Polyimide-Polysiloxane Segmented Copolymers for Fuel Cell Applications

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Sulfonated perfluoropolymers (e.g. Nafion) are currently used in fuel cell applications due to their high proton conductivity, chemical resistance, and mechanical stability [1-3]. There is a great demand to develop less expensive non-fluorinated polymers that exhibit equally high performance [4-6]. We are developing nanostructured aromatic polyimides as an approach to fulfill this need. Polyimides have high strength, film-forming ability, superior chemical resistance, and can easily be sulfonated. Here we report on the one-pot synthesis and characterization of sulfonated polyimide-polysiloxane segmented copolymers. Our synthetic approach is described in Figure 1.

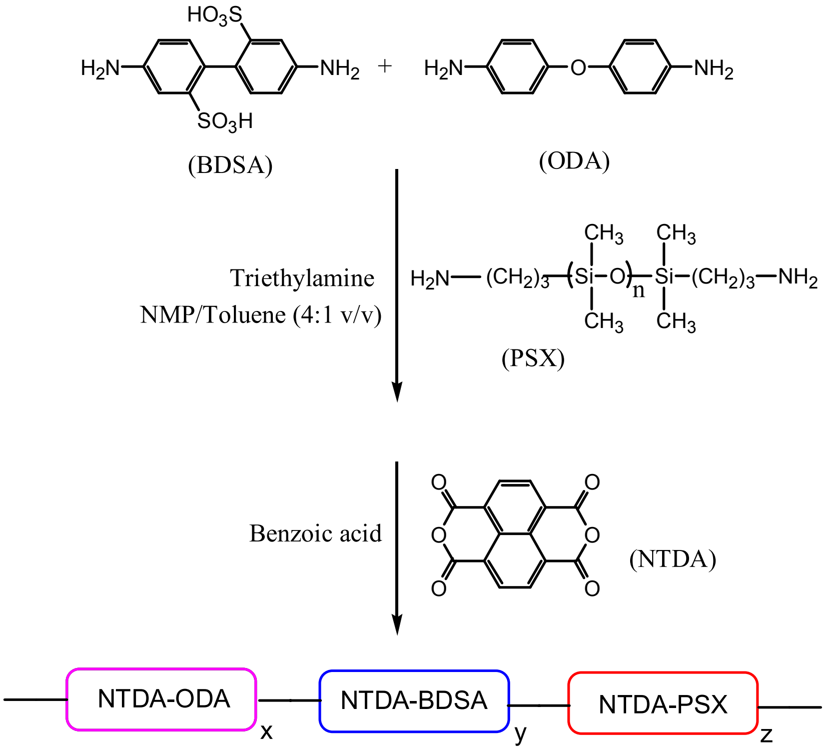

Figure 1. One-pot synthesis scheme leading to sulfonated polyimide-polysiloxane copolymers.

This approach enables tuning of both the siloxane content and the degree of sulfonation. All resulting materials were soluble in selective solvents and could be solvent-cast into films. Free-standing films were obtained for sulfonated polyimides that did not contain siloxane segments. On the other hand, copolymers containing siloxanes adhered strongly to glass; they were also lighter in color, and less viscous in solution.

Materials were characterized by infrared, nuclear magnetic resonance spectroscopies, dynamic light scattering and thermal gravimetric analysis. Water uptake (WU), ion exchange capacity (IEC) and proton conductivity of synthesized films have been measured. The underwater proton conductivity of membrane NTDA-BDSA/ODA is shown in Figure 2. Proton conductivity increased with increasing temperature and approached 0.13 S/cm at 97°C. Table 1 shows the IEC and WU values for samples with different ionic contents and compositions. As expected, the WU value was found to increase with ionic content, but the presence of a hydrophobic siloxane block inhibited water uptake.

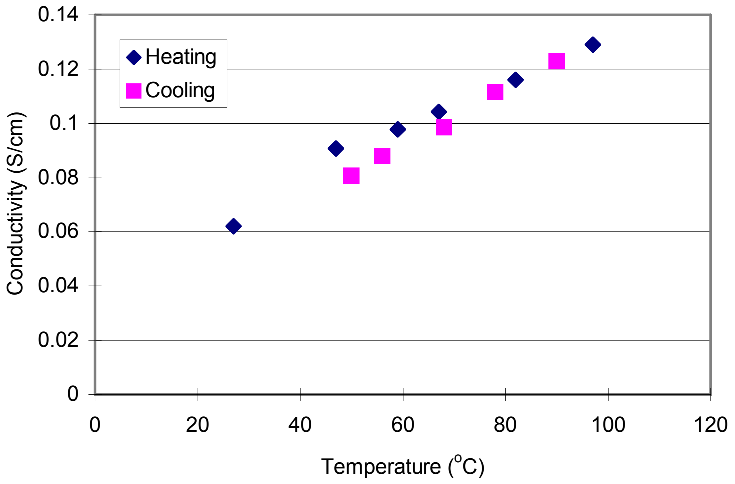

Figure 2. Underwater proton conductivity of sample NTDA-BDSA/ODA plotted against temperature. This sample contains no siloxane content.

Table 1. IEC and water uptake values for sulfonated polyimide copolymers[a].

Samples	IEC (meq/g)	WU (%) @ RT
NTDA-ODA (1:0:0)	-	-
NTDA-ODA/BDSA (1:1:0)	1.57	54.8
NTDA-ODA/BDSA/PSX (1:1:0.5)	1.28	24.6
NTDA-BDSA (0:1:0)	2.32	163.2

a) numbers in parenthesis show the molar fraction of diamine monomer component (ODA:BDSA:PSX)

In summary, we have developed methodology to prepare sulfonated polyimides containing specified amounts of linear siloxanes. Our present focus is to understand the interrelationship between proton conductivity, ionic content, and morphology in these copolymers. Future experiments will include dynamic water sorption analysis, in situ impedance measurements, and electron microscopy. This research was supported by the University of Rochester, Department of Chemical Engineering.

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