

SYNTHESIS, CHARACTERIZATION AND MORPHOLOGICAL INFLUENCE OF BISPHENOL STRUCTURE ON THE DIRECT SYNTHESIS OF SULFONATED POLY(ARYLENE ETHER SUFLONE)S

William Harrison, F. Wang, Y-S. Kim, M. Hickner,
and
J.E. McGrath*

Department of Chemistry and the Materials Research
Institute Virginia Tech, Blacksburg, VA 24061

Introduction

Polymer exchange membrane fuel cells (PEMFC) have gained world-wide interest as alternative power sources. Of crucial interest is the development of cost effective polymeric membrane material that will allow for efficient fuel cells for transportation and portable power applications. Proton exchange membranes (PEMs) are essential to the operation and the advancement of the fuel cell technology as they serve as a gas separator and the electrolyte. Sulfonated polymers / solid polyelectrolytes lead the frontier in PEMs. Alternatives to expensive perfluorinated copolymer, such as DuPont's Nafion®, are needed to expand the operation temperature, fuel efficiency, and fuel options (ie., alcohol proton sources like methanol) for PEMFCs. The properties and performance of polymers in any application can be traced to the choices and/or selection of monomers. Here we report on various bisphenols: bisphenol A, hexafluoroisopropylidene (6F) bisphenol A, 4,4'-biphenol, and hydroquinone in the syntheses of sulfonated poly(arylene ether)s and their respective influence on membrane properties of high molecular weight, film forming copolymers synthesized via traditional condensation polymerization with various compositions of both unsulfonated and disulfonated 4,4'-difluorodiphenylsulfone monomer, as generalized in Figure 2. We will survey the morphologically influence due to bisphenol structure and changes in ionic content using Tapping mode -Atomic Force Microscopy (AFM).

Characterization

Intrinsic viscosities were determined in NMP at 30°C using an Ubbelohde viscometer. Proton (¹H) and carbon (¹³C) NMR spectroscopy of monomers and polymers were conducted using a Varian 400 MHz instrument. Thermal gravimetric analyses (TGA) were performed in air at a heating rate of 10°C/min using a Perkin-Elmer TGA 7. FTIR spectra were recorded using a Nicolet Impact 400 FT-IR spectrometer. Tapping mode -Atomic Force

Microscopy (AFM) is performed using a Digital Instrument Dimension 3000 on dehydrated films converted to their acid form

Conclusions

Polymers with controlled amounts of sulfonated dihalide comonomer have been synthesized and characterized using intrinsic viscosity, FTIR, and TGA. These copolymers have high calculated ion-exchange capacities and protonic conductive equal to and even higher than the commercial reference material. Thermal gravimetric analysis of the free acid form of the copolymers does not display weight loss for any polymer composition before 220°C, while the sodium salt form does display higher thermal stability as expected. Short-term water sorption / uptake of the sulfonated polymers can be up to 60 weight percent of its dry weight.

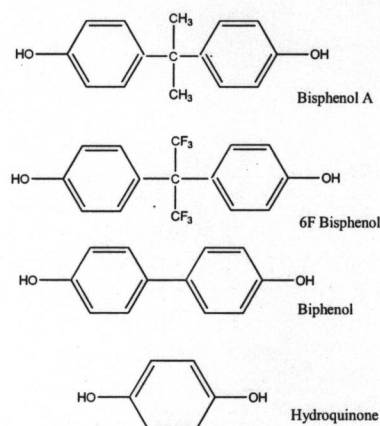


Figure 1. Structures of Investigated Bisphenols

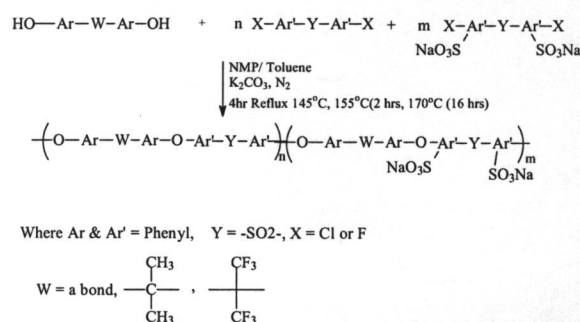


Figure 2. General synthesis of sulfonated poly(arylene ether)s

Acknowledgements: The authors would like to thank the Department of Energy and National Science Foundation for support of this research effort. William Harrison would like to thank the NSF funded Hampton University / Virginia Tech Trainee Fellowship.