

INTRODUCTION

Sulfonated polyimides have attracted much attention for their potential use as proton exchange membranes (PEMs) due to their excellent thermal, chemical, and mechanical stability. Preparation of sulfonated polyimides from a combination of sulfonated and non-sulfonated monomers allows for the preparation of polymers with varying ion exchange capacity (IEC). Block copolyimides, prepared by utilizing a sequential addition of sulfonated and non-sulfonated monomers, lead to phase-separated membranes with both hydrophilic (sulfonic acid-containing) and hydrophobic (non-sulfonated) domains (1,2).

Perfluorosulfonic acid membranes, such as DuPont's Nafion membrane, which are typically used as polymer electrolytes in PEM fuel cells, are known to have ion-rich domains that form proton transport channels (3). In this work, a series of sulfonated polyimides have been prepared from bisphenol-A dianhydride (BPADA) and a combination of 4,4'-oxydianiline (ODA) and oxydianiline disulfonic acid (ODADS). Both random and block copolymers have been prepared in order to study the effect of hydrophilic block size on the formation of proton conducting domains.

RESULTS AND DISCUSSION

A series of polyimides have been prepared from BPADA, ODA, and ODADS by solution polycondensation reactions as shown in Figure 1. Random copolymers were prepared by combining all of the required monomers at the beginning of a given reaction while block copolymers were prepared with an initial charge of ODADS plus one equivalent of BPADA followed by a second, later addition of ODA plus one equivalent of BPADA.

Table 1 lists the polyimides with their compositions and IEC values. The IEC values were measured by titrations of the acid form of polymers in dimethylacetamide solution. The measured IEC values are all in agreement with the expected values and the presence of sulfonic acid groups was also verified by FTIR and H^1 NMR spectroscopy.

The polymers were prepared with the sulfonic acid groups in triethylammonium salt form. Films of the salt form of the polymers will not undergo complete ion exchange in aqueous acid, but when dissolved in 1-methyl-2-pyrrolidinone they can be readily converted to their acid form with H_2SO_4 . The one exception to this observation was a film of the 6:4 block copolymer which did completely ion exchange in aqueous acid. These results imply that the polymer backbone has sufficient flexibility to form low free volume structures that resist ingress of water and exchange. In the 6:4 block copolymer, this resistance to water ingress is countered by the formation of large hydrophilic domains that allow ion exchange to take place.

Water uptake measurements (Figure 2) show that the block copolymers absorb more water than their

random analogs. This shows that in addition to the IEC value, the water uptake and ion exchange abilities of these films depends on hydrophilic domain size. It is expected that film conductivities will show a similar relationship to domain size. Conductivity measurements as well as synthesis of block copolyimides with higher IEC values are currently in progress.

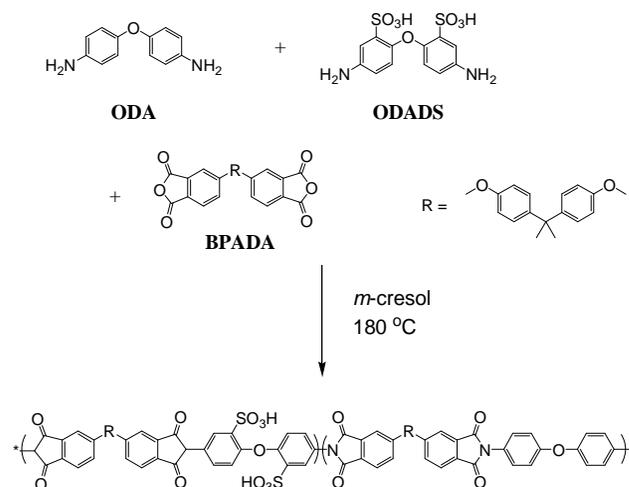


Figure 1. Scheme of Copolymer Synthesis.

Table 1. Copolyimides and IEC Values

ODA:ODADS	Theoretical IEC (mmol/g)	Measured IEC (mmol/g)
9:1 (random)	0.29	0.30
8:2 (random)	0.56	0.61
5:5 (random)	1.31	1.35
8:2 (block)	0.56	0.58
6:4 (block)	1.07	1.25

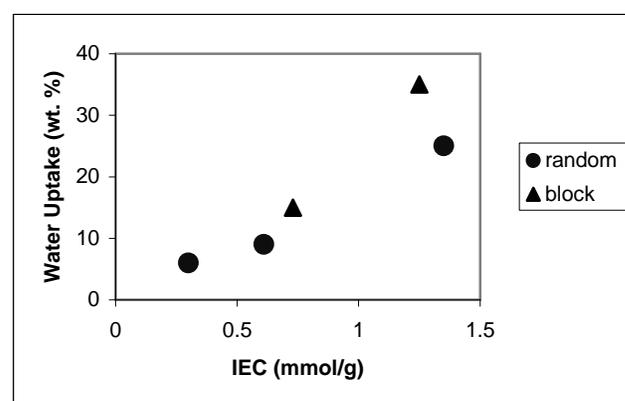


Figure 2. Water Uptake vs. Measured IEC.

REFERENCES

1. E. Vallejo, G. Pourcelly, C. Gavech, R. Mercier, M. Pineri, *J. Mem. Sci.*, **160**, 127 (1999).
2. F. Piroux, E. Espouche, M. Escoubes, R. Mercier, M. Pineri, *Macromol. Symp.*, **188**, 61 (2002).
3. F. Wang, M. Hickner, YS Kim, TA Zawodzinski, JE McGrath, *J. Mem. Sci.*, **197**, 231 (2002).