Investigation of nanostructures and properties of sulfonated poly(arylenethioethersulfone) copolymer as proton conducting materials by small angle neutron scattering

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ABSTRACT

Sulfonated poly(arylenethioethersulfone) copolymer (SPTES-50), a promising candidate material for proton exchange membrane fuel cell (PEMFC), exhibited excellent thermal stability, high proton conductivity (135 mS/cm at 85 °C, 85% relative humidity), and electrochemical property. Small angle neutron scattering (SANS) of fully hydrated SPTES-50 membranes revealed the presence of embedded spherical nanodomains containing ionic group and water within the polymer membranes. The polydispersity of the nanoscale structure limited scattering contrast between the polymer backbone and sulfonated groups, and precluded analysis of intermediate and large scattering vectors in terms of the polymer–water interface structure. Inter-cluster correlations associated with the large extent of water absorption in the fully hydrated SPTES-50 membranes were accounted by Percus–Yevick liquid-like ordering of polydispersed hard sphere model with Schulz polydispersity approximation. Approximation of their low q upturn with an exponential decay results in a decay of -3 at 25 °C accounted for inter-cluster correlations which changed to a decay of -1.1 at 55 °C and 77 °C. This indicated a change in morphology upon increase of temperature such as to fractal morphology or an interconnected cylindrical network. The scattering patterns don't exhibit any further changes within examined range of q when the temperature increased from 55 °C to 77 °C. The number density of ionic clusters remained approximately constant ($\sim 1.1818 \times 10^{17}$ cm^3), which indicated that additional water adsorbed by the polymer at the elevated temperature did not result in substantial coalescence of the clusters. Transmission electron microscopy (TEM) observation of the silver exchanged SPTES-50 membranes exhibited aggregates of Ag$^+$ embedded within the dry membranes which can be approximated by isolated spheres.

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1. Introduction

The increasing demand for the new source of energy for internal combustion engine of vehicles, telecommunication and portable devices, laptops, and cell phones requires developing new green methods of energy generation such as fuel cells. Proton exchange membrane (PEM) is a critical component of hydrogen fuel cell which separate gases from mixing while maintaining a path for proton transport. Key properties of PEM materials are high proton conductivity, good electrochemical properties, durability, excellent thermal stability, low permeation to reactant gases (hydrogen and oxygen) and small dimensional variations upon hydration–dehydration cycles. Nafion membranes are limited by high cost, high permeation of methanol, loss of proton conductivity at high temperatures (>80 °C) and low relative humidity (<50%). The last two effects result from membrane dehydration and low glass transition temperature of Nafion (T_g: 110–130 °C) [1,2]. A range of sulfonated polymers with aromatic phenyl ring in the backbone such as sulfonated polyetherether ketone (SPEEK) [3], sulfonated polyimide (SPI) [4,5], sulfonated polysulfones [6,7] and sulfonated polybenzimidazole [8] have been developed and investigated to overcome Nafion's limitations. Proton conductivity of these membranes depends on the degree of sulfonation, number of water molecules associated with one sulfonic group and their activity. These polymers in general possess higher thermal stability and lower methanol crossover (for direct methanol fuel cells).

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Sulfonated poly(arylenethioethersulfone) copolymer (SPTES-50) membranes have good processability, and excellent thermal and electrochemical properties as well as low cost to make [9–11]. SPTES-50 is a sulfonated poly(arylenethioethersulfone) copolymer with equal ratio of hydrophobic and hydrophilic chain segment ratio (see Fig. 1). It posses key characteristics of high proton conductivity (135 mS/cm at 85 °C, 85% relative humidity (RH)), low gas permeation rate, and thermal stability ($T_g \sim 200$ °C). The presence of sulfonated groups on the backbone containing aromatic phenyl rings leads to lower segregation of hydrophobic and hydrophilic compared to Nafion where the sulfonated groups are in the pendant chain of a flexible polymer backbone. The polycondensation synthesis of SPTES copolymers with tailored hydrophobic and hydrophilic chain segment ratio has been described elsewhere [10,11]. SPTES-50 membrane can be incorporated into a membrane electrode assembly for hydrogen fuel cell operations and it can operate at elevated temperatures (>100 °C) when water molecules are present.

Sulfonated polymers phase separate to form hydrophobic domains and aggregates of sulfonic groups which contain water molecules and hydronium ions [12]. The macromolecular architecture and the degree of sulfonation control the size and structure of the phases. The dynamics and transport of proton and hydronium ions depend on the strength of the ionic interactions between hydronium ions and sulfonic groups, water activity, inter-aggregate distance and connectivity of the aggregates. Characteristics of Nafion have been examined extensively including proton conductivity and its dependence on temperature and humidity, diffusion coefficient by pulsed-gradient NMR and structural models by SANS and combination of experimental structural analysis and simulations of reconstruction by SAXS [13–16].

Numerous models such as sphere [17], core–shell [18], parallelpiped [19], and local order model [5,20,21] have been introduced to explain cluster size and water aggregate network formation at high water contents semi-quantitatively. More recently, it was shown that Nafion forms randomly packed inverted micelle cylindrical structure [22,23]. The effects of external counter ion on the internal structure of the ionomeric aggregates and clusters of Nafion have been studied extensively. Few studies on a range of swollen states from dry to solution have suggested an inverted micelle model for low water content and a network of rod-like polymer aggregates for dilute solution [13]. There is no semi-quantitative information available regarding the structure of sulfonated poly(arylenethioethersulfone)s to the best of our knowledge. Preliminary X-ray scattering (SAXS) and AFM studies of the SPTES copolymer (SPTES-70) membranes indicated a phase separation between hydrophobic and hydrophilic segments [9], and significant differences between the nanostructures of SPTES membranes in comparison to Nafion. SAXS studies of the SPTES-70 revealed the presence of a broad maximum corresponding to the sulfonic aggregates where the size depends on the membrane hydration. Presence of a broader peak suggests a lower degree of segregation between hydrophobic and hydrophilic domains. This could be attributed to the lower flexibility of the polymer chain and the presence of sulfonic groups on the polymer backbone. This study attempts to investigate and quantify the nanostructure of hydrated SPTES-50 membrane and to provide a correlation between its phase morphology and its proton conductivity.

2. Experimental

2.1. Materials

A solution (~ 10 wt%) of SPTES-50 (equivalent weight of 610 g/eq.) in dimethyl acetamide (DMAc, Sigma Aldrich) was filtered several times, cast in a flat dish and placed in vacuum oven with a gradual temperature increase to 100 °C for 24 h and 120 °C for 2 h. The resulting uniform flat membranes immersed in deionized water for 2 h and dried under vacuum (24 h, 80 °C) after they were acidified in sulfuric acid (4 M, 24 h) to ensure complete conversion of sulfonic groups to their protonated forms.

2.2. Characterization

Membranes were dried in vacuum (80 °C and 20 mb) (W_{dry}), and then immersed in DI water at 25 °C, 55 °C, and 77 °C (accuracy of 0.5 °C) for 2 h until constant weight was achieved (W_h). The reported water uptake of the membrane was determined from the weight of the hydrated membrane and weight of the dry membrane as follow equation (1):

$$\text{Water uptake} = \frac{W_h - W_{dry}}{W_{dry}} \times 100\% \tag{1}$$

The volume fraction of water (ϕ_w) was obtained from the equation (2):

$$\phi_w = \rho_p W_w / \left(\rho_{H_2O} W_{dry} + \rho_p W_w \right) \tag{2}$$

where W_w is the weight of water, ρ_p and ρ_{H_2O} are the density of dry polymer and water, respectively. Reported water volume fractions are average of three independent measurements. Compared to a previous study [9], we have obtained a higher water volume fraction which may be associated with a different rate of solvent evaporation during film formation or differences in polymer batches such as monomer sequence in the copolymer backbone, degree of polymerization, and polydispersity.

Measurements of the proton conductivity were performed using AC impedance spectroscopy with an Alpha High Resolution Dielectric/Impedance Analyzer (Novo Control), over frequency range of (10 Hz–1 MHz) using a standard 4-electrode setup. The impedance values in a range of zero phase angles were used to calculate the proton conductivity (σ), as follow equation (3):

$$\rho = l/RS \tag{3}$$

where l is the distance between electrodes in cm, R is the resistance, S is the cross sectional area in cm^2 and σ is proton conductivity in S/cm.

The SANS experiments were performed at the National Institute of Standards and Technology (NIST), Neutron Center for Research on the 30 m NG-7 SANS instrument with a neutron wavelength, λ, of 6 Å ($\Delta\lambda/\lambda = 10\%$) and three sample-to-detector distance of 1.5 m, 10 m ($\lambda = 6$ Å), and 15 m ($\lambda = 8$ Å), $0.001 < q < 0.3168$ Å^{-1} at 25 °C, 55 °C, and 77 °C (accuracy of 0.5 °C). Hydrated membranes were placed in demountable 1 mm thick titanium liquid cells filled with D$_2$O after equilibrium in D$_2$O (24 h). Scattered intensities were reduced, corrected for the transmission and background and placed on absolute scale. Then, circularly averaged to produce absolute scale scattering intensity, $I(q)$, as a function of the wave vector, q,
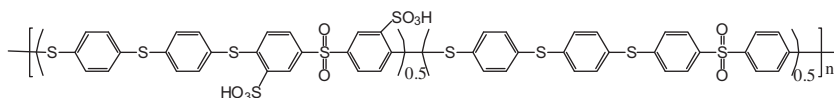

Fig. 1. Chemical structure of sulfonated endcapped poly(arylenethioethersulfone) copolymer (SPTES-50).