



# Morphology of sulfonated polyarylenethioethersulfone random copolymer series as proton exchange fuel cells membranes by small angle neutron scattering

Mitra Yoonessi<sup>a,b,\*</sup>, Hendrik Heinz<sup>c</sup>, Thuy D. Dang<sup>d</sup>, Zongwu Bai<sup>e</sup>

<sup>a</sup> Ohio Aerospace Institute, Cleveland, OH 44142, USA

<sup>b</sup> NASA Glenn Research Center, Cleveland, OH 44135, USA

<sup>c</sup> Department of Polymer Engineering, University of Akron, Akron, OH 44325, USA

<sup>d</sup> Air Force Research Laboratory, AFRL/RXBN, Wright-Patterson AFB, OH 45433, USA

<sup>e</sup> University of Dayton Research Institute, 300 College Park Drive, Dayton, OH 45469, USA

## ARTICLE INFO

### Article history:

Received 27 June 2011

Received in revised form

23 September 2011

Accepted 28 September 2011

Available online 4 October 2011

### Keywords:

Fuel cells membrane

Morphology

Neutron scattering

## ABSTRACT

Sulfonated polyarylenethioethersulfone (SPTES) copolymers with high proton conductivity (100–215 mS/cm at 65 °C, 85% relative humidity) are promising potential proton exchange membrane (PEM) for fuel cells. Small angle neutron scattering (SANS) of the hydrated SPTES copolymer membranes at 25 °C exhibit a nanostructure which can be approximated by correlated polydisperse spherical aggregates containing water molecules with liquid-like ordering (Percus Yevick approximation) and large scale water pockets. The ionic domain radius and the volume packing density of the aggregates present in the hydrated SPTES copolymer membranes at 25 °C increased with increasing degree of sulfonation. SPTES-80 with highest degree of sulfonation (71.6%) showed a Guinier plateau at the very low  $q$  range ( $q < 1 \times 10^{-4} \text{ 1/\AA}$ ) indicating presence of isolated large scale morphology ( $R_g = 1.3 \pm 0.18 \text{ micron}$ ). The radius of spherical ionic aggregates present in the hydrated SPTES-50 and SPTES-60 copolymer membranes increased with increasing temperature to 55 °C, but the large scale morphology changed to a fractal network. Further increase of the sulfonation degree to 63.3% and 71.6% (SPTES-70 and SPTES-80) resulted in a substantial morphology change of the spherical aggregates to an irregular bicontinuous hydrophobic/hydrophilic morphology for the hydrated SPTES-70 and SPTES-80 copolymer membranes at 55 °C. Presence of ionic maxima followed by a power law decay of  $-4$  for SPTES-70 and SPTES-80 copolymer membranes was attributed to the bicontinuous phase morphology at high degree of sulfonation and elevated temperature (55 °C). The disruption of the larger scale fractal morphology was characterized by significant decrease in the intermediate scattering intensity. Hydrophobic and hydrophilic domains were separated distinctly by sulfonic groups at the interface showing as power law decay of  $-4$  for all hydrated SPTES copolymers.

© 2011 Elsevier Ltd. All rights reserved.

## 1. Introduction

Ionomers are important class of polymeric materials with ionizable groups on the polymer backbone or in the pendant which can phase separate to hydrophobic and hydrophilic domains [1,2]. Ionomers with ionizable acidic groups have potential application as polyelectrolyte membranes in fuel cells. Hydrogen fuel cell is an electrochemical reactor in which the proton transport from anode to cathode leads to a reaction at the cathode catalyst interface [3–5]. Therefore, transport of protons and hydronium ions through proton

exchange membrane (PEM) is the key factor on the performance of a hydrogen fuel cell. High proton conductivity, impermeability to reactant gases, high thermal and mechanical stability both in the dry and hydrated states, water uptake, dimensional stability, and low cost are fundamental characteristics of PEM for hydrogen fuel cells. The structure, dynamics, and transport characteristics of Nafion<sup>®</sup> as commercially utilized PEM have been studied by small angle neutron scattering (SANS) [6–11], small angle x-ray scattering (SAXS) [12–16], quasi-elastic neutron scattering (QENS) [17], and nuclear magnetic resonance spectroscopy (NMR) [18].

Transport properties and nanostructure of sulfonated polyimide (SPI) membranes have been studied using pulsed field gradient NMR and NMR quadrupolar relaxation rates determinations [19,20], and small angle scattering methods (SAXS and SANS), respectively [21,22].

\* Corresponding author. Ohio Aerospace Institute, Cleveland, OH 44135, USA. Tel./fax: +1 9376265333.

E-mail address: [mitra.yoonessi@nasa.gov](mailto:mitra.yoonessi@nasa.gov) (M. Yoonessi).