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Communications to the Editor

A Simple Transformation of Polyethylenes to Environmentally Benign Acid Catalysts and Lithium Conductive Polymeric Electrolytes[†]

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There has been considerable interest to develop strong polymeric acids as environmentally benign catalysts and their lithium salts as polymeric electrolytes for lithium batteries to replace hazardous, corrosive, and difficult to recover materials such as HF, H_2SO_4, and $LiPF_6$. Although Nafion resins, perfluorinated sulfonic acid ionomers, are superior to polystyrene-based sulfonic acids such as Dowex and Amberlite in terms of acidity, they have high equivalent weight, high cost, and relatively low catalytic activity in nonpolar media.[1] In addition, the lithium salt form of the Nafion membrane is difficult to process and does not absorb enough quantities of organic solvents to achieve high ion conductivity. However, the polymeric lithium salts can offer significant advantages over conventional electrolytes. The most noticeable features of polymeric lithium electrolytes are fast cation transport and anion exclusion, and they do not require added thermally and hydrolytically unstable lithium salts such as $LiPF_6$.[2] We have demonstrated that the catalytic activity, the ionic conductivity, and processability of these materials could be improved by manipulation of the microstructure of polymers.[3] Herein we report environmentally benign active polymeric acid catalysts and conductive polymeric lithium electrolytes by simply grafting polyethylene (**1**) with an α-olefin containing fluorosulfonyl fluoride (**2**).

The activities of solid acid catalysts are generally determined by the acid strength, surface area, or accessibility of the catalysts. Perfluoroalkanesulfonic acid is one of the strongest acids due to the electron withdrawing of the perfluoroalkyl group.[4] Homogeneous catalysts usually exhibit high activity whereas heterogeneous catalysts also could exhibit excellent properties if they have a high surface area or swell in the reaction media.[5] Although Nafion showed low catalytic activity, nanocomposites of Nafion with silica exhibited enhanced reactivity due to the increase of surface area.[6] A covalent bonding fluorosulfonic acid to silica as a solid acid catalyst also showed excellent activity.[7] Polystyrene-based fluorinated acid as a swellable catalyst was also reported, but it was expensive to make.[8] Swellability of polymeric lithium electrolytes in selected organic solvents is particularly important for high ionic conductivity. In addition to having good electrochemical stability and low cost, lithium electrolytes suitable for commercial applications also require that the electrolytes have excellent mechanical properties and processability to fabricate a functional multilayered laminate with the battery solvents.[2,9a] A practical and cost-effective method for introducing the fluorosulfonic acid groups to polymers is to graft alkenes containing fluorosulfonyl acid onto low-cost commodity polymers, such as polyethylene. Grafting polyethylenes with functional monomers under free radical, photo, and irradiation conditions in solution or molten state are well documented.[10] We anticipate that the radical grafting of a fluorinated olefin onto PE is particularly efficient since an electron-rich radical readily adds to electron-poor double bond and the fluoroolefin **2** is not homopolymerizable.[11]

We have grafted high-density polyethylene (HDPE, **1a**), wax polyethylene (W-PE, **1b**), and branched polyethylene (B-PE, **1c**) made by α-dimine Ni catalysts[12] with α-olefins containing fluorinated sulfonyl fluoride (**2**) with an organic peroxide as an initiator in solution (see Scheme 1). Typically, PE, **1**, and **2** were first

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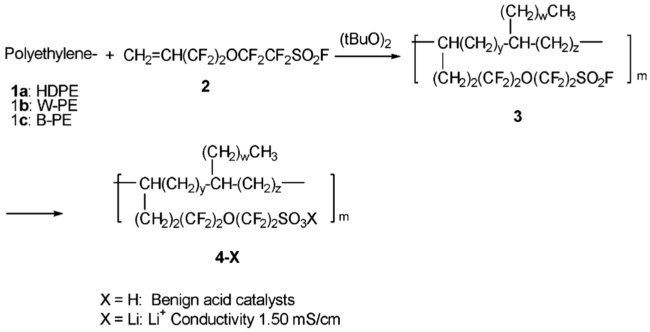
Table 1. Polymerization of THF with Acetic Anhydride

entry	THF (g)	Ac_2O (g)	catalyst	cat. (g)	time (h)	conv (%)	$M_w \times 10^4$ (PDI)
1	10.00	0.56	**4a**	0.526	1	60.25	1.64 (1.70)
2	10.00	0.56	**4a**	0.526	2	73.07	1.67 (1.77)
3	10.10	0.56	Nafion NR50	0.57	1	6.8	1.60 (2.64)
4	10.10	0.62	Nafion NR50	0.37	2	12.7	2.90 (2.14)
5	10.10[a]	0.50	**4a**	0.50	1	30	1.68 (1.48)
6	10.00[a]	0.50	**4a**	0.50	2	45	2.29 (1.87)
7	10.00[a]	0.50	Nafion NR50	0.50	2	20	1.97 (2.04)

[a] 3Me-THF copolymerization, approximately 30 mol % in initial THF solution, via ^{1}H NMR the resulting polymer contains 14 mol % 3-Me-THF.

Scheme 1



dissolved in 1,2-dichlorobenzene at about 130 °C, and then a solution of *tert*-butyl peroxide in 1,2-dichlorobenzene was slowly added to the mixtures at 120 °C for 8−10 h. The hot solution was poured into acetone to precipitate the polymer, filtered, washed with acetone for four times, and dried to give the grafted PE, **3**. The IR spectrum of **3** indicated the presence of SO_2F at 1460 cm^{-1} and fluorocarbon at 1205−1190 cm^{-1}. Elemental analyses indicated 5.2−5.4 mol % of **2** in polymer **3** with mp 115−118 °C for **1a** and **1b** and mp 94 °C for **1c** by DSC. The grafted PE exhibited good thermal stability, and 10% weight loss is at about 380 °C under N_2 as observed in TGA. During grafting, polymer chain cleavage was also observed, but cross-linking and other side reactions occurred. **1a**, which had a M_w of 1.27×10^5, gave **3a** with M_w of 6.57×10^4 and 5 Me per 1000 carbon units based on ^{13}C and ^{1}H NMR analysis. **1c** containing 92 Me per 1000 CH_2 units ($M_w = 2.51 \times 10^5$) resulted in **3c** with M_w of 2.04×10^4 containing 113 Me per 1000 CH_2. Despite chain cleavage, the grafted polyethylene could be readily pressed into thin films or other shaped articles at 150−250 °C with reasonably good mechanical strength.

The films or pellets of grafted PEs 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 of the fluorinated group, these polyethylene grafted acids showed superacid properties. Unlike highly branched ethylene copolymer superacids,[3a] the grafted polymeric acids **4a** and **4b** are not soluble but swellable in THF and can be used as heterogeneous superacid catalysts. Although homogeneous catalysts exhibit excellent activity for some acid-catalyzed reactions, heterogeneous catalysts offer advantages in the isolation step since the catalysts could be isolated by simple filtration and reused in the next batch reaction. Therefore, the heterogeneous acid catalysts could lead to significant reduction of the liquid and solid wastes due to the elimination of the posttreatments typically associated with the hazardous homogeneous acids. We have demonstrated that these catalysts exhibit excellent catalytic activities in industrially important polymerization of THF.[13] Table 1 summarized the polymerization of THF with acetic anhydride with the new polyethylene−sulfonic acid catalysts to generate diacetate-capped polyethers. The polymerization of THF occurred readily with a catalyst containing low mole percentage of **2**. With catalyst **4a** containing 5.4 mol % of comonomer **2**, polymerization occurred rapidly to give a conversion of 60% within 1 h, whereas 6.8% conversion was observed with Nafion resin catalyst. 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 due to the fact that the new catalysts swell more in THF solution and active sites are more accessible. The other remarkable feature with the new catalyst is that molecular weight (M_n) of polyethers did not change significantly although depolymerization occurred over long periods of times. Conversion of THF reached a peak to 73% within 2 h and then slowly decreased to 70% within 6 h and to 57.45% after 20 h. The molecular weight (M_n) of the polymer kept almost constant during 20 h, and M_n is within ranges of 9.68×10^3 and 10.3×10^3. More importantly, the new catalyst also catalyzed the copolymerization of THF and 3-methyl-THF, which is usually difficult to achieve with other acid catalysis. As shown in entries 5 and 6 in Table 1, the new polyethylene−sulfonic acid catalyst at a loading of 0.50 g gave a conversion of 30% in 1 h and 45% within 2 h. Nafion catalyst gave a conversion of 20% in 2 h under the same conditions. Isolation was easy, and the polymer can be readily separated from catalyst by addition of a mixture of ether, THF, and water to the reaction mixture. Since the catalyst is not soluble, simple filtration also separated products from the catalyst. We have also run continuous polymerization of THF with fixed bed catalyst to give polymers with desired properties. More importantly, the new catalysts led to the formation of polymers of designed molecular weights with narrow polydispersity (PDI less than 2), whereas polymers made with Nafion catalysts have broad bimodal molecular weight distributions under the same conditions.

After conversion into lithium form, the tough thin films of grafted PE are thermally stable up to 330 °C. The preliminary results have demonstrated that the ionomer **4a** (X = Li) has showed uptake of solvent and lithium ion conductivity, but the amounts of solvent absorption were less than that of more branched PE since the grafted PE is much less branching and has only 5 methyl per 1000 carbons (Table 2). The films swell moderately in selected organic solvents such as propylene carbonate (PC), a mixture of PC and 1,2-dimethoxyethane, γ-butyrolactone (GBL), DMSO, and DMF from 39 to 56 wt % at room temperature but still

Table 2. Li^+ Conductivity and Solvent Uptake of 4a

entry	solvent	solvent uptake[a] (%)	conductivity[b] (mS/cm)
1	PC	39	0.066
2	PC/DME	39	0.229
3	GBL	47	0.234
3	DMSO	56	1.22
4	DMF	47	1.50

[a] Weight increased. [b] Measured at 25 °C.

have good mechanical properties. The lithium ion conductivity was dependent on the absorbed solvent. In PC, the conductivity was only 0.066 mS/cm, which was much lower than moderately branched polyethylene-based electrolytes.[3b] The low conductivity may be attributed to low amorphous domain in the films due to low branched structure and low solvent uptake. However, when the films absorbed similar amounts of 1:1 PC/DME or pure GBL, conductivities increased 3.5-fold. The most remarkable observation was that when DMSO or DMF was used as solvents, the conductivity jumped another 6.5-fold and reached 1.22−1.50 mS/cm at 25 °C. These examples indicated that the grafted PE ionomer has excellent lithium ionic conductivity in these solvents. Ionomers with highly branched structures made from highly branched PE, **1c**, resulted in poor mechanical properties. Optimization of the degree of branching and grafted fluorosulfonate monomer content would be expected to increase conductivity even further, especially for the poorer solvents such as PC.

In conclusion, a simple and cost-effective method has been demonstrated for the production of environmentally benign superacid catalysts and polymeric lithium ion conducting electrolytes for lithium battery applications using principles of polymer grafting chemistry. The PE grafted polymeric acid catalysts showed enhanced catalytic activity for industrially important polymerization of THF and are expected to be used as excellent catalysts for other acid-catalyzed reactions. The lithium ionomers not only have high conductivity in selected solvents but good mechanical properties as well in addition to low cost.

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Supporting Information Available: Experimental procedures for synthesis of monomer, grafting of PE, polymerization of THF, thin film process, measurement of solvent uptake, and ion conductivity. This material is available free of charge via the Internet at http://pub.acs.org.

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