

High-Temperature Polymer Electrolyte Fuel Cell Electrolytes based on Dendronized Polymers

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Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) using perfluorinated sulfonic acid (PFSA) polymers, such as NAFION[®], are being developed as high efficiency power sources for vehicle traction and residential power. However, these polymers require high humidity levels to sustain proton conductivity, limiting the operating temperature to <100°C and adding complexity, size, weight, and cost to the fuel cell power system. Our approach to developing membrane electrolytes with high proton conductivity at low relative humidity and temperatures above 100°C is to utilize sulfonated polyaryl ether dendritic building blocks (highly branched macromolecules) attached to polymer backbones to enable film formation and to eliminate water solubility. The thermal stability and proton conductivity of these dendronized polymers will be discussed.

Experimental

Dendronized polymers for each generation of polyaryl ether dendron (G1 through G4) have been prepared by grafting onto polyepichlorohydrin (PECH, mol.wt. ~100,000) via a typical etherification reaction (Fig. 1). The grafting approach using an excess amount of the corresponding dendron was chosen over the macromonomer technique to overcome steric effects and to utilize as many chlorine sites as possible. The dendronized polymer was sulfonated using chlorosulfonic acid in chloroform. The ion exchange capacity (IEC) of the sulfonated polymers was determined by titration. The thermal stabilities of G2 and G3 dendronized polymers, before and after sulfonation, were determined by thermal gravimetric analysis (TGA) using an SII EXSTAR 6000. Membranes were prepared by tape-casting, followed by hot pressing at 75–90°C. The ionic conductivities of the membranes were determined under various temperature and humidity conditions using a four-point probe AC impedance apparatus equipped with a PAR 273A Potentiostat/Galvanostat and a Solartron 1250 Frequency Response Analyzer.

Results and Discussion

Figure 2 shows TGA traces for the second generation (G2) and the third generation (G3) polyepichlorohydrin-based dendronized polymers before and after sulfonation (designated PECH-G2, PECH-G3, PECH-G2-SO₃H, and PECH-G3-SO₃H, respectively). The initial weight loss for PECH-G2, PECH-G3 and PECH-G3-SO₃H is attributed to remnant dimethyl formamide used during the grafting reaction. The PECH-G2-SO₃H (IEC ~4 meq/g) shows no weight loss up to nearly 250°C. This material was brittle and, thus, solvent could be easily removed. On the other hand, PECH-G3-SO₃H (IEC ~4.1 meq/g) was too flexible for conductivity measurements. However, a homogeneous and tough film was obtained by solvent blending these two materials in the ratio G2/G3 ~20/80 wt%, and then hot pressing. The conductivity of

this polyelectrolyte blend, as a function of temperature and relative humidity, is shown in Table 1. These data show that the blended dendronized PECH membrane, unlike the PFSA membranes, maintains proton conductivity at elevated temperatures and at relative humidity less than 100%. Continuing work is focused on synthesizing polymers with the desired mechanical and conductivity characteristics using the generation one to generation four polyaryl ether dendrons without blending.

Acknowledgement

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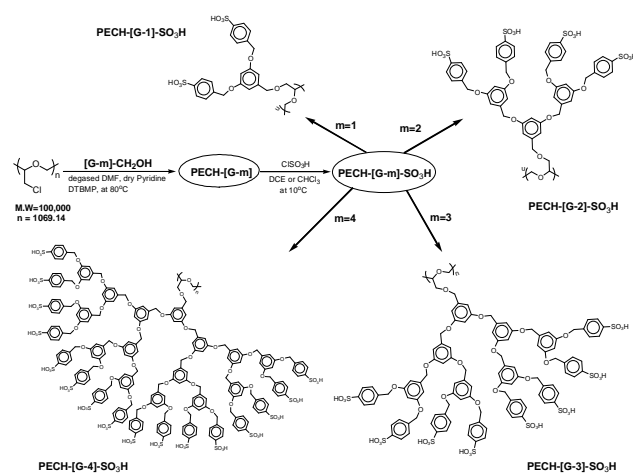


Fig. 1. Synthetic procedure for sulfonated polyepichlorohydrin-based dendronized polymers.

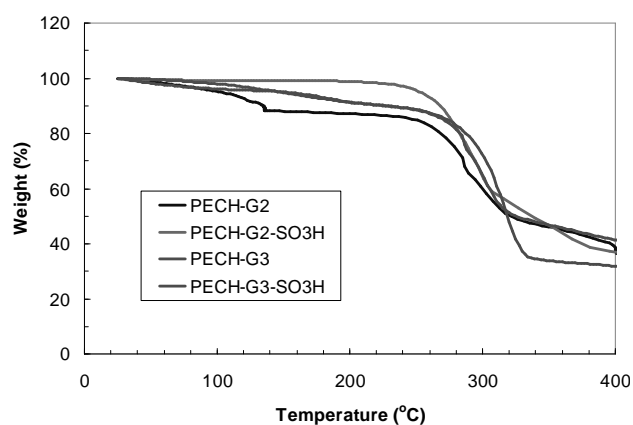


Fig. 2. Thermal Gravimetric Analysis (TGA) of polyepichlorohydrin-based dendronized polymers before and after sulfonation.

Table 1. Measured ionic conductivities of a blend of PECH-G2-SO₃H and PECH-G3-SO₃H

Temperature (°C)	RH (%)	σ (S/cm)
21	90	0.031
56	95	0.081
73	59	0.036
98	22	0.022