolymeric acids **4**-*x* showed super acid properties (*x* refers to the entry numbers in Table 1, thus indicating how the acids were obtained). The highly branched polymeric sulfonic acids **4**-1 and **4**-2 (Table 1, entries 1 and 2) are elastic materials and soluble in polar solvents such as THF. Thus, these materials can be used as homogeneous polymeric super-acid catalysts in certain polar solvents. While polymeric super acids **4**-4–10 (from entries 4–10) are usually not soluble in organic solvent, they can be swelled and used as heterogeneous super acid catalysts. Although homogenous catalysts exhibit excellent activity for some acid-catalyzed reactions, heterogeneous catalysts offer advantages in the isolation step as simple filtration can remove the catalysts from the reaction mixture and the recovered catalyst can be reused. We have demonstrated that these catalysts exhibit excellent catalytic activities in several types of industrially important reactions.[15,16] Table 2 tabulates the polymerization of THF with acetic anhydride with the new polyethylene/sulfonic acid catalysts to generate diacetate-capped polyethers. The polymerization of THF occurs readily with a catalyst that contains a low mole percent of **1**. Thus with catalyst **4**-3, which only contains 2.9 mole% of comonomer **1**, the polymerization occurs rapidly to give a conversion of 45% after 2 h. With catalyst **4**-2, 50% conversion was observed within 2 hrs. More importantly, the catalyst **4**-2 also catalyzed the copolymerization of THF and 3-methyl THF, which is usually difficult to achieve with other acid catalysis. Although the new catalysts contain much less sulfonic acid comonomer than the standard Nafion resin, which contains 16 mol% of fluorosulfonic acid comonomer, the new catalysts are more active than the Nafion resin. This is probably because the new catalysts swell more or are soluble in the THF solutions. After one hour at a loading of 0.57 g the new polyethylene/sulfonic acid catalyst gave a conversion of 39% compared to 6.8% for Nafion (Table 2, entries 2, 3, 6, and 7).

Table 2: Polymerization of THF with acetic anhydride.

Entry	THF [g]	Ac_2O [g]	Catalyst	Quantity[a] [g]	Time [h]	Conv. [%]	$\bar{M}_w \times 10^{-4}$[b] (PDI)
1	10.00	0.53	**4**-3	0.66	20	74.4	2.2 (1.80)
2	10.10	0.65	**4**-3	0.57	1	39.2	2.6 (1.48)
3	10.10	0.56	**4**-3	0.37	2	45.1	4.2 (1.65)
4	10.08	0.50	**4**-2	0.43	2	50.0	5.2 (1.57)
5	10.15[c]	0.50	**4**-2	0.35	18	56.2	3.5 (1.76)
6	10.10	0.56	Nafion NR50	0.57	1	6.8	1.6 (2.64)
7	10.10	0.62	Nafion NR50	0.37	2	12.7	2.9 (2.14)

[a] Quantity of catalyst present. [b] $\bar{M}_w$ is the weight average molecular mass. [c] 3-Me-THF copolymerization, approximately 30 mole% in initial THF solution. From ^1H NMR spectroscopy the resulting polymer contains ca. 14 mole% 3-Me-THF.

After the quantity of catalyst was decreased to 0.37 g and the polymerization time increased to two hours, Nafion gave a conversion of 13 % and the catalyst **4**-3 gave a conversion of 45 %. Isolation was easy and the polymer was readily separated from catalyst by the addition of a mixture of ether, THF and water to the reaction mixture. More importantly, the new catalysts gave polymers of designed molecular weight with narrow polydispersity (PDI less than 2), whereas polymers made with Nafion catalysts have broad bimodal molecular weight distributions.

We also tested catalytic activity of **4**-6 in acylation of substituted-benzenes with acyl chloride and isomerization of olefins. We found that the new catalyst is not soluble but it is more active than Nafion and other acid catalysts. For example, in the benzoylation of *m*-xylene at 140 °C, the reaction rate with 0.25 g of **4**-6 was 380 mM g^{-1} of catalyst h^{-1}, whereas the rate with 1.0 g of Nafion and 1.0 g of SAC-13A (Nafion/silica composite) was 108 and 68 mM g^{-1} of catalyst h^{-1}, respectively. Upon isomerization of 1-dodecene at 75 °C, the rate with **4**-6 was 45 times faster than that with Nafion, four times faster than that with Amberlst-15 and more than 88 times faster than with 70 % H_3PO_4/SiO_2.

After they have been converted into lithium form, the strong and tough thin films of copolymers made with Ni catalysts have almost the same melting point as the nonionic copolymers and are thermally stable up to 350 °C. Our preliminary results have demonstrated that branching in ionomers remarkably affects the uptake of solvent and lithium ion conductivity. The films swell in selected organic solvents such as propylene carbonate (PC) but still have excellent mechanical properties. The more branched the polymers are, the more solvent they absorb although contents of comonomer **1** (or equivalent weight) also have a pronounced effect (Table 3). The relatively high-branching ionomer of entry 2 exhibited the same conductivity as the ionomer of entry 3, which had 50 % more of the comonomer **1**, but less branching. More interestingly, the film **4** containing 6.8 mol % of **1** with 20 methyl groups per 1000 CH_2 units was 3.7 fold more conductive than the film of Table 3, entry 5, which contained 10.8 mol % **1** but only eight methyl groups per 1000 CH_2 units, although they absorbed similar amounts of PC. These examples have indicated that moderate branching in the ionomers significantly improved ionic conductivity and overall properties. Ionomers with highly branched structures made from the Pd catalyst resulted in poor mechanical properties, while ionomers with little alkyl branches exhibited poor conductivity and low uptake of solvents.

Table 3: Lithium ion conductivity and PC uptake of ionomer films.

Entry	Content of **1** [mol %] in **4**	CH_3 per 1000 CH_2	T_m [°C]	PC uptake [%]	Conductivity [mS cm^{-1}]
1	3.7	11	124	56	0.233
2	4.4	49	93	70	0.369
3	6.9	6	120	84	0.341
4	8.0	20	118	84	0.702
5	10.8	8	125	87	0.189

The molecular architecture design of copolymers of ethylene described here provides new opportunities for green solid super-acid catalysts and polymeric lithium-ion-conducting electrolytes. In principle, various polymeric molecular structures can be synthesized by tailoring the polymerization catalysts and the polymerization conditions with commodity monomers, which offers a promising approach for making new materials at low cost. We have demonstrated that the materials with new structures exhibit desirable properties to meet specific applications. The polymeric acid catalysts from copolymers of ethylene showed enhanced catalytic activity for industrially important reactions and their lithium ionomers not only have excellent conductivity but can also be processed more easily, have better mechanical properties, and are inexpensive.

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[1] a) M. A. Harmer, Q. Sun, *Appl. Catal. A* **2001**, *221*, 45, and references therein; b) G. A. Olah, S. I. Pradeep, G. K. S. Prakash, *Synthesis* **1986**, 513.

[2] M. E. Doyle, M. G. Lewittes, M. A. Roelofs, S. A. Perusich, *J. Phys. Chem. B* **2001**, *105*, 9387.

[3] a) J. M. Tarascon, M. Armand, *Nature* **2001**, *414*, 359; b) G. S. MacGlashan, Y. G. Andreev, P. Bruce, *Nature* **1998**, *398*, 792; c) F. Croce, G. B. Appetecchi, L. Persi, B. Scrosati, *Nature* **1998**, *394*, 456.

[4] a) O. W. Webster, *Science* **1991**, *251*, 887; b) K. Ishizu, K. Tsubaki, A. Mori, S. Uchida, *Prog. Polym. Sci.* **2003**, *28*, 27.

[5] a) Z. Guan, P. M. Cotts, E. F. McCord, S. J. Mclain, *Science* **1999**, *283*, 2059; b) Z. Guan, *J. Am. Chem. Soc.* **2002**, *124*, 5616.

[6] C. W. Bielawski, D. Benitez, R. H. Grubbs, *Science* **2002**, *297*, 2041.

[7] J. M. Frechet, M. Henmi, I. Gitsov, S. Aoshima, M. R Leduc, R. B. Grubbs, *Science* **1995**, *269*, 1080.

[8] A. W. Bosman, R. Vestberg, A. Heumann, J. M. Frechet, C. J. Hawker, *J. Am. Chem. Soc.* **2003**, *125*, 715.

[9] a) K. Ishihara, A. Hasegawa, H. Yamamoto, *Angew. Chem.* **2001**, *113*, 4201; *Angew. Chem. Int. Ed.* **2001**, *40*, 4077; b) K. Ishihara, A. Hasegawa, H. Yamamoto, *Synlett* **2002**, 1296.

[10] D. J. Cole-Hamilton, *Science* **2003**, *299*, 1702.

[11] a) A. Feiring, S. K. Choi, M. E. Doyle, E. R. Wonchoba, *Macromolecules* **2000**, *33*, 9262; b) A. U. Schnurer, N. R. Holcomb, G. L. Gard, D. G. Castner, D. W. Grainger, *Chem. Mater.* **1996**, *8*, 1475.

[12] a) L. K. Johnson, C. M. Killian, M. Brookhart, *J. Am. Chem. Soc.* **1995**, *117*, 6414; b) S, Mecking, L. K. Johnson, L. Wang, M. Brookhart, *J. Am. Chem. Soc.* **1998**, *120*, 888; c) D. P. Gates, S. A. Svejda, E. Onate, C. M. Killian, L. K. Johnson, P. S. White, M. Brookhart, *Macromolecules* **2000**, *33*, 2320; d) P. Preishuber-Pflugl, M. Brookhart, *Macromolecules* **2002**, *35*, 6074.

[13] S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169, and references therein.

[14] T. R. Younkin, E. F. Connor, J. I. Henderson, S. K. Friedrich, R. H. Grubbs, D. A. Bansleben, *Science* **2000**, *287*, 460.

[15] F. E. Bailey, J. V. Koleske, *Ullmann's Encyclopedia of Industrial Chemistry, Vol. 28*, 6th ed., VCH, Weinheim, **2003**, p. 497.

[16] M. Schneider, K. Zimmermann, F. Aquino, W. Bonrath, *Appl. Catal. A* **2001**, *220*, 51.

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