Hydrophilic–hydrophobic multiblock copolymers based on poly(arylene ether sulfone)s as novel proton exchange membranes – Part B

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ABSTRACT

There has been growing evidence, both experimental and theoretical, that block copolymer systems with well-defined sulfonated regions may provide enhanced proton transport, especially at low relative humidity. We have recently demonstrated a novel way to make hydrocarbon hydrophobic–hydrophilic block copolymers. While the chemical structure and chemical compositions are very similar to random copolymers, the microstructure and the morphology are very different. The self-diffusion coefficients of water, as measured by Pulse Gradient Stimulated Echo (PGSE) NMR techniques, have indicated a significant improvement in water transport after reaching a particular block length. At that block length (10 kg/mol:10 kg/mol), the multiblocks display better proton conductivity under partially hydrated conditions than the random copolymers. The presence of increased free water content in the multiblocks with increasing block lengths was confirmed by states of water analysis. A significant change in the distribution of three types of water was also observed compared to the random copolymers. This paper will discuss the structure–property relationships of these multiblock copolymers for potential application as proton exchange membranes.

1. Introduction

Ion containing polymeric membranes has been widely used as proton exchange membranes (PEM) in fuel cells. The nature of the ionic groups, chemical composition, and copolymer microstructure all play important roles in controlling the desired properties. One important criterion for a PEM is to have sufficient proton conductivity under partially hydrated conditions. Nafion®, a commercially available PEM developed by DuPont, has met that criterion to a certain extent. However, it has several disadvantages such as mechanical and oxidative stability and reduced performance at elevated temperatures (above 100 °C). More importantly, Nafion® displays high gas and methanol cross-over rates [1]. Sulfonic acid group containing hydrocarbon based random copolymers have been proposed as alternative membranes [2]. Our research group had been engaged over the past several years in synthesizing and characterizing biphenol based partially disulfonated poly(arylene ether sulfone) (BPSH-xx) random copolymers as potential PEMs [2–5]. In BPSH-xx, the BP stands for Biphenol, S for sulfone, H for the acidified form and xx is the degree of disulfonation. The copolymers have demonstrated superior performance at elevated

temperatures and higher hydration levels when compared to Nafion® [4]. However, the random architecture results in the formation of isolated domains which significantly restricts proton transport at low hydration levels [6].

Ion containing block copolymers with better phase-separated microstructures are reported to have better performance than random copolymers at low hydration levels [6,7]. Recently, our group has synthesized thermally stable multiblock copolymers with varying chemical structures and compositions [6,8–11]. These have included highly fluorinated and partially fluorinated systems, as well as hydrocarbon based copolymers—all of which feature the same hydrophilic units. Transport properties have scaled with the block lengths of the copolymers, irrespective of the nature of the backbone. An increase in block length for a given series of block copolymers under the same ionic concentration has been associated with an increase in the self-diffusion coefficients of water, as well as improved proton conduction under partially hydrated conditions, especially when compared to BPSH-xx random copolymers [6,9,11]. Nanophase separation or the extent of connectivity between the hydrophilic domains, which has been shown to be a function of block lengths, lowers the morphological barrier for transport. However, the chemical structure of the multiblock copolymers studied was different from the random BPSH-xx copolymer [6,9,11]. Hence a true understanding of the influence of block copolymer microstructure on

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the properties over the random copolymer microstructure is yet to be achieved.

We have recently demonstrated a novel way to make hydrocarbon hydrophobic–hydrophilic block copolymers. The detailed synthesis and fundamental polymer characterization studies have been reported separately [12]. In contrast to random copolymers, the block copolymer chemistry involves decafluorobiphenyl as a coupling agent to facilitate a low temperature coupling reaction (100 °C) between the hydrophilic and hydrophobic blocks. The decafluorobiphenyl unit is present in very small amounts, only about 1–2% on a weight basis; hence, the chemical structure will be very similar to BPSH-xx [3] random copolymers. However, the microstructure and the morphology are very different. In this paper, BPSH-xx random copolymers of varying ionic compositions will be compared with BPSH block copolymers of varying block lengths and ionic compositions. This will provide a better understanding of the effect of the differences in random and block copolymer morphology on the transport properties under both fully and partially hydrated conditions.

The nature of water, i.e., the different states of water existing in the hydrophilic domains, is of great fundamental importance in understanding the influence of chemical structure on transport properties [13,14]. As has been documented, there are at least three states of water that have been associated with water residing in the hydrophilic phases of polymers [13,15–17]. The presence and nature of these three states are defined by the thermal properties. *Non-freezing bound water*, also referred to as *tightly bound water*, is firmly bound to the polymer and depresses its T_g, but the water shows no melting endotherm by differential scanning calorimetry (DSC). *Freezable bound water* is weakly bound to the polymer (or loosely bound to the non-freezing water), and displays a broad melting behavior around 0 °C. *Free water* exhibits a sharp melting point at 0 °C. A strong relationship between the states of water and transport properties is known to exist [13]. In this paper, the characterization and quantification of the different types of water will be reported as a function of block and random copolymer morphology. A more complete understanding of the relationships between chemical composition, microstructure, states of water, and transport properties will lead to synthesizing tailored PEMs with improved performance capabilities.

2. Experimental

2.1. Materials

Highly purified 4,4′-dichlorodiphenyl sulfone (DCDPS) was provided by Solvay Advanced Polymers. Biphenol (BP) was obtained from Eastman Chemical. All these monomers were well dried under vacuum prior to use and dried *in vacuo* before copolymerization. Decafluorobiphenyl (DFBP) was obtained from Lancaster and used as received. Disulfonated derivatized comonomer (SDCDPS) was synthesized according to modified literature methods [18] and dried *in vacuo* before copolymerization. The solvent *N,N*-dimethylacetamide (DMAc, Fisher) and *N*-methyl-2-pyrrolidinone (NMP, Fisher) were vacuum-distilled from calcium hydride onto molecular sieves. Potassium carbonate (Aldrich) was dried *in vacuo* before copolymerization. Toluene, sodium chloride, 30% fuming sulfuric acid and methanol were obtained from Aldrich and used as received. The fuming sulfuric acid was further analyzed for active SO_3 concentration [18,19]. Nafion® 112 was obtained from ElectroChem, Inc. and used as received.

2.2. Multiblock and random copolymer syntheses

A series of segmented disulfonated multiblock copolymers based on poly(arylene ether sulfone) were synthesized.

The multiblock copolymers were prepared by a coupling reaction between phenoxide terminated fully disulfonated poly(arylene ether sulfone) (BPSH100) and decafluorobiphenyl (DFBP) end-capped unsulfonated poly(arylene ether sulfone) (BPS00) as hydrophilic and hydrophobic blocks, respectively. BPSH100 hydrophilic oligomers with phenoxide end-groups were prepared with varying block lengths ranging from 3 kg/mol to 20 kg/mol via step growth polymerization. DFBP end-capped unsulfonated BPS00 hydrophobic oligomers were prepared via a two-step reaction. First, phenoxide terminated BPS00 oligomers with the same molecular weight range of the hydrophilic oligomers were synthesized. Second, the oligomers were end-capped with DFBP. Synthesis of the multiblock copolymers was facilitated by a low temperature coupling reaction (100 °C) between the phenoxide end-groups on the hydrophilic oligomers and the fluorine containing end-groups on the hydrophobic oligomers, producing high molecular weight multiblock copolymers. A detailed synthesis for producing these copolymers and fundamental polymer properties has been published elsewhere [12]. Random BPSH-xx copolymers were synthesized using the procedures described earlier [3].

2.3. Membrane preparation

Salt form copolymers were redissolved in NMP to afford transparent solutions with 5% solids and then the solutions were cast onto clean glass substrates. The films were dried for 2 days with infrared heat at gradually increasing temperatures, and then dried under vacuum at 110 °C for 2 days. The membranes were converted to their acid form by boiling in 0.5 M H_2SO_4 for 2 h, and were then boiled in deionized water for 2 h.

2.4. Determination of water uptake

The water uptake of all membranes was determined gravimetrically. First, the membranes were soaked in water at 30 °C for 2 days after acidification. Wet membranes were removed from the liquid water, blotted dry to remove surface droplets, and quickly weighed. The membranes were then dried at 120 °C under vacuum for at least 24 h and weighed again. The water uptake of the membranes was calculated according to Eq. (1) where $mass_{dry}$ and $mass_{wet}$ refer to the mass of the dry membrane and the wet membrane, respectively.

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

The hydration number (λ), namely, the number of water molecules absorbed per sulfonic acid group, can be calculated from the mass water uptake and the ion content of the dry copolymer. This is shown in Eq. (2), where MW_{H_2O} is the molecular weight of water (18.01 g/mol) and IEC is the ion exchange capacity of the dry copolymer in equivalents per gram.

$$\lambda = \frac{\left(mass_{wet} - mass_{dry}\right)\big/ MW_{H_2O}}{IEC \times mass_{dry}} \tag{2}$$

The volume fraction of water or the hydrophilic phase was determined from the given expression [20],

$$\phi = \left(\frac{M_{H_2O}/\rho_{H_2O}}{\left[M_{H_2O}/\rho_{H_2O} + EW/\lambda \rho_{ionomer}\right]} \right) \tag{3}$$

where Φ is the volume fraction of water, ρ is the density, and EW is the equivalent weight of the ionomer.

2.5. Determination of swelling ratio, density and ion exchange capacity

The water swelling ratio of all of the membranes was determined from the dimensional changes from wet to dry states both in-plane and through-plane. Initially, samples were equilibrated in water and the wet dimensions were measured. The dried dimensions were obtained by drying the wet membrane at 80 °C in a convection oven for 2 h. Density was also calculated from the volume and weight of the dried membranes [21]. An average of four samples was obtained for each measurement. The ion exchange capacity (IEC) values of the acid form copolymers were determined by titration with 0.01 M NaOH.

2.6. Measurement of proton conductivity

Proton conductivity at 30 °C and at full hydration (in liquid water) was determined in a window cell geometry [22] using a Solartron 1252 + 1287 Impedance/Gain-Phase Analyzer over the frequency range of 10–1 MHz following the literature procedures [23]. For determining proton conductivity in liquid water, membranes were equilibrated at 30 °C in DI water for 24 h prior to testing. In order to determine proton conductivity under partially hydrated conditions, membranes were equilibrated in a humidity–temperature oven (ESPEC, SH-240) at the specified RH and temperature for 5 h before each measurement.

2.7. Determination of self-diffusion coefficient of water

The self-diffusion coefficients of water were measured using a Varian Inova 400 MHz (for protons) nuclear magnetic resonance spectrometer with a 60 G/cm gradient diffusion probe. Corresponding experimental procedures were reported earlier [6].

2.8. Differential scanning calorimetry (DSC) and nuclear magnetic resonance (NMR)

The DSC experiments were performed in a TA DSC instrument using liquid nitrogen as cooling medium for subambient operation. The samples were equilibrated in a relative humidity oven (ESPEC SH-240) to achieve desired hydration levels. The samples were placed in thermally sealed pans capable of withstanding pressure of 100 atm. Samples were cooled to -70 °C and then heated at a rate of 5 °C min^{-1} under a N$_2$ atmosphere.

The proton spin relaxation time, T_2, was measured in a Varian Inova 400 spectrometer using Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence [13]. The 90° pulse was of 13.8 μs and the 180° pulse of 27.6 μs. A total of 200 decay points was collected over 8 ms. Samples were equilibrated at room temperature in water. Just before the experiment, they were removed from water, blotted to remove the surface water and placed in the NMR probe.

3. Results and discussion

3.1. Summary of the copolymers synthesized

The multiblock copolymers examined in this study are listed in Table 1. The copolymers are identified as BPSH–BPS (A:B) multi-blocks, where A represents the hydrophilic (BPSH) block lengths in kg/mol and B represents the hydrophobic (BPS) block length in kg/mol. The hydrophilic block is a 100% disulfonated system. The multiblock copolymers are classified in two different categories. The first one represents an equal block length series with lower and similar IEC values as shown in Table 1. The second category represents multiblocks of unequal block lengths. The hydrophilic block lengths were purposefully synthesized to be longer than the

Table 1
Summary of the properties of copolymers

Copolymer	Ion exchange capacity (IEC)[a] (meq/g)	Water uptake (%)	Water volume fraction	Self-diffusion coefficients of water[b] (10^{-6} cm^2 s^{-1})	Proton conductivity[c] (mS/cm)	Density (g/cc)
Nafion® 112	0.90	25	0.30	4.0	90	2.1
BPSH–BPS (3:3)	1.33	30	0.28	1.9	65	1.3
BPSH–BPS (5:5)	1.39	33	0.32	2.2	88	1.4
BPSH–BPS (10:10)	1.28	60	0.45	9.1	95	1.4
BPSH–BPS (10:5)	1.83	100	0.60	–[d]	160	1.5
BPSH–BPS (15:10)	1.71	90	0.57	–[d]	140	1.5
BPSH–BPS (20:15)	1.71	70	0.49	9.5	120	1.4
BPSH 40	1.73	60	0.45	5.1	100	1.3
BPSH 35	1.50	36	0.33	3.1	70	1.3
BPSH 30	1.34	29	0.22	1.6	40	1.2

[a] Obtained from titration with NaOH.
[b] Measurements were conducted in fully hydrated state at 25 °C, ±10%.
[c] Measurements were conducted in water at 30 °C, ±5%.
[d] Not measured, because of their high water uptake.

hydrophobic segments in order to achieve higher IEC values. The multiblocks were then compared to the random copolymers with very similar chemical structures represented by BPSH-xx, where xx stands for the degree of disulfonation. The random copolymers were varied in terms of ionic compositions. Nafion® 112 was used as a control for the study. The structures of BPSH–BPS (A:B) and BPSH-xx are given in Fig. 1.

3.2. Physical properties: IEC, density, water uptake and water volume fraction

The titrated ion exchange capacity (Table 1) values were similar for each of the three equal block length materials. Because the ionic compositions were similar, any change in properties with increasing block length would inevitably result from the expected increase in phase separation between the hydrophobic and hydrophilic phases in these multiblock copolymers. Water uptake values increased with increasing block length. The observed increase in the water volume fraction (calculated) with increasing block length suggests the formation of distinct phase separated and associated hydrophilic domains. In our earlier publication, we have demonstrated the presence of distinct anisotropic water swelling behavior with increasing block lengths for these multiblock copolymers [12]. All the multiblock copolymers showed similar in-plane swelling. However, the through-plane swelling increased significantly for the BPSH–BPS (10:10) copolymers. This can be correlated with TEM findings which revealed the formation of an ordered co-continuous lamella-like morphology with increasing block length—BPSH–BPS (10:10) [24].

The multiblock copolymers with unequal blocks and higher IECs showed significantly higher water uptake. In addition to the morphology effect, higher IEC values corresponded to increased water uptake. For the random copolymers, water uptake was mainly a function of the ion exchange capacity as shown in Table 1. In comparing the random copolymers and the multiblocks at similar IEC values, the multiblocks with higher block lengths absorbed more water than the random copolymers. This also indicates the presence of a better phase separated and associated
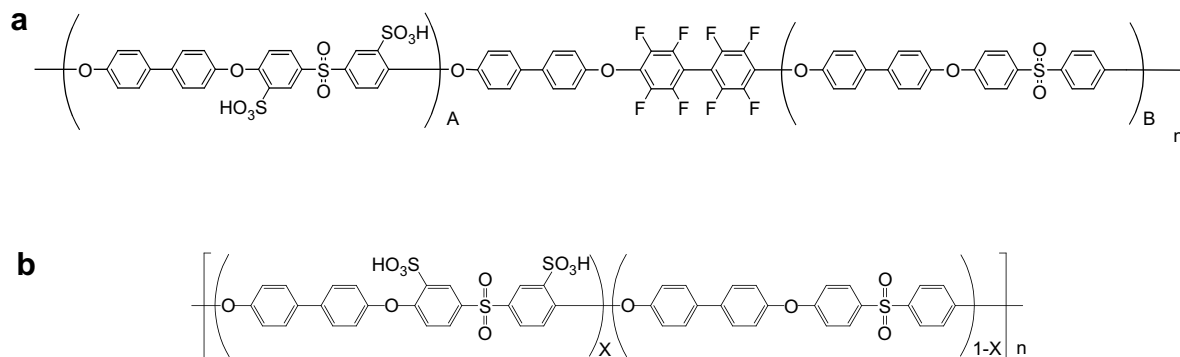
a

b

Fig. 1. Chemical Structure of (a) BPSH–BPS (A:B) multiblock and (b) BPSH-xx random copolymers.

hydrophilic–hydrophobic domain microstructure in multiblocks, when compared with the random copolymers.

3.3. Water and proton transport

Microstructural difference were clearly observed from the self-diffusion coefficient of water values measured at 25 °C under fully hydrated conditions between the multiblocks with equal block lengths and the random copolymers (Table 1). Specifically, for the multiblocks, a significant fivefold increase in diffusion values was observed with increasing block lengths. In addition to the TEM study, the higher diffusion coefficient value for the BPSH–BPS (10:10) copolymer confirms the presence of co-continuous hydrophobic–hydrophilic morphological network with a lower morphological barrier for transport. In contrast, at similar IECs, the random copolymers with significantly lowered water transport values represent an isolated morphological structure with a higher morphological barrier for transport. Understanding these microstructural differences is important in addressing the proton transport issue under partially hydrated conditions.

Proton conductivity for the multiblocks in liquid water at 30 °C was determined and the resulting values are listed in Table 1. For the random copolymers, proton conductivity normally scales with ion exchange capacity. For the multiblocks, however, an increase in conductivity values with both block lengths and IEC was observed. The increased phase separated morphology with increasing block lengths is expected to increase the available volume fraction for

transport. As a result, proton transport in multiblock copolymers seems to be dependent on the volume fraction of the water or the hydrophilic phase (Fig. 2). This clearly emphasizes the importance of morphology on proton transport. In addition, the BPSH–BPS (5:5) multiblock copolymers showed much higher proton conductivity at lower water uptake than the random BPSH 35 copolymers. Although the chemical structures and compositions are fairly similar, the differences in the microstructure and morphology make the multiblock copolymers more selective.

The activation energy for proton transport in liquid water was studied over a temperature range of 30–80 °C for the equal block length materials. Because the equal block length materials all had similar IEC values, any change in the activation energy would essentially be a function of morphology. Fig. 3 depicts plots of temperature vs. conductivity for the three equal block length copolymers and the random BPSH 35 copolymer. The slopes represent activation energy and value is given within the box as units of kJ/mol. A significant decrease in activation energy was observed as block lengths increased from 5000 g/mol to 10,000 g/mol. The activation energy of the BPSH–BPS (10:10) multiblock copolymer was significantly lower than the BPSH 35 random copolymer. The morphological transition taking place over that particular block length regime decreased the morphological barrier, thereby lowering the activation energy for proton transport.

Proton conductivity as a function of relative humidity (RH) at 80 °C was studied and the results are displayed in Fig. 4. As shown,
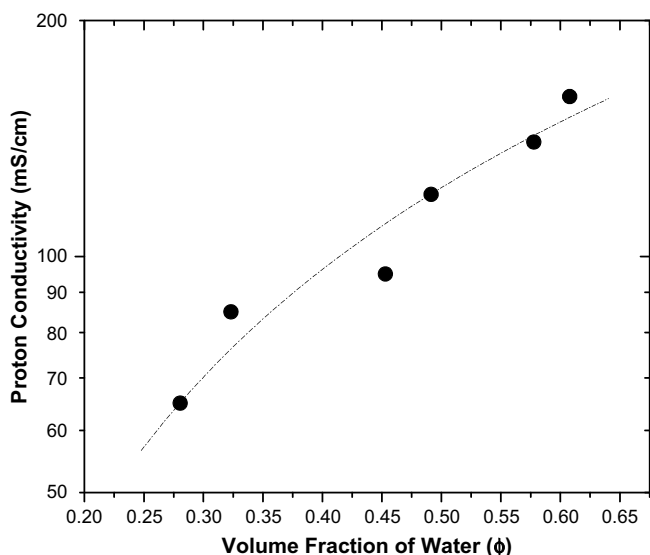
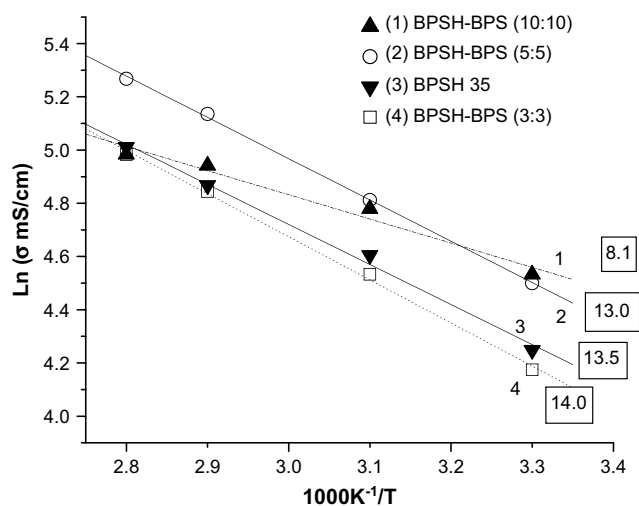Fig. 2. Proton conductivity scales with the volume fraction of water.

Fig. 3. Influence of temperature on proton conductivity as a function of block length; activation energy in kJ/mol represented within boxes decreases with increasing block length.
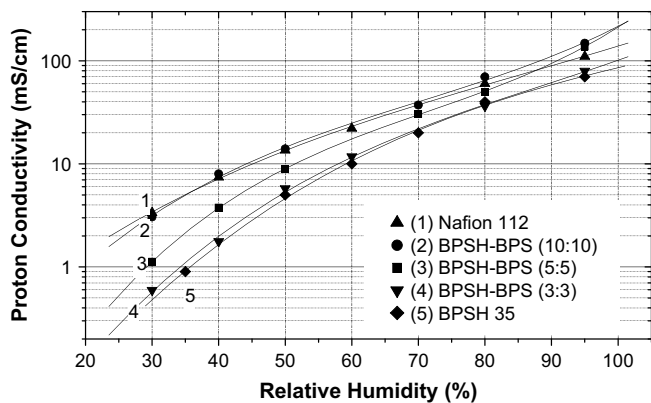
Fig. 4. Proton conductivity under partially hydrated conditions increases with increasing block lengths at 80 °C.

proton conductivity dropped significantly at lower RH values for the BPSH 35 random copolymers. Random copolymers show acceptable performance under fully hydrated conditions since there are sufficient water molecules to provide proton transport. Due to the scattered hydrophilic domains in the copolymer, however, they lack the connectivity among sulfonic acid groups for proton transport under partially hydrated conditions. In contrast, the performance of the multiblock copolymers under partially hydrated condition improved with increasing block lengths. The performance of BPSH–BPS (10:10) was comparable to that of commercially available Nafion® 112. This performance improvement is related to the formation of long, co-continuous channels at higher block lengths, through which protons can be transported along with the sulfonic acid groups and water molecules. The distinct phase separated co-continuous hydrophilic domain morphology, as supported by the diffusion coefficient, TEM and water sorption studies, lowers the morphological barrier for proton transport and improves the proton transport at low water content. Although the multiblocks and random copolymers have identical chemical structures, the difference in their chemical microstructures, particularly at higher block lengths, improves proton transport under partially hydrated conditions.

Proton conductivity was measured for the unequal block length materials as a function of relative humidity as shown in Fig. 5. Both the higher IEC values and the higher volume fraction of hydrophilic units were expected to improve connectivity within the hydrophilic domains compared to the lower IEC materials. Performance was improved significantly and was shown to be better than the benchmark Nafion® 112. However, the copolymers exhibited higher water uptake.
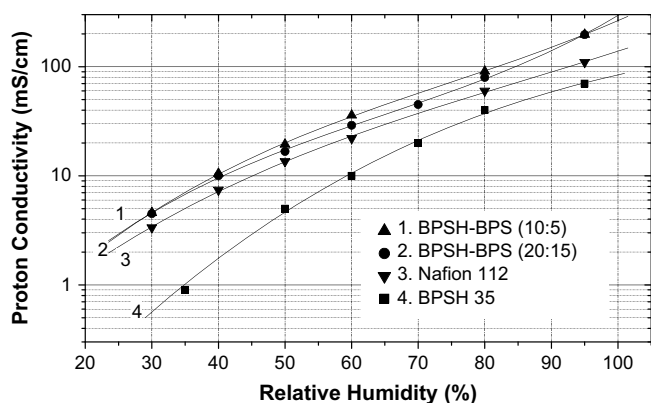

Fig. 5. Proton conductivity as a function of relative humidity for the multiblocks with higher IECs at 80 °C.
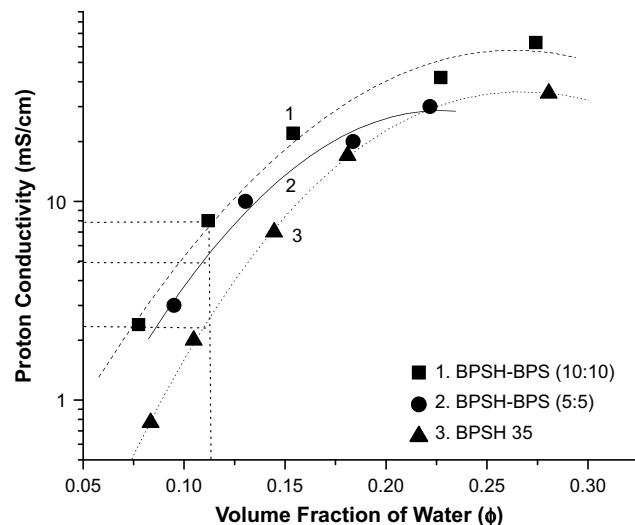

Fig. 6. Proton conductivity as a function of volume fraction of water in the copolymers at 30 °C; morphology dominates transport at low water content.

Apart from the ionic content, as seen, proton conductivity is a strong function of the water content in the copolymers [25,26]. Hence in order to understand the true effect of morphology on proton transport, the effect of water and ionic content on proton conductivity needs to be normalized. Proton conductivity values of the equal block length multiblocks and the random BPSH 35 copolymers with similar IECs were compared over a wide range of water volume fractions. The copolymers were equilibrated with different water contents, after which proton conductivity was measured at 30 °C.

It follows that even under similar water content level, proton transport is a function of block length, which is confirmed in Fig. 6. Although the multiblock copolymers showed improved proton conductivity over a wide range of water content compared to the BPSH 35 random copolymers, the effect was more pronounced in lower water content regions. Interestingly, the BPSH–BPS (10:10) with the best phase separated morphology required the least amount of water to achieve similar proton conductivity results. Hence, the morphological difference between the block and random copolymer can be assigned as the primary factor for controlling proton transport at low water content.

3.4. States of water

The states of water of the BPSH–BPS (A:B) multiblock copolymers were characterized and quantified using DSC and NMR T_2 relaxation methods. Our earlier investigations of the states of water of BPSH random copolymers indicated a strong relationship between ionic content and the nature of water [13]. Free water was found to develop within the BPSH random copolymers after attaining a particular IEC value. Specifically, an increase in block length has been associated with increasing free water. This paper will extend this analysis to the BPSH–BPS block copolymers.

3.4.1. Water absorption

Water uptake values expressed in terms of a hydration number were measured over a wide range of water activity levels for the multiblocks with equal block lengths. Nafion® 112 and BPSH 35 were included for comparison (Fig. 7). At low water activity, the BPSH–BPS (10:10) and the random BPSH 35 showed similar absorption characteristics. However, after 0.7 water activity, a sharp increase in water absorption was observed for the BPSH–BPS (10:10) in contrast to the random copolymers. This suggests that
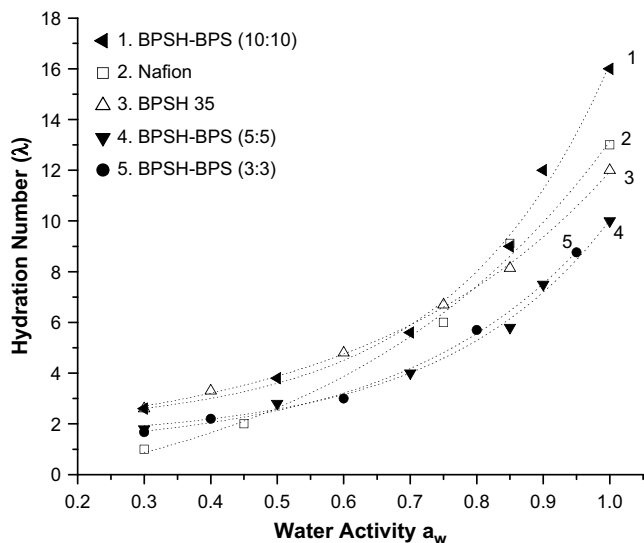
Fig. 7. Water absorption of copolymers under partially hydrated conditions.

Fig. 8. DSC thermograms of the melting endotherm of water as a function of block lengths.

the observed change in the type or state of water for the multiblock was influenced by the morphology of the copolymer. The higher hydration value for the BPSH–BPS (10:10) compared to all the other copolymers at higher water activity levels indicates the presence of more free water. The multiblock copolymers with lower block lengths, i.e. BPSH–BPS (5:5) and BPSH–BPS (3:3), showed very similar water absorption characteristics. Hence, the distribution of the types of water is thought to be similar in these systems.

3.4.2. DSC studies

The melting endotherm of water as a function of block length was characterized from DSC experiments as shown in Fig. 8. A significant increase in the area under the curve was observed for the BPSH–BPS (10:10) multiblock as block lengths were increased from 5000 g/mol to 10,000 g/mol. It should be noted that the IEC values of the multiblocks were comparable. The increased area under the peak with increasing block lengths corresponds to increased freezing water (free and loosely bound water) content. The co-continuous, ordered, phase separated morphology for the BPSH–BPS (10:10) multiblocks allows the retention of more loosely bound water and, more importantly, the retention of free water in the system. The calculated ΔH_{fus} values from the melting endotherm peaks are given in Table 2. A higher ΔH_{fus} value represents better water–water interactions. The value increased with increasing block lengths. The high ΔH_{fus} value for the BPSH–BPS (10:10) copolymer indicates presence of increased fraction of free water and better water–water interaction. However, with decreasing block length—particularly for the BPSH–BPS (3:3) sample—the melting endotherm peak shifted towards to the left or to a lower temperature. This indicates the water is more bound to the sulfonic groups, as evidenced by the significantly decreased ΔH_{fus} values.

As discussed earlier, DSC can be used to quantify the types of water present in copolymers. For example, tightly bound water content can be determined quite accurately in this way. Previous work has shown that DSC thermograms are a function of water content for polymers, showing the melting endotherms of both loosely bound water and free water [13]. Tightly bound water can be correlated to the maximum amount of water for which there is no melting endotherm. Quinn et al. [16] proposed a better mathematical technique to estimate the distribution of each type of water. They showed that if the integrated change in enthalpy (per gram of dry polymer) from the DSC thermogram is plotted against
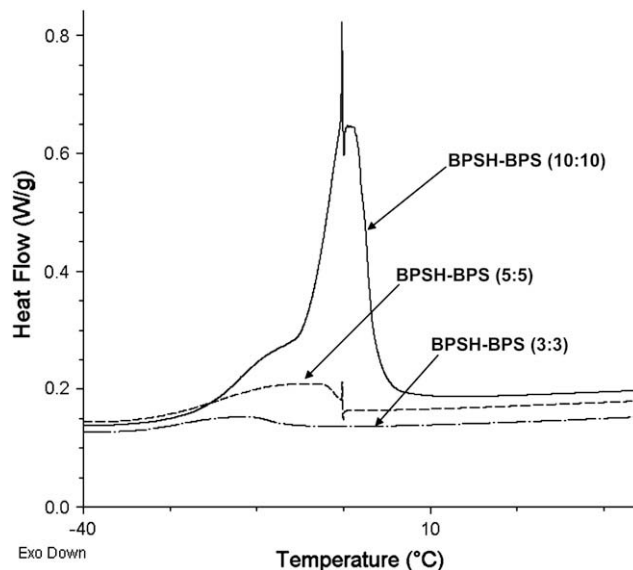
total water content, the intercept corresponds to the amount of tightly bound water. By subtracting the tightly bound water from the total water, the combined content of the loosely bound water and free water can be obtained.

Fig. 9 depicts representative plots of DSC thermograms for BPSH–BPS (10:10) multiblocks with increasing water content. The percentages in the figure represent the respective water uptake on a mass basis. The thermogram corresponding to maximum water uptake represents the fully hydrated state. A sharp and broad melting endotherm was observed, indicating the presence of both loosely and free water content. When the water uptake was decreased to 27%, the area under the peak decreased, as did the percentage of free water content. However, no melting endotherm was observed when water uptake was decreased to 18%. This corresponds to the presence of only tightly bound water in the system and can be quantified easily. DSC can successfully quantify the non-freezing water (tightly bound) and freezing water (loosely bound and free water) separately. It should be noted that it was difficult to quantify the loosely bound and free water separately only using DSC. This is due to the fact that the two melting

Table 2
States of water quantification for the BPSH–BPS (A:B) multiblocks and BPSH-xx random copolymers

Sample	IEC[a] (meq/g)	Total water content (λ)	Tightly bound water (λ)	Loosely bound water (λ)	Free water (λ)	ΔH_{fus} water (J/g of water)[c]
Nafion® 112	0.90	17	3	9	5	210
BPSH–BPS (3:3)	1.33	12	7	5	0	151
BPSH–BPS (5:5)	1.39	13	8	5	0	42
BPSH–BPS (10:10)	1.28	26	10	8	8	14
BPSH 50[b]	2.18	33	5	24	4	–
BPSH 40[b]	1.73	18	5	11	2	–
BPSH 30[b]	1.34	12	4	8	0	–

[a] Obtained from titration with NaOH.
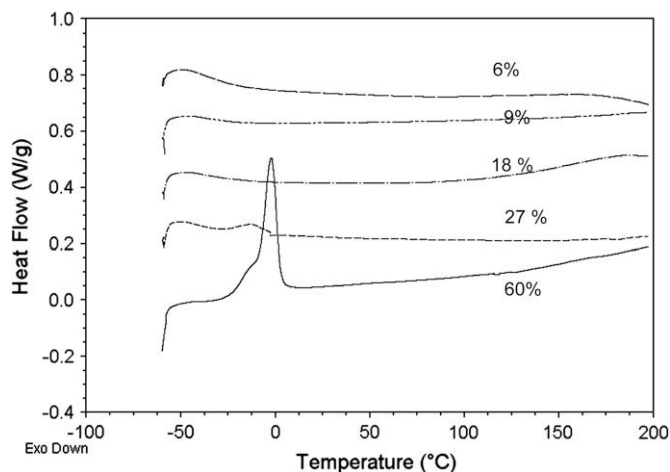[b] Data obtained from Ref. [13].
[c] Obtained from DSC.

Fig. 9. DSC thermograms of BPSH–BPS (10:10) multiblock at various water content; the numbers represent the water uptake on mass basis.

Fig. 10. ^{1}H NMR T_2 relaxation (triexponential fit) behavior of BPSH–BPS (10:10) multiblock copolymer with 60% water uptake.

endotherms of free and loosely bound water overlapped with each other. Hence, other experimental techniques should be used in conjunction with DSC to properly quantify the states of water.

3.4.3. NMR relaxation measurements

In order to quantify the loosely bound and free water content, T_2 NMR relaxation experiments were conducted. The mechanism for the T_2 relaxation in sulfonic acid containing copolymers is believed to be an exchange process between the water molecules and the exchangeable protons in the sulfonic acid groups [27]. Hence, the water molecules (tightly and loosely bound) associated with the sulfonic groups will relax faster than the ones (free water) which are not associated. However, for the copolymers studied, T_2 data could not distinguish between the shortest and the intermediate components. Loosely bound and tightly bound water are believed to exist in the same hydrophilic domain, and a rapid exchange can occur in between the two environments. For the BPSH–BPS (3:3) and BPSH–BPS (5:5) multiblock copolymers, the T_2 relaxation was found to follow a mono exponential decay function. No free water was detected in these materials. By subtracting the tightly bound water content (obtained from DSC) from the total water content, it was possible to determine the content of loosely bound water.

However, for the BPSH–BPS (10:10) multiblocks, the T_2 relaxation was triexponential in nature (Fig. 10). A unique, longer relaxation time was associated with the presence of free water in the system. The relative proportion of the corresponding coefficient of the exponent term allowed the quantification of the free water component. The sharp peak observed in the melting endotherm of the BPSH–BPS (10:10) multiblock as evidenced by DSC also supports the presence of free water. The free water content was then quantified by NMR, while the tightly bound water was quantified by DSC. Subtracting the free and tightly bound water from total water content allows proper estimation of loosely bound water content. Hence, the use of NMR in conjunction with DSC allows one to accurately quantify the states of water, as shown in Table 2.

The three different types of water quantified for the multiblocks, along with the ΔH_{fus} of water, are given in Table 2. The data for BPSH–xx were obtained from our earlier publications [13]. The method used to quantify the states of water was similar to the methods described in this paper. Nafion® 112 was used as the control.

The content of tightly bound water was found to be higher in the multiblocks than in the random copolymers. And while free water
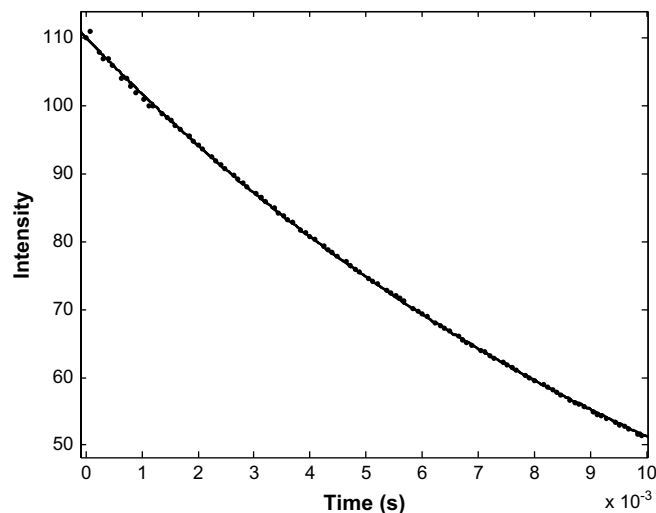
content developed after reaching a particular IEC for the random copolymers, for the multiblock copolymers it developed with increasing block length without having any increase in the IEC. In comparing the multiblock copolymers to the random copolymers at a given IEC (1.3), the BPSH–BPS (10:10) multiblock copolymer displayed significantly higher free water content than the random copolymer. The higher ionic content in the random copolymers induced microstructural changes, leading to the formation of water-assisted phase separated morphology. Hence free water develops in random copolymers only at higher IECs. In contrast, the chemically phase separated morphology of the multiblocks is responsible for the formation of free water even at a low IEC. As a comparison, Nafion® also has higher free water content at low IEC, indicating a similar phase separation characteristic to the multiblock copolymers.

4. Conclusions

The influence of microstructure/sequence distribution on the performance properties of proton exchange membranes was investigated. The BPSH–xx random copolymers and the BPSH–BPS (A:B) multiblock copolymers have a similar chemical structure. At a same IEC, the acidity and the concentration of sulfonic groups are similar in these two systems. They differ only in microstructure or sequence distribution. The microstructure of the multiblocks was varied by changing the molecular weights of the individual blocks. The random copolymer morphology resulted in lower water uptake and reduced proton and water transport. The lower block length multiblocks displayed properties similar to the random copolymers at a given IEC. However, proton and water transport increased significantly with increasing block length as observed for the BPSH–BPS (10:10) multiblock copolymers. The observed transition behavior corresponds to the formation of a co-continuous hydrophilic–hydrophobic morphology with enhanced phase separation as seen from TEM and swelling studies.

The enhanced phase separated morphology of the multiblocks improved the desired proton conductivity under partially hydrated conditions, when compared at similar water and ionic content. Thus, one can conclude that under partially hydrated conditions proton transport is controlled by the morphology and not by the acidity of the system. Hence, by changing the chemical architecture from a random to a phase separated domain network, significant improvements in PEM properties can be achieved.

Fundamental morphological differences between the random and multiblock architectures were also investigated by states of water analysis. Significant differences were observed between the two systems in the distribution of the three types of water. Specifically, a random morphology resulted in lower free water content, suggesting a closed, isolated morphological structure. Phase separated morphology in the block copolymer encouraged the formation of free water, even at lower IEC values. Free water content and the ΔH_{fus} of water increased with increasing block length under similar ionic concentrations. This can be qualitatively related to improvement of the water and proton transport for the multiblocks with increasing block lengths, highlighting the importance of free water on transport properties. Hence, in spite of their lower IEC values, the presence of free water in the BPSH–BPS (10:10) copolymers enhanced their performance as compared to the random copolymers.

All these facts support the presence of a "favored or facilitated" morphology in the multiblocks, which is conducive to improved proton and water transport.

Acknowledgements

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