

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

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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.

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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[®] 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].

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The microstructure of sulfonated polyetherether ketone (sPEEK) has been investigated by SAXS [12]. We recently reported a class of ionomers based on aromatic hydrocarbon copolymers with high proton conductivity and excellent thermal mechanical stability both in the dry and hydrated states [22–29]. Sulfonated polyarylenethioethersulfone (SPTES) copolymers have following chemical structures (Fig. 1).

SPTES copolymers including SPTES-50, SPTES-60, SPTES-70 and SPTES-80, have equivalent weight (EW) and IEC (mequiv./g) values of 610, 515, 459, 417, and 1.64, 1.94, 2.18, and 2.4, respectively [22]. They exhibited proton conductivity of 100, 145, 175, and 215 mS/cm respectively, at 65 °C and 85% relative humidity [22]. Their excellent proton conductivity at high temperatures combined with their high glass transition temperature (~ 200 °C) and mechanical stability (both in the dry and hydrated states) make them excellent potentials as high temperature PEM materials for fuel cells. SPTES-50 copolymer membrane has successfully been fabricated to membrane electrode assemblies and exhibited polarization curves and durability up to 400 h [29]. Their successful operations at 90–100 °C were limited by boiling point of water (100 °C at 1 atm). Replacing water molecules with heterocycles such as imidazolium where the charge carrier has a very low vapor pressure can result in proton conductivity at higher temperatures. Despite excellent electrochemical properties, excessive water uptake of SPTES-70 and SPTES-80 copolymer membranes provide difficulties to be made as membrane electrode assembly [22,27]. The proton transport and performance of SPTES copolymers highly depend on the presence of water molecules. In addition to the number of sulfonic groups, their acidity (pK_a) ability to dissociate water molecules to proton, water activity coefficient, and number of water molecules associated with each sulfonic group, the supermolecular structure of the hydrophobic and hydrophilic phases is also defined by polymer chain characteristics such as chain persistent length, and presence of sulfonic group on the backbone or in the side chains. We reported the presence of ionic nanodomains containing water molecules in the SPTES-70 using *in-situ* x-ray scattering [27]. The morphology and the nanostructure of SPTES-50 were approximated by correlated polydisperse spherical aggregates and a larger scale water domain network and were quantified by modeling of the SANS spectra with polydisperse hard sphere model with Percus Yevick liquid-like ordering [29]. This study reports the nanostructure and morphology of sulfonated polyarylenethioethersulfone (SPTES) copolymer membranes which is directly related to the proton transport through the membrane in terms of their degree of sulfonation and temperature dependency.

2. Materials and methods

2.1. Materials

Visually observed defect free films of SPTES copolymers were prepared by dissolving the purified copolymer in dimethyl acetamide (DMAc, Sigma Aldrich) (5–10 wt%) filtering, placing in a flat dish in a vacuum oven with a gradual temperature rise to 100 °C for 24 h and 120 °C for 2 h. The resulting uniform flat films were immersed for 2 h in deionized water 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

SANS experiments were performed at the National Institute of Standards and Technology (NIST), Neutron Center for Research using 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, and 55 °C (accuracy of 0.5 °C). Hydrated membranes were placed in demountable 1 mm thick titanium liquid cells filled with D₂O after equilibrium in D₂O (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 , where $q = (4\pi/\lambda)\sin(\theta/2)$ and θ is the scattering angle. Calculations were performed using Igor Pro® software [30,31]. USANS experiments covered a q -range of $0.00005 < q$ (Å⁻¹) < 0.01 , corresponding to a real-space length scale of 0.1 micron–10 micron.

3. Results and discussions

3.1. Hydrated SPTES copolymers at 25 °C

SPTES copolymers have high proton conductivity at high relative humidities and elevated temperatures; e.g. 65 °C and 85% RH of 100, 145, 175, and 215 mS/cm for SPTES-50, -60, -70, and -80 copolymers, respectively [27]. The degree of sulfonation increases for SPTES-50, -60, -70 and -80 copolymers in the order of 45.04, 54.9, 63.3, and 71.6%, respectively. SPTES-50 copolymer has the lowest the degree of sulfonation and SPTES-80 copolymer has the highest degree of sulfonation in this class of copolymers [22,27]. The scattering spectra of the fully hydrated (D₂O) SPTES-50, -60, -70, and -80 copolymers at 25 °C show a scattering behavior of a two phase structure (Fig. 2a). The contribution of sulfonic groups to the scattering is considered to be negligible due to their small volume compared to the polymer and the water phase volume. It was visually observed that membranes do not dissociate when fully hydrated in the examined temperature. It was also determined by weight measurement that the membranes maintain the weight after deswelling. Therefore, the hydrophobic polymeric structure is the supporting network even at high water content and increased temperatures. Fig. 2a presents enhanced scattering intensity data (vertically shifted) for the hydrated SPTES-60, -70, and -80 copolymer membranes in the order of 20X, 1000X, and 2×10^5 X for the clarity of data presentation. The absolute scale scattering intensities in the medium q range of $0.02 < q$ (1/Å) < 0.1 are almost in the same intensity range for all SPTES copolymers. The high q scattering spectra for all copolymers exhibit a feature which is attributed to the presence of ionic domains containing water molecules. According to the scattering results, the morphology of all hydrated SPTES-50, -60, -70, and -80 copolymer membranes at 25 °C can be approximated as correlated polydisperse spherical aggregates with liquid-like ordering (P.Y. ordering) and a power law decay [29]. The scattering data for the hydrated SPTES-50, -60, -70, and -80 copolymer membranes at 25 °C were compared and quantified using polydisperse (Schulz polydispersity) hard sphere model with Percus Yevick liquid-like ordering [32–34] and a low q power law decay [29]. The modeling of the SPETS 50 nanostructure and its properties have been reported elsewhere but presented here for

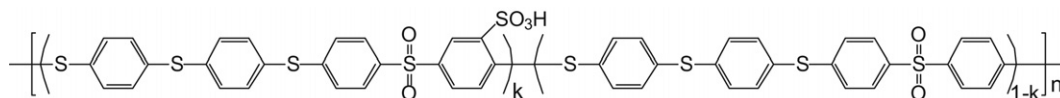


Fig. 1. Chemical structure of the highly sulfonated endcapped polyarylenethioethersulfone, SPTES-50, -60, -70, -80 ($k = 0.5, 0.6, 0.7, 0.8$).

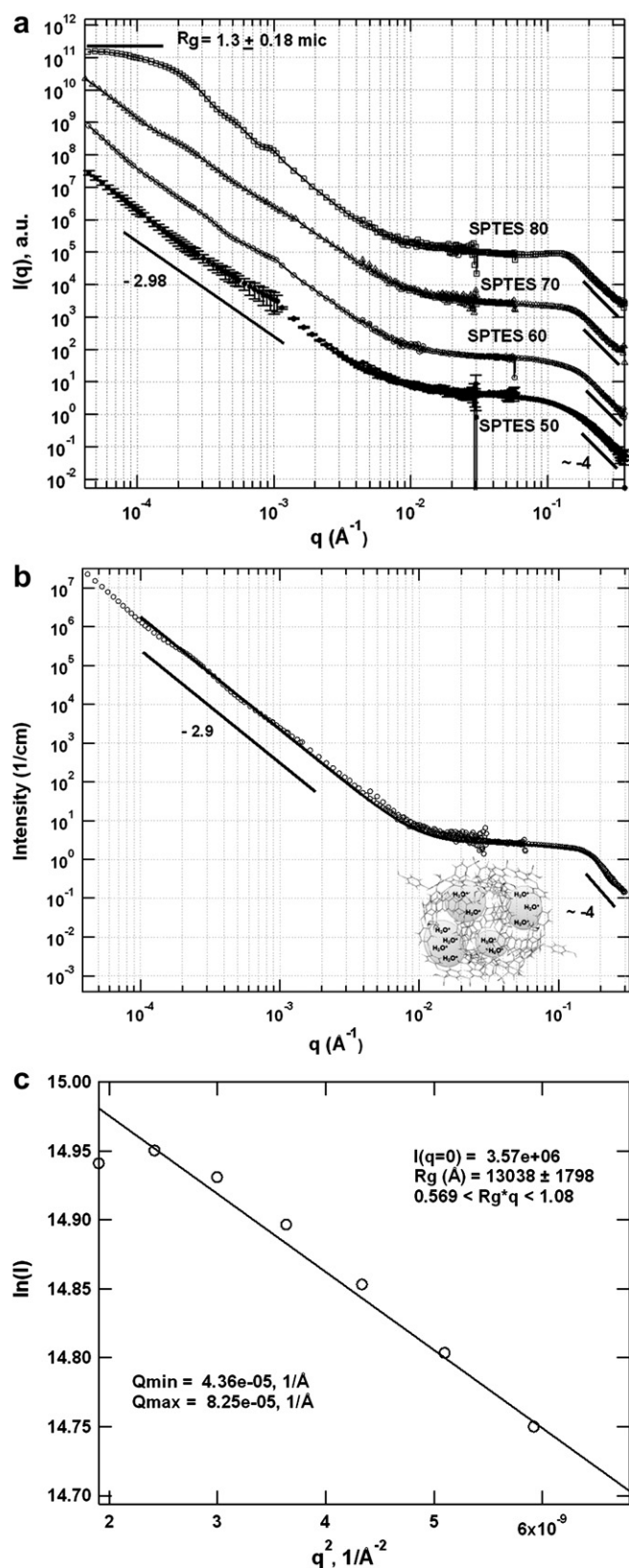


Fig. 2. Scattering spectra of fully hydrated (D_2O) SPTES copolymer series at 25 °C 2a) Scattering spectra of SPTES-50 (●), SPTES-60 (○), SPTES-70 (△), and SPTES-80 (□); Scattering intensity for hydrated SPTES-60, SPTES-70 and SPTES-80 were shifted vertically for clarity (SPTES-60: 20X, SPTES-70: 1000X, SPTES-80: 2×10^5 X). 2b) Experimental scattering spectra of SPTES 70 compared with polydisperse hard sphere model with liquid-like ordering and a power law decay of -2.9 . 2c) The plot of $\ln(I)$ vs. q^2 in the $4.36 \times 10^{-5} < q$ ($1/\text{\AA}$) $< 8.25 \times 10^{-5}$.

clarity and completeness of the SPTES series analysis [29]. Fig. 2b shows the experimental scattering spectra of the hydrated SPTES-70 copolymer membrane at 25 °C compared with the theoretical calculations of the model (solid line). The results of the comparison of the hydrated SPTES-50, -60, -70 and -80 copolymer membranes scattering data with the model are summarized in Table 1. According to this modeling the domain radius increased with increasing degree of sulfonation in the order of 13.45, 14.9, 15.4, and 16.9 Å for SPTES-50, -60, -70 and -80 copolymer membranes. The hard sphere packing density increased with increasing degree of sulfonation in the order of 19.8%, 23%, 25%, 29% for SPTES-50, -60, -70, and -80 copolymer membranes. This could indicate that ionic domains are capable of holding more water molecules with the presence of more sulfonic groups on the polymer backbone (increasing the degree of sulfonation). The high- q scattering spectra exhibits onset of a peak formation when the degree of sulfonation was increased to 71.6% for SPTES-80 copolymer. Presence of scattering maxima can be due to the scattering from an ordered structure (periodicity) or the oscillations resulted from the structural factor effects or the excluded volume effect arising from short range liquid-like ordering. The onset of peak formation is attributed to the excluded volume effects related to the liquid-like ordering [33–35]. The low- q power law decay of nearly -3 was observed for all SPTES copolymers in the range of $1 \times 10^{-4} < q$ ($1/\text{\AA}$) $< 3 \times 10^{-3}$. The power law decay of -3 is attributed to the presence of interacting three-dimensional fractal morphology. In addition, a Guinier plateau [35] was present for the hydrated SPTES-80 copolymer at the very low q (q ($1/\text{\AA}$) $< 9 \times 10^{-5}$). This is in addition to the nearly identical scattering intensity in the intermediate q -range ($0.02 < q$ ($1/\text{\AA}$) < 0.1). It can be concluded that the change in the degree of sulfonation had little or no effect on the intermediate and low angle scattering wave vector. The low- q power law decay was nearly -3 ± 0.1 for all SPTES copolymers. The presence of sharp interface between hydrophobic and hydrophilic domains was deduced from the power law decay of -4 at large angle wave vectors for all hydrated SPTES copolymer membranes. All scattering data presented in Fig. 2a shows a power slope of -3.85 to -4.15 which is approximated as ~ -4 . The presence of Porod behavior (decay of -4) has been attributed to the two immiscible phase with a sharp boundary [35–37]. This shows that the hydrophobic and hydrophilic domains are separated with a distinct interface containing sulfonic groups.

Presence of a plateau in the scattering spectra is characteristics of isolated scatterers [35]. The radius of gyration (R_g) of the isolated scatterers can be approximated by $I(q) = I_0 \exp((-q^2 R_g^2)/3)$, where I_0 is the extrapolated zero scattering intensity (Guinier approximation) [35]. Presence of the Guinier plateau in the q range of $4.3 \times 10^{-5} < q$ ($1/\text{\AA}$) $< 8.2 \times 10^{-5}$ for SPTES-80 copolymer suggests segregation of the isolated large scale hydrophilic water pockets when the degree of sulfonation increased to 71.6%. Radius of gyration of the isolated larger scale water pockets in fully hydrated

Table 1

Structural characteristics of SPTES copolymer membrane predicted by polydisperse hard sphere with Percus Yevick liquid-like ordering and a low- q decay.

Material	R (Å)	Vol. fraction	Polydispersity	Low q decay
Hydrated Membranes at 25 °C				
SPTES-50	13.45 ± 0.2	0.2	0.43	-3
SPTES-60	14.9 ± 0.5	0.23	0.36	-2.9
SPTES-70	15.4 ± 0.5	0.25	0.32	-2.9
SPTES-80	16.9 ± 0.5	0.29	0.31	-3.1
Hydrated Membranes at 55 °C				
SPTES-50	26.4 ± 0.5	0.28	0.35	—
SPTES-60	32 ± 0.2	0.33	0.31	—

SPTES-80 copolymer membrane was 1.3 ± 0.18 micron which was calculated from this approximation (Fig. 2c).

3.2. Hydrated SPTES copolymers at 55 °C

Based on the physical observations, water saturated membranes at 55 °C were swollen films without visual dissociation. Fig. 3 exhibits the scattering spectra of the fully hydrated (D_2O) SPTES-50, -60, -70 and -80 copolymer membranes at 55 °C. The intermediate scattering intensity decreased with increasing degree of sulfonation in the order of SPTES-50, -60, -70, and -80 copolymers. The scattering spectra of the fully hydrated SPTES-60, -70, and -80 copolymer membranes start to form scattering maxima at high q range when the degree of sulfonation increased. This indicated the increase in the excluded volume due to the increase in the volume of the scatterers at higher degree of sulfonation and increased temperature (55 °C). The presence of scattering maxima is more significant for SPTES-70 copolymer and SPTES-80 copolymer with 63.3 and 71.6% degree of sulfonation. The large angle scattering feature shows scattering maxima at q_{\max} of 0.103 and 0.1108 $1/\text{\AA}$ for SPTES-70 and SPTES-80 copolymers which correspond to spatial characteristics lengths ($l = 2\pi/q_{\max}$) of 60.97 and 56.7 Å due to concentration fluctuations of hydrated domains (hard spheres). The scattering spectra of the hydrated SPTES-50, -60, -70, and -80 copolymer membranes changed significantly with increasing degree of sulfonation. This indicates a substantial change in the hydrophobic/hydrophilic morphology with increasing degree of sulfonation at 55 °C which is more pronounced for SPTES-70 and SPTES-80 copolymers (degree of sulfonation 63.3 and 71.6%, respectively). Hydrophobic and hydrophilic regions are segregated distinctly by the sulfonic groups at the interface which is represented by the Porod behavior, asymptotic behavior of ~ -4 for all SPTES copolymers [35–37]. The morphology of these membranes is complex and controlled by interfacial phenomena. The number of sulfonic groups per repeat unit volume and their acidity complemented with the chain persistent length and chain mobility are governing factors in the formed morphology. This study approximates the morphology of the fully hydrated SPTES-50 and SPTES-60 copolymer membranes at 55 °C are approximated as spherical nanodomains containing water molecules with liquid-like ordering similar to their morphology at 25 °C. It is also proposed that this morphology changed to fractal morphology with increasing temperature (increasing the intermediate scattering decay). The domain radius and the sphere packing density were increased from 26.4 Å and 28% for SPTES-50 copolymer to 32 Å and 33% for SPTES-60 copolymer while the intermediate scattering intensity decreased. The domain radius and packing density of the hydrated SPTES-50 copolymer membrane increased from 13.45 Å and 19.8% to 26.4 Å and 28% when the temperature increased from 25 °C to 55 °C with this approximation. The same increasing trend of 14.9 Å–32 Å for the average domain radius and 23%–33% of the sphere packing density was observed. The decrease in the intermediate scattering of the hydrated SPTES-60 copolymer membrane compared to the hydrated SPTES-50 copolymer membrane is attributed to the disruption of the large scale morphology. The low q power law decay of the hydrated SPTES-60 copolymer membrane was close to the decay of the hydrated SPTES-50 copolymer membrane.

The increase in the degree of sulfonation of SPTES-60, -70, and -80 copolymers from 54.9, to 63.3 and 71.6% resulted in a shift in the position of the high q scattering maxima of the hydrated membranes toward the large angle scattering regime. This peak formation is more prominent for SPTES-70 and SPTES-80 copolymers with higher sulfonation degree. The decrease in the intermediate scattering intensity in the order of SPTES-50, -60, -70 and

-80 copolymers is attributed to the loss of the large scale water network, intermediate fractal morphology within the polymer and onset of a morphology change to a two large scale phase morphology. The closed domain morphology of polydisperse spherical aggregates containing water molecules with fractal network were present for fully hydrated SPTES-50 and SPTES-60 copolymer membranes at 55 °C (Figs. 3 and 4a). However, substantial changes in the morphology of fully hydrated membranes occurred when the degree of sulfonation is increased to 63.3 and 71.6% for SPTES-70 and SPTES-80 copolymers at higher temperature of 55 °C. Combination of high temperature, high density of sulfonic groups, and significant amount of water molecules within the polymer backbone could have resulted in the coalescence of the small spherical ionic domains and fractal water network into a larger scale bicontinuous network of intermeshed hydrophobic and hydrophilic morphology for fully hydrated SPTES-80 copolymer membrane at 55 °C. The bicontinuous model originally proposed for micro-emulsion of two immiscible phases of water and oil with comparable amount based on Landau theory [38,39]. This model describes two irregular shapes with distinct boundary and has been used for intermesh of hydrophobic and hydrophilic structure when the particle shape is not well-defined [40,41]. This model proposes $I(q) = (a_2 + c_1q + c_2q^2)^{-1}$ for $a_2 > 0$, $c_1 < 0$, and $c_2 > 0$, a single broad scattering maxima, and power law decay of -4 at large scattering angles. Two characteristics lengths of d and ξ are deduced from this analysis having a_2 , c_1 , and c_2 [39,40], d is the domain periodicity or interdomain distance and ξ is the correlation length which has been attributed to the dispersion of d . According to this theory, c_1 is negative due to the surfactant. The absolute values of c_1 and the ratio of ξ/d should increase with increasing surfactant. The specific internal surface area can be derived from the ratio of $S/V = 4\phi(1-\phi)/\xi$ [38,39].

The scattering spectra of the hydrated SPTES-70 copolymer membrane has a low- q upturn, a lower intermediate scattering intensity compared to the hydrated SPTES-60 and SPTES-50 copolymers, and a large angle maxima followed by a power law decay of -4 . This indicates the onset of the coalescence of the ionic aggregates, disruption of the fractal water network, and the formation of the two irregular large scale bicontinuous phase morphology. The high q range ($q > 0.037$ $1/\text{\AA}$) of the scattering

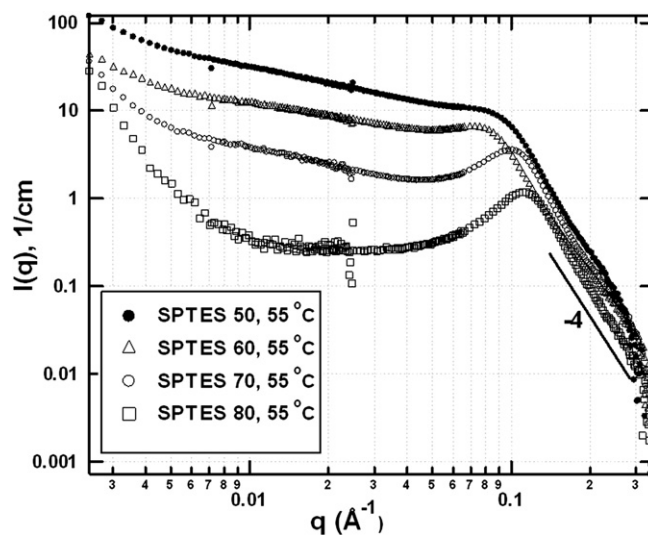


Fig. 3. Scattering spectra of fully hydrated (D_2O) SPTES copolymers at 55 °C. The high q scattering exhibit a power law decay of -4 . High q range maxima position of hydrated SPTES-60, SPTES-70 and SPTES-80 shifts toward higher q with increasing degree of sulfonation.

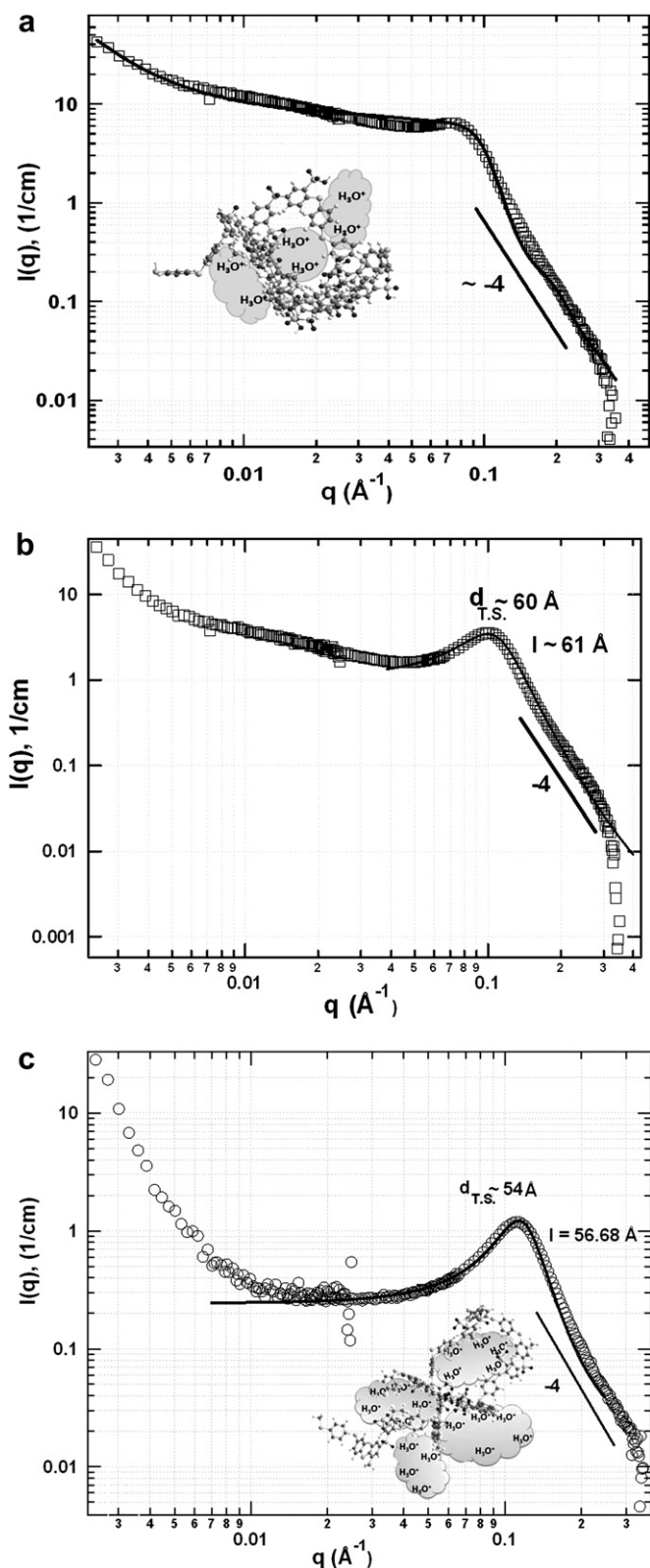


Fig. 4. Experimental SANS data of fully hydrated (D_2O) SPES-60 (lower degree of sulfonation), SPES-70 and SPES-80 (highest degree of sulfonation) membranes at 55 °C. High q scattering spectra exhibits a power law decay of -4 indicating a sharp ionic interface for all hydrated polymer membranes. 4a) SANS spectra of hydrated SPES-60 at 55 °C (\circ) is compared with the polydisperse hard sphere model with liquid-like ordering and a power law decay. 4b) SANS spectra of the SPES-70 indicates that the domain aggregates and fractal domains start to collapse and form bicontinuous irregular two immiscible phase morphology. Bicontinuous model was compared with SANS spectra in the q range of ($q > 0.037$ 1/Å). 4c) Experimental scattering data of fully hydrated SPES-80 (\circ) at 55 °C compared with Tuebner Strey bicontinuous phase model.

spectra of the hydrated SPES-70 copolymer membrane at 55 °C was compared with the T.S. bicontinuous model (Fig. 4b). This simulation resulted in a periodicity, d , of 59.9 Å which is in excellent agreement with the one obtained from the scattering maxima position, 60.97 Å. According to this simulation, the correlation length (ξ) is 31.14 Å. The medium- q range scattering still exhibits the larger scale morphology which is not completely converted to the bi-continuous phase morphology. However, they are partially collapsed characterized by a lower scattering intensity in the intermediate q range. The high q maxima followed by a power law decay of -4 is approximated as bicontinuous morphology. The low and medium q ($q < 0.037$ 1/Å) scattering spectra of the SPES 70 is due to the presence of fractal network of waters which have not coalesce yet.

The scattering spectra of the SPES-80 copolymer are consistent with a bicontinuous two phase structure of irregular shapes with sulfonic groups as interfacial ionic region. The scattering experimental data of the hydrated SPES-80 copolymer membrane was compared with this model ($q > 0.015$ 1/Å), (Fig. 4c and Table 2). The periodicity of the water domains (or hydrophobic domains), d , predicted by this model is ~ 54 Å which is in excellent agreement with the one obtained from the scattering maxima (q_{max}), 56.7 Å. This value is the distance between water domains. The correlation length (ξ) obtained from this model is 37.86 Å which is a measure of dispersion.

The distance between the water phases, periodicity, was decreased from 59.9 Å to 54 Å with increasing degree of sulfonation. The correlation length, ξ , was increased from 31.14 Å to 37.86 Å when the degree of sulfonation increased. Increasing the interfacial area results in an increase in the ξ/d ratio. The presence of the upturn in the low range of the hydrated SPES 70 and 80 at 55 °C (Fig. 4b and c) is attributed to the fractal morphology of the large scale features.

3.3. Discussions

Scattering data of series of SPES membranes were obtained in the full hydration state with increasing the sulfonation degree in the order of 45.04, 54.9, 63.3, and 71.6% for SPES-50, -60, -70, and -80 copolymer membranes. Complete study was performed to provide understanding membranes morphology with increasing the temperature of the hydrated membranes from 25 °C to 55 °C. Proposed model assumes spherical nanodomains containing water molecules forming from clustering of the sulfonation groups. This assumption was performed based on previously reported study which showed spherical nanodomains in the dry SPES 50 membrane under HR-TEM [29]. The scattering spectra of the membranes with high degree of sulfonation (SPES 70, and 80) changed significantly when the temperature increased to 55 °C. The morphology is approximated as bi-continuous system where the hydrocarbon is the main support network containing water. This model has been recently proposed by Wnek et al. [40], Gebel [8], and Kreuer [12], Wnek also provided visualization of the hydrophobic cluster using SYBYL version 6.7 (Tripos) and HINT (Hydrophobic INTERactions) computational modeling software [40]. Despite the support of the transport studies of this model [42],

Table 2

Structural characteristics of fully hydrated SPES-70 and SPES-80 at 55 °C described by Tuebner Strey model.

Material	d (Å)	ξ (Å)	ξ/d	I (Å)
Hydrated Membranes at 55 °C				
SPES-70	59.9 ± 0.2	31.1 ± 0.4	0.52	61 ± 0.3
SPES-80	$\sim 54 \pm 0.3$	37.8 ± 0.6	0.7	56.7 ± 0.2

Table 3
Summary of membrane structural changes (SPTES 50, 60, 70, and 80 at 25 °C, and SPTES 50 and 60 at 55 °C) as a function of degree of sulfonation and temperature by polydisperse hard sphere model with liquid-like ordering (P.Y. ordering). T.S. bi-continuous model was approximated for higher sulfonation degree copolymers, SPTES 70 and 80, at 55 °C.

Sulfonation Level, % Temperature, °C Morphology	SPTES 50			SPTES 60			SPTES 70			SPTES 80		
	45.04	25	55	54.9	25	55	63.3	25	55	71.6	25	55
	P.D. hard sphere, P.Y. ordering	P.D. hard sphere, P.Y. ordering	P.D. hard sphere, P.Y. ordering	P.D. hard sphere, P.Y. ordering	P.D. hard sphere, P.Y. ordering	P.D. hard sphere, P.Y. ordering	P.D. hard sphere, P.Y. ordering	P.D. hard sphere, P.Y. ordering	T.S. bi-continuous model	P.D. hard sphere, P.Y. ordering	P.D. hard sphere, P.Y. ordering	T.S. bi-continuous model
Radius, Å	13.45 ± 0.2	26.4 ± 0.5	26.4 ± 0.5	14.9 ± 0.5	32 ± 0.2	32 ± 0.2	15.4 ± 0.5	15.4 ± 0.5	31.1 ± 0.4	16.9 ± 0.5	16.9 ± 0.5	37.8 ± 0.6
Correlation length (ξ), Å												

there is no direct visualization method for this proposed approximation. The T. S. model is also supported by high proton conductivity of the hydrated SPTES 70 and 80 membranes at 55 °C where a larger number of hydronium ions in a larger domain can facilitate proton transport. A summary of the structural evolution of the SPTES membranes as a function of temperature and degree of sulfonation is illustrated in Table 3. This study attempted to study a full range of SPTES membrane nanostructure for the first time and provide an understanding of large membrane water uptakes, and their morphology and their relation with high conductivity of the membranes using both liquid like ordering of polydisperse nanospheres and bi-continuous T.S. model approximation.

4. Conclusions

A series of SPTES copolymers with high proton conductivity of 100–215 mS/cm at 65 °C and 85% relative humidity as potential fuel cells membranes were studied. SANS studies of fully hydrated membranes showed that the nanostructure of the fully hydrated SPTES-50, -60, -70, and -80 copolymer membranes at 25 °C in agreement with ionic aggregates containing water molecules with a large scale morphology network of water pockets morphology. This model predicted that the increase in the degree of sulfonation resulted in an increase in the radius of ionic domains and an increase in the volume packing density of water in the aggregates. It was assumed that the same morphology of polydisperse correlated spherical ionic domains were present in the SPTES-50 and SPTES-60 copolymers when the temperature increased to 55 °C. Increase in the degree of sulfonation for fully hydrated SPTES-70 and SPTES-80 copolymer at 55 °C led to a substantial reorganization of the membrane morphology which was described by a bi-continuous hydrophobic/hydrophilic network.

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References

- [1] Schlick S. Ionomers: characterization, theory and applications. FL: CRC Press; 1996.
- [2] Tant MR, Mauritz KA, Wilkes GL, editors. Ionomers: synthesis, structure, properties and applications. London: Chapman and Hall; 1997.
- [3] Larminie J, Dicks A, editors. Fuel cells systems explained. London: John Wiley & Sons; 2003.
- [4] Cleghorn SJC, Ren X, Springer TE, Wilson MS, Zawodinski C, Zawodinski TA, et al. Int J Hydrogen Energy 1997;22:1137–44.
- [5] Hoogers G. Fuel cell technology handbook. CRC Press LLC; 2003. MA.
- [6] Eisenberg A, Yeager HL. ACS symposium series 180. Washington, DC: American Chemical Society; 1982.
- [7] Kim MH, Glinka CJ, Grot SA, Grot WG. Macromolecules 2006;39:4775–87.
- [8] Gebel G, Lambard J. Macromolecules 1997;30:7914–20.
- [9] Rollet AL, Diat OR, Gebel G. J Phy Chem B 2002;106:3033–6.
- [10] Young SK, Trevino SF, Beck Tan NC. J Polym Sci. Part B Polym Phys 2002;40:387–400.
- [11] Rollet AL, Gebel G, Simonin JP, Turq P. J Polym Sci. Part B Polym Phys 2001;39:548–58.
- [12] Kreuer D. J Mem Sci 2001;185:29–39.

- [13] Elliott JA, Hanna SA, Elliott MS, Cooley GE. *Macromolecule* 2000;33:4161–71.
- [14] Schmidt-Rohr K, Chen Q. *Nat Mater* 2007;7:75–83.
- [15] Haubold HG, Vad Th, Jungbluth H, Hiller P. *Electro Acta* 2001;46:1559–63.
- [16] Elliott JA, Hanna SJ. *Appl Crystallogr* 1999;32:1069–83.
- [17] Pivovar AM, Pivovar BS. *J Phys Chem B* 2005;109:785–93.
- [18] Nosaka AY, Nosaka YJ. *J Power Sources* 2008;180:733–7.
- [19] Rollet AL, Blachot JF, Delville A, Diat O, Guillermo A, Porion P, et al. *Eur Phys J* 2003;12:130–4.
- [20] Rollet AL, Porion PT, Delville A, Diat O, Gebel G. *Mag Res Imag* 2005;23:367–8.
- [21] Blachot JF, Diat O, Putaux JL, Rollet AL, Rubatat L, Vallois C, et al. *J Mem Sci* 2003;214:31–42.
- [22] Bai Z, Durstock MF, Dang TD. *J Mem Sci* 2006;281:508–16.
- [23] Bai Z, Price GE, Yoonessi M, Juhl SB, Durstock MF, Dang TD. *J Mem Sci* 2007;305:69–76.
- [24] Yoonessi M, Bai Z, Dang TD, Durstock MF, Vaia RA. *Proceeding of American Institute of chemical Engineers (AIChE)*, 2005.
- [25] Dang T, Bai Z, Dalton MJ, Fossum E. 27th ACS National Meeting, 2004 Anaheim, CA.
- [26] Bai Z, Williams LD, Durstock MF, Dang TD. *Polym Preprints (American Chem Soc Division Polym Chemistry)* 2004;45:60–1.
- [27] Yoonessi M, Bai Z, Dang TD. *J Polym Sci. Part B Polym Phys* 2007;45:2813–22.
- [28] Bai Z, Dang TD. *Macro Rapid Comm* 2006;27:1271–7.
- [29] Yoonessi M, Heinz H, Dang TD, Wheeler R, Bai Z. *Polymer* 2010;51:1585–92.
- [30] Kline S. SANS data reduction tutorial. Gaithersburg, MD: NIST Center for Neutron Research; 2001.
- [31] Hammouda B. http://www.ncnr.nist.gov/staff/hammouda/the_SANS_toolbox.pdf, April, 2008.
- [32] Kinning DJ, Thomas EL. *Macromolecules* 1984;17:1712–8.
- [33] Percus JK, Yevick GJ. *Phys Rev* 1958;110:1–13.
- [34] Percus JK. *Phys Rev Lett* 1962;8:462–3.
- [35] Guinier A, Fournet G. *Small-angle scattering of x-rays*. NewYork: John Wiley and Sons; 1955.
- [36] Porod G. In: Glatter O, Kratky O, editors. *Small-angle x-ray scattering*. London: Academic Press; 1982.
- [37] Higgins JS, Benoit HC. *Polymers and neutron scattering*. Oxford: Clarendon Press; 1994.
- [38] Teubner M, Strey R. *J Chem Phys* 1987;87:3195–7.
- [39] Schubert KV, Strey R, Kline SR, Kaler EW. *J Chem Phys* 1994;101:5343–56.
- [40] Serpico JM, Ehrenberg SG, Fontanella JJ, Jiao X, Perahia D, McGrady KA, et al. *Macromolecules* 2002;35:5916–21.
- [41] Nieh MP, Guiver MD, Kim DS, Ding J, Norsten T. *Macromolecules* 2008;41:6176–82.
- [42] Edmondson CA, Fontanella JJ, Chung SH, Greenbaum SG, Wnek GE. *Electrochim Acta* 2001;46:1623–8.