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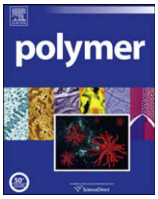

Novel hydrophilic–hydrophobic multiblock copolyimides as proton exchange membranes: Enhancing the proton conductivity

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ABSTRACT

A series of novel multiblock copolymers based on sulfonated copolyimides were developed and evaluated for use as proton exchange membranes (PEMs). In these multiblock copolyimides, the hydrophilic blocks were composed of the sulfonated dianhydride and the sulfonated diamine, with sulfonic acid groups on every aromatic ring (i.e., fully sulfonated). This molecular design was implemented to effectively enhance the proton conductivity. The properties of the multiblock copolyimides with varying IEC values or block lengths were investigated to obtain a better understanding of the relationship between molecular structure and properties of proton exchange membranes. The water uptake and proton conductivity were found to be highly dependent upon their structure. The block copolymers displayed significantly higher proton conductivities, especially at low relative humidity than the random copolymers with a similar IEC. The results indicated that the distribution of sulfonic acid and the length of the blocks play a key role on properties of proton exchange membranes.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have attracted much attention in the last few years as promising power sources for transport, stationary, and portable applications due to their low pollution levels and high conversion efficiency [1–3]. Proton exchange membranes (PEMs), which act as an electrolyte to transport protons from the anode to the cathode, are the key component of PEM fuel cell systems. Among various requirements for PEMs, the most essential property is proton conductivity. The state-of-the-art PEM is perfluorosulfonic acid membranes such as Nafion, because of their superior chemical and electrochemical stabilities, in addition to high proton conductivity with relatively low ion exchange capacity (IEC). However, some specific limitations exist for Nafion membranes including high cost, high gas permeability, and loss of the preferable properties at high temperature (>80 °C) [2,4]. This stimulated many efforts in the development of alternative PEMs.

There has been considerable effort on PEMs based on sulfonated aromatic polymers since they are thermally stable, easy to modify chemically, and inexpensive [5–8]. Generally, sulfonated aromatic polymers can achieve conductivities that are comparable to those of Nafion only with high IECs, resulting in a high water uptake (WU) and the loss of mechanical properties. It is widely recognized that the lower proton conductivity of sulfonated aromatic polymer is attributed to the lack of ion channels and the lower acidity of Ar-SO_3H [9–13]. The model suggested by Kreuer [10] for a sulfonated poly(ether ketone) confirms less pronounced ionic/nonionic separation than that of Nafion, i.e., a morphology with narrower channels than those in Nafion but with highly branched channels and many dead-end channels. Therefore, increasing the hydrophilic/hydrophobic separation to obtain a good microphase separation structure, and thus enhance proton conductivities are desired [14–16].

Various strategies have been pursued to form efficient ionic networks for enhancing the proton conductivity [12,17], include the concentration of the ionic groups on short side chains to increase the hydrophilic–hydrophobic separation [18–24], the incorporation of highly ionic blocks and grafts to favor a microphase separation [25–29], and the use of polymer main chains containing highly hydrophobic fluorinated chains to enhance the hydrophobic–hydrophilic incompatibility [17,25,29]. Among these strategies, the block copolymers is of interest due to their self-organization behaviors which could offer the opportunity for precise control of the membrane morphologies through the manipulation of chemical compositions and relative volumes of the constituent blocks [30,31]. Certain block copolymers based, for example, on sulfonated

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polyimide or sulfonated poly(arylene ether sulfone), have been claimed to display higher proton conductivities than the corresponding random copolymers [32–37]. Unfortunately, the so-called hydrophilic blocks of the block copolymers are composed not only of sulfonated but also of unsulfonated (or actually partly sulfonated) aromatic rings, a consequence of their lower hydrophilicity [38,39]. Furthermore, for a given IECs, the partly sulfonated block results in a relatively small volumes of the hydrophobic block, and thus an insufficient hydrophobicity. This in combination with the lower hydrophobicity of the aromatic ring leads to a less pronounced hydrophilic/hydrophobic separation, and thus a low-level microscale organization of the phase-separated nanodomains. The potential advantages of using these materials to enhance the proton conductivity in PEM have therefore not been fully realized. It is important, herein, to design an aromatic ionomer membrane with pronounced hydrophilic–hydrophobic separation, and to subsequently investigate this membrane to completely elucidate the intrinsic effect of the hydrophilic–hydrophobic separation on water uptake and proton transport of the membrane.

The current paper, thus presents a study on novel multiblock-sulfonated polyimides in which the hydrophilic blocks were composed of sulfonated dianhydride and sulfonated diamine monomers, with sulfonic acid groups on every aromatic ring (fully sulfonated), in order to dramatically enhance the hydrophilicity. For a given IEC, the fully sulfonated hydrophilic blocks resulted in the relatively large volumes of the hydrophobic blocks. Such an architectonically novel class of multiblock copolymer was expected to increase the hydrophilic/hydrophobic separation and microphase separation of non-polar and ionic moieties, and thus enhance the proton conductivity. The effect of block lengths water uptake and proton conductivity was studied in detail to further examine the structure–property relationships.

2. Experimental

2.1. Materials

4,4′-Diamino-3,3′-dimethyldphenylmethane (DMMDA) was purchased from Aldrich and used as received. 4,4′-Binaphthyl-1,1′,8,8′-tetracarboxylic dianhydride (BTDA) [41] and 6,6′-disulfonic acid-4,4′-binaphthyl-1,1′,8,8′-tetracarboxylic dianhydride (SBTDA) [42] were prepared according to the method previously reported. All other reagents were obtained from commercial sources and used as received.

2.2. Monomer and polymer syntheses

2.2.1. Synthesis of 3,3′-dimethyl-4,4′-methylenedianiline-6,6′-disulfonic acid (DMMDADS)

To a 100 mL three-necked flask equipped with a mechanical stirring device was charged with 2.26 g (10 mmol) of 4,4′-diamino-3,3′-dimethyldphenylmethane (DMMDA). The flask was cooled in an ice bath, and then 1.7 mL of concentrated sulfonic acid (95%) was slowly added with stirring. After DMMDA was completely dissolved, 3.5 mL fuming (SO_3 60%) sulfonic acid was slowly added to the flask. The reaction mixture was stirred at 0 °C for 2 h and then slowly heated to 60 °C and kept at this temperature for additional 2 h. After cooling to room temperature, the slurry solution was carefully poured into 20 g of crushed ice. The resulting white precipitate was filtered off and then redissolved in a sodium hydroxide solution. The basic solution was filtered, and the filtrate was acidified with concentrated hydrochloric acid. The solid was filtered off, washed with water and methanol successively, and dried at 80 °C in vacuum. Then 3.05 g of white product was obtained (yield: 85%); ^1H NMR (DMSO-d_6; Et_3N was added for dissolution in DMSO): 7.10 (2H, s), 6.66 (2H, s), 4.48 (2H, s), 4.28 (4H, $-NH_2$), 1.87 (6H, s). ^{13}C NMR: 144.4 (2C, Ar), 143.5 (2C, Ar), 133.9 (2C, Ar), 129.6 (2C, Ar), 122.6 (2C, Ar), 113.2 (2C, Ar), 32.5 (1C, $-CH_2-$), 18.1 (2C, $-CH_3$).

2.2.2. Synthesis of random sulfonated copolyimides

A typical procedure for the random copolymerization is as follows (2.69–*r*). To a 100 mL completely dried three-necked flask were added 0.5 mmol of DMMDADS, 8 mL of *m*-cresol, and 1.2 mmol of triethylamine successively under nitrogen flow with stirring. After DMMDADS was completely dissolved, 0.5 mmol of SBTDA, 0.5 mmol of BTDA, 0.5 mmol of DMMDA, 1.2 mmol of triethylamine and 2 mmol benzoic acid were added. The mixture was stirred at room temperature for a few minutes and then heated at 80 °C for 4 h and 180 °C for 20 h. After cooling to 80 °C, additional 5 mL of *m*-cresol was added to dilute the highly viscous solution, and then the solution was poured into 200 mL acetone. The precipitate was filtered off, washed with acetone thoroughly, and dried in vacuum oven for 12 h at 150 °C.

2.2.3. Synthesis of block-sulfonated copolyimides

A typical procedure for the block polymerization is as follows [39,40]. In one flask, the diamine-terminated oligomers were prepared by the reaction of DMMDADS and SBTDA in the presence of triethylamine in *m*-cresol (8 mL) at 80 °C for 4 h and 180 °C for 18 h. In another flask, the dianhydride-terminated oligomers were prepared from BTDA and an excess of DMMDA in *m*-cresol (8 mL) at 80 °C for 4 h and 180 °C for 18 h. Benzoic acid and the two mixtures containing each oligomer were mixed and copolymerized at 180 °C for 24 h. After cooling to 80 °C, the solution was poured into a large of acetone. The precipitate was filtered off, washed with acetone thoroughly, and dried in vacuum oven at 150 °C for 12 h.

2.3. Membrane preparation and proton exchange

A series of tough, ductile copolymer membranes were prepared with a controlled thickness of 40–50 μm. The polymers with triethylammonium salt form were dissolved in DMSO to form 8–10% solution at 80 °C. The solution was filtered and cast onto glass plates at 120 °C for 12 h. The as-obtained membranes were dried in vacuum at 150 °C for 12 h to remove the residual solvent, and then treated with 1.0 N sulfonic acid at room temperature for 4 days for proton exchange. The proton-exchanged membranes were thoroughly washed with de-ionized water and then dried in vacuum at 100 °C for 10 h.

2.4. Polymer characterization

2.4.1. Measurements

^1H NMR spectra were measured at 300 MHz on an AV300 spectrometer. FT-IR spectra were obtained with a Bio-Rad Digilab Division FTS-80 FT-IR spectrometer. The thermogravimetric analyses (TGA) were obtained in nitrogen with a Perkin–Elmer TGA-2 thermogravimetric analyzer at a heating rate of 10 °C/min. Molecular weight was measured with gel permeation chromatography (GPC) equipped with two Shodex KF-805 columns and a Jasco 805 UV detector (270 nm) with DMF containing 0.01 M LiBr as eluent. Molecular weight was calibrated with standard polystyrene samples. Ion exchange capacity (IEC) of the membrane was determined by titration. In the titration method, the membranes in the H^+ form were immersed in a 1 M NaCl solution for 24 h to liberate the H^+ ions (the H^+ ions in the membrane were replaced by Na^+ ions). The H^+ ions in solution were then titrated with 0.01 M NaOH using phenolphthalein as an indicator.

2.4.2. Water content

The membrane (30–40 mg per sheet) was dried at 100 °C under vacuum for 6 h until constant weight of dry material was obtained. It was immersed into de-ionized water at room temperature for 4 h. Then the membranes were taken out, wiped with tissue paper, and quickly weighted on a microbalance. Water uptake of the membranes was calculated from:

$$\text{Water content (wt\%)} = \text{WU} = (W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}} \quad (1)$$

Proton concentration in wet membrane was calculated using Eq. (2).

$$[\text{H}^+] = [W_{\text{dry}}(\text{g})/\text{Vol}_{\text{wet}}(\text{cm}^3)] \times \text{IEC(mequiv/g)} \quad (2)$$

Effective proton mobility in wet membrane (μ_{eff}) was estimated using Eq. (3).

$$\mu_{\text{eff}} = \sigma/(\text{F} \times [\text{H}^+]) \quad (3)$$

2.4.3. Stability testing

Hydrolytic stability was evaluated by treating the membrane samples in water at 140 °C for 24 h as an accelerated testing and the change in molecular weight of the test samples was recorded.

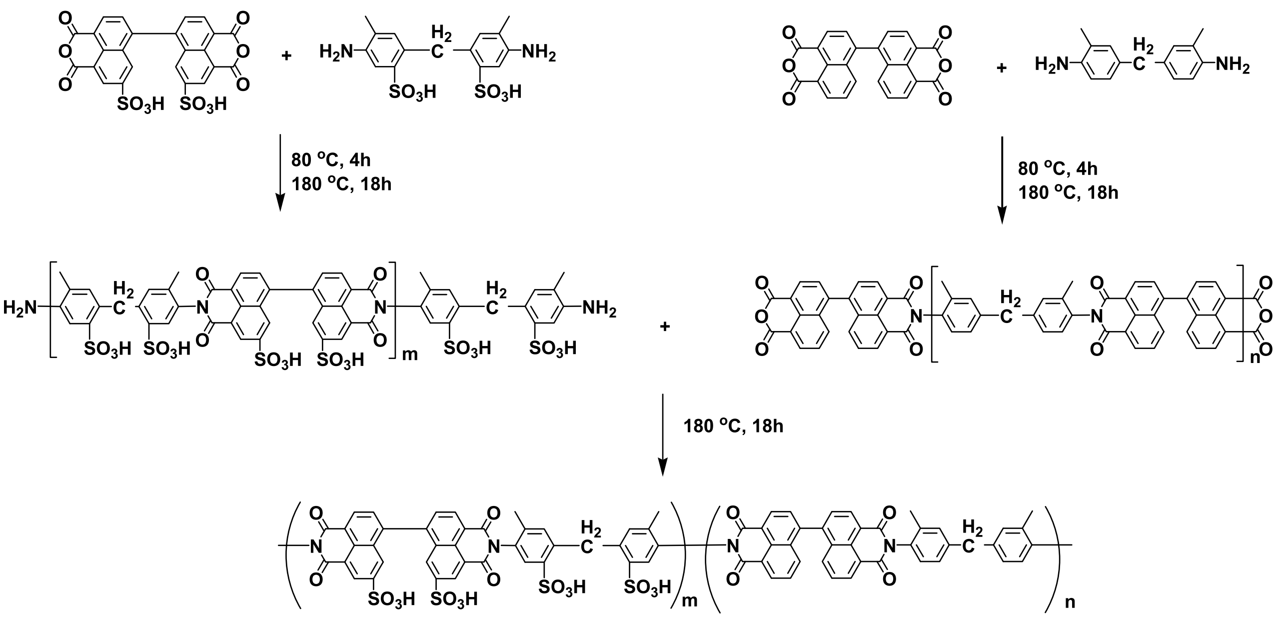
2.4.4. Proton conductivity

The proton conductivity (σ, S/cm) of each membrane coupon (size: 1 cm × 4 cm) was obtained using $\sigma = d/L_s W_s R$ (d: distance between reference electrodes, and L_s and W_s are the thickness and width of the membrane, respectively). The resistance value (R) was measured by four-point probe alternating current (ac) impedance spectroscopy using an electrode system connected with an impedance/gain-phase analyzer (Solatron 1260) and an electrochemical interface (Solatron 1287, Farnborough Hampshire, ONR, UK). The membranes were sandwiched between two pairs of gold-plate electrodes. The membranes and the electrodes were set in a Teflon cell and the distance between the reference electrodes was 1 cm. The cell was placed in a thermo-controlled chamber in liquid water for measurement. Conductivity measurements under fully hydrated conditions were carried out with the cell immersed in liquid water. All samples were equilibrated in water for at least 24 h before the conductivity measurements. At a given temperature, the samples were equilibrated for at least 30 min before any measurements. Repeated measurements were then taken at that given temperature with 10-min interval until no more change in conductivity was observed.

3. Results and discussion

3.1. Synthesis and characterization of the sulfonated copolyimides (random and block copolymers)

Important properties required for fuel cell applications, including the proton conductivity, depend on various factors such as the distribution of sulfonic acid groups along the chain and morphological structures. This paper was primarily focused on studying the effect of such factors on the proton conductivity as well as on other properties. For this purpose, a series of block-sulfonated copolyimides with the different IEC values were synthesized, as shown in Scheme 1. Random copolyimide PI (x–r) (where x refers to the IEC values) was prepared by a one-step method in the presence of Et_3N and benzoic acid. The block-sulfonated copolyimides with the different block chain lengths were synthesized by two-pot procedure, which was similar to the published work [39,40]. As illustrated in Scheme 1, a hydrophilic amine-terminated SPI oligomer was first prepared from SBTDA and excessive DMMDADS before the hydrophobic anhydride-terminated PI oligomer which was comprised of BTDA and DMMDA was introduced. The hydrophobic blocks and hydrophilic blocks were kept in the reactive flask and not precipitated before the next-step block copolymerization that can ensure the high molecular weights of resulting block copolymers. The sequence length of the hydrophilic blocks was adjusted by changing the amount of excess monomer. These block-sulfonated copolyimides PI(x–m) possess varying IEC and length of the hydrophilic blocks, where x corresponds to the IEC and the m refers to the length of the hydrophilic blocks. The resulting block copolyimides had a unique structural feature in which the hydrophilic blocks were comprised of the sulfonated dianhydride (SBTDA) and the sulfonated diamine (DMMDADS). Moreover, the hydrophobic blocks were non-sulfonated dianhydride (BTDA) and non-sulfonated diamine



Scheme 1. The synthesis of the block-sulfonated copolyimides.

Table 1
Molecular weight and ion exchange capacity (IEC) of the sulfonated copolyimides.

Polymer	m:n[a]	m:n[b]	$M_n \times 10^4$	$M_w \times 10^4$	M_w/M_n	IEC[c] (mequiv/g)	IEC[d] (mequiv/g)
2.69–r	–	–	12.3	28.7	2.3	2.69	2.70
2.69–5	5:5	5.1:4.7	13.2	25.4	1.9	2.69	2.61
2.69–10	10:10	10:9.5	9.7	21.2	2.2	2.69	2.57
2.69–20	20:20	21:19.9	12.7	24.2	1.9	2.69	2.59
2.69–50	50:50	58:63	13.9	26.4	1.9	2.69	2.52
2.01–r	–	–	9.8	25.4	2.7	2.01	1.98
2.01–5	5:9.3	5:9	10.5	23.1	2.2	2.01	2.02
2.01–10	10:18.6	11:19	9.2	21.3	2.3	2.01	1.91
2.01–20	20:37	21:40	11.2	25.2	2.2	2.01	1.99
2.01–50	50:93	60:110	14.2	29.3	2.1	2.01	1.90
1.51–r	–	–	9.1	22.8	2.6	1.51	1.49
1.51–5	5:15	5:16	13.6	28.8	2.2	1.51	1.39
1.51–10	10:30	10:33	10.8	23.2	2.2	1.51	1.42
1.51–20	20:60	22:69	9.9	22.6	2.3	1.51	1.46
1.51–50	50:150	62:178	13.9	23.9	1.7	1.51	1.41

[a] Calculated from the feed monomer ratio.
[b] Calculated from the GPC results.
[c] Obtained from the titration.
[d] Calculated from the feed monomer ratio.

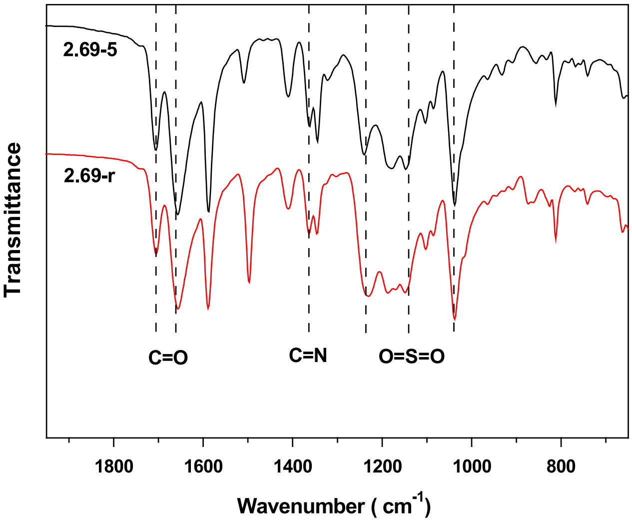


Fig. 2. FT-IR spectra of copolyimide membranes.

(DMMDA). The molecular weights and IEC values of the copolyimides are shown in Table 1. The experimental m and n values calculated from the molecular weights of the dianhydride-terminated oligomers and the diamine-terminated oligomers were almost consistent with the theoretical values which indicated the multiblock copolyimides prepared successfully with the desired lengths. In addition, all the prepared sulfonated copolyimides showed high molecular weights ($M_n > 9.0 \times 10^4$, $M_w > 20.0 \times 10^4$).

The as-synthesized sulfonated copolyimides in TEA salt form were soluble in polar aprotic solvents such as DMF, DMAc, NMP and DMSO. Tough, flexible, and transparent membranes were prepared by solution casting. These polyimide membranes were in the TEA form and were converted to their proton form by being treated with 1.0 M sulfonic acid. The structure of the copolyimides was confirmed by ^{1}H NMR and IR. As a typical example, the ^{1}H NMR spectrum of proton-exchanged PI(2.69–5) membrane was given in Fig. 1. The peaks at 7.95 and 8.76 ppm were attributed to the 1,2 and 3,4 hydrogen, respectively, of the SBTDA moieties, whereas the peak at 4.24 ppm was assigned to the j hydrogen of the DMMDA moieties. Based on the intensity ratios of the former to the latter peaks, the IEC value was calculated to be 2.71 mequiv/g for PI(2.69–5), a value that was in good accordance with its theoretically calculated counterpart. The representative IR spectrum of PI(2.69–r) and PI(2.69–5) is shown in Fig. 2. The strong absorption bands around 1709 and 1667 cm^{-1} were assigned to the stretch vibration of carbonyl groups of imide rings. The broad band around 1233 cm^{-1} and the band around 1040 cm^{-1} corresponded to the stretch vibrations of sulfonic acid groups. The fact that no absorption bands at 1780 and 1730 cm^{-1} which was corresponding to the C=O stretching vibration in a six-membered anhydride were identified can be considered as good evidence of complete copolymerization of hydrophilic blocks and hydrophobic blocks. These results indicated that the block copolyimides were obtained successfully by two-pot procedure.

The thermal stabilities of these sulfonated polyimide membranes in their proton form were investigated by TGA (Fig. 3). It can be seen that the block and random copolyimide membranes displayed quite similar TGA curves [41]. The first stage weight loss (below 130 °C) was due to the evaporation of water absorbed in the membranes. The second stage weight loss ranging from ~278 °C to ~480 °C was ascribed to the thermal decomposition of the sulfonic acid groups. Finally, the third stage weight loss above 520 °C was the result of decomposition of the polymer backbone.

3.2. Water uptake

Water uptake within the membrane is a critical parameter influencing the performance of PEM materials. Water serves as a carrier of the protons thus maintaining the high proton conductivity. The water uptake is typically a function of the degree of sulfonation or the ion exchange capacities (IECs), which is a measure of the exchangeable protons in the material. As shown in Fig. 4a, the water uptake of both in random- and block-copolymer membranes increased with increasing IEC values. A higher water uptake was observed for the block copolyimides with both high and low IECs as opposed to corresponding result of the random copolyimides (Fig. 4a). However, the proportional increase in the water uptake of the high-IEC copolyimides was relatively large as compared to their lower-IEC counterparts. The water uptake of the block membrane PI(2.69–5) was 108%, a value almost two times that of its random counterpart (62.5%). For the samples with lower

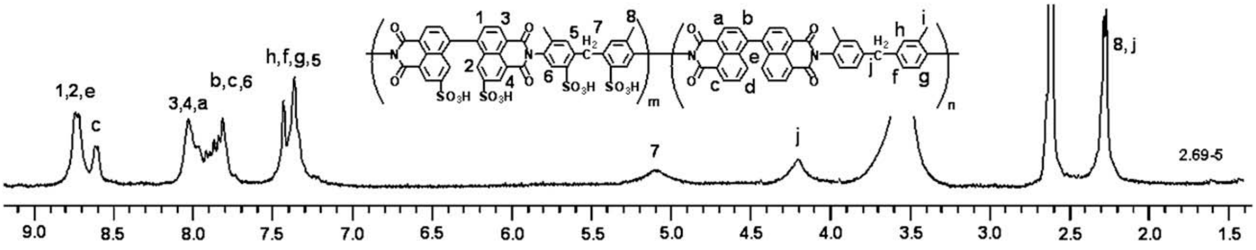


Fig. 1. The ^{1}H NMR spectra of copolyimides PI(2.69–5) in DMSO-d_6.

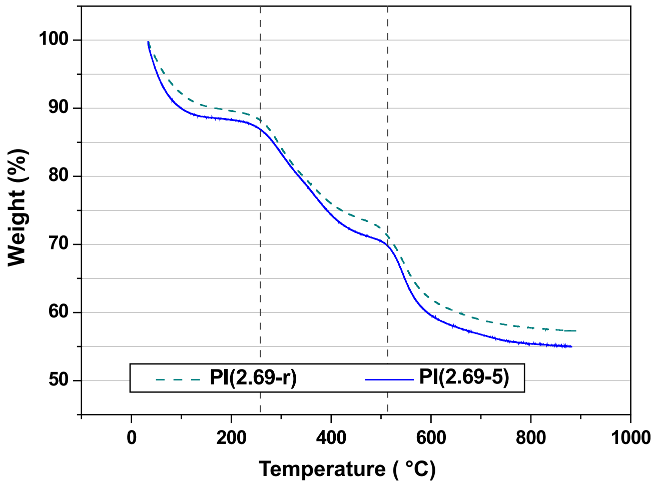


Fig. 3. The TGA curves of copolyimides PI(2.69–*r*) and PI(2.69–5) in dry N_2.

IECs, the PI(1.50–5) membrane demonstrated a water uptake of 34.8%. This value was only slightly higher than that of its corresponding random copolyimides (i.e., PI(1.5–*r*): 31.2%). Moreover, the water uptake of the high-IEC block copolyimides increased with increasing length of the hydrophilic blocks, whereas an almost constant water uptake of approximately 34.0% was observed for the low-IEC block samples (1.50 mequiv/g).

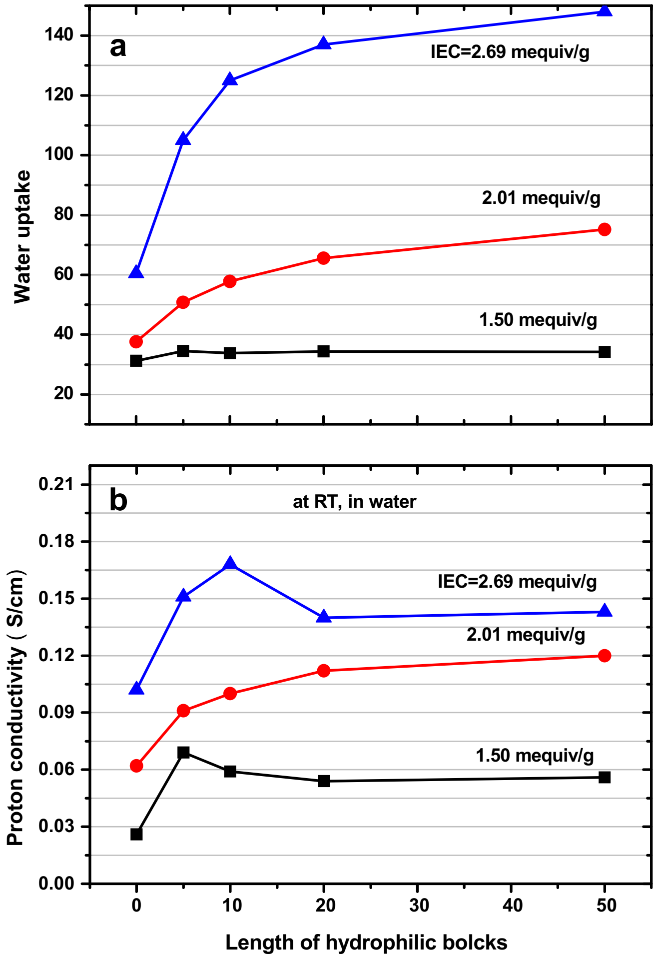


Fig. 4. Plots of (a) water uptake *vs* length of hydrophilic blocks, (b) proton conductivity at 20 °C in water *vs* length of hydrophilic blocks.

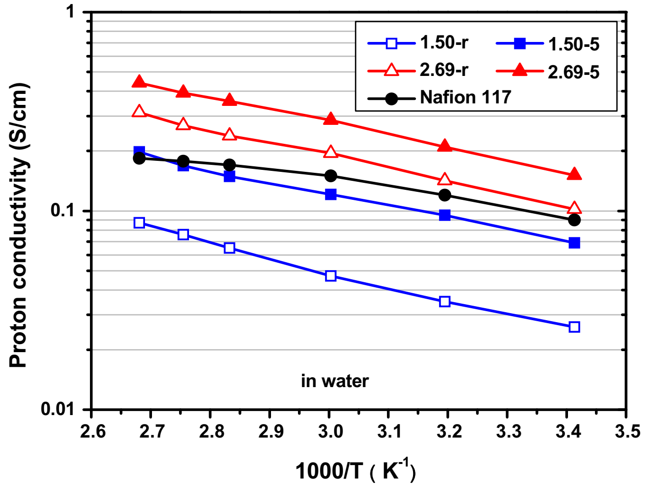


Fig. 5. The proton conductivity of the SPI membranes, as well as of Nafion 117, as a function of temperature.

3.3. *Proton conductivity*

Traditionally, a high water uptake in polymers leads to the high proton conductivities. As shown in Fig. 5, the block membranes displayed significantly higher proton conductivities than their random counterparts. More specifically, the block copolymers possessing high-IEC values (2.69 mequiv/g) exhibited proton conductivities of 0.14–0.17 S/cm at room temperature as opposed to 0.10 S/cm for the random copolymer. For higher IEC copolymers, the proton conductivities of the block copolymers revealed the similar trend of the water uptake and increased with increasing block lengths. For example, with IEC value of 2.01 mequiv/g block copolymers, as the block length increased from 5 to 50, the proton conductivities increased from 0.062 to 0.120 S/cm. Such superior values were maintained when the temperature was raised to 100 °C, as shown in Fig. 5. The highest proton conductivity (0.43 S/cm, at 100 °C in water) was obtained for the PI(2.69–5) membrane. Moreover, the proton conductivity at 50% RH, 70 °C was also measured. As shown in Fig. 6, the proton conductivity dropped significantly at lower RH values for the random copolymers. In contrast, the proton conductivity of the block copolymers under partially hydrated condition improved with increasing block

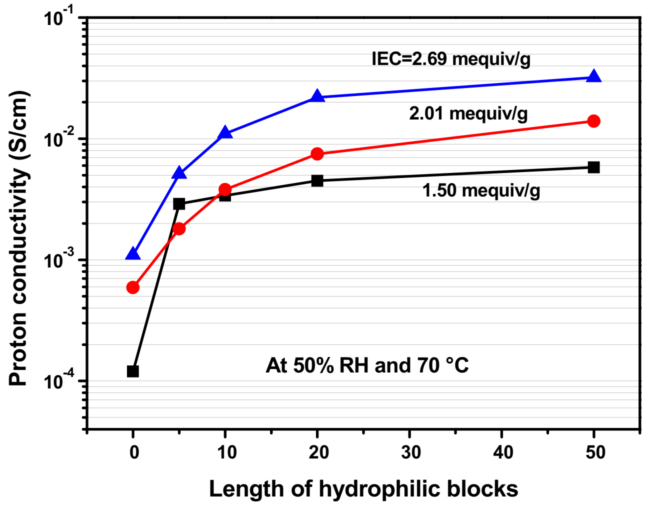


Fig. 6. The proton conductivity of the SPI membranes as a function of length of hydrophilic blocks at 50% RH and 70 °C.

lengths. The proton conductivity of PI(2.69–50) was 3.22×10^{-2} S/cm at 70 °C and 50% RH, which was about twenty times higher that that of the PI(2.69–*r*) (1.10×10^{-3} S/cm).

For the low-IEC copolymers, there was a significant difference between the proton conductivity of the PI(1.50–*r*) and its corresponding block copolymers, despite of the fact that no distinct differences were observed with respect to in their water uptakes. 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. Furthermore, the result was different from other multiblock-sulfonated copolyimides in which the highly enhanced proton conductivity was achieved for the longer block length more than 50 [39,40]. The result was contributed to the fully sulfonated hydrophilic blocks of the novel multiblock copolyimides which increased the volume the hydrophobic blocks as mentioned above and shortened the distance of the sulfonic acid groups. The shortened distance of the sulfonic acid presumably promoted the proton transport in the block copolyimide membranes. Since the proton-bearing, positively charged species (e.g., H_3O^+, $H_2O_5^+$, and/or $H_4O_9^+$ ions) [43] were transported between the negatively charged, tethered $-SO_3^-$ groups, the transport would be facilitated if the distances were shortened [10,44,45].

To further elucidate the proton-conducting properties of the SPI membranes, the *effective* proton mobility (μ_{eff}) through the membranes was estimated from the measured proton conductivity and the measured analytical [H^+] in hydrated membranes [46,47]. As shown in Fig. 7, the μ_{eff} of the block membranes was much higher than that of their random counterparts, but the analytical [H^+] was lower as a consequence of their high water uptake. The high μ_{eff} could be the result of an increasing water content leading to an increased dissociation of the protons from the SO_3^- groups. Although a higher water uptake enabled greater dissociation of protons and hence a higher mobility (Fig. 7a), the effect on [H^+] of a significant increase in water uptake was represented by a dilution of the available sulfonic acid groups (Fig. 7b). Thus, as compared to the random membranes, the high-IEC block membranes possessing a high relative water uptake showed a low relative proton conductivity, as shown in Fig. 8.

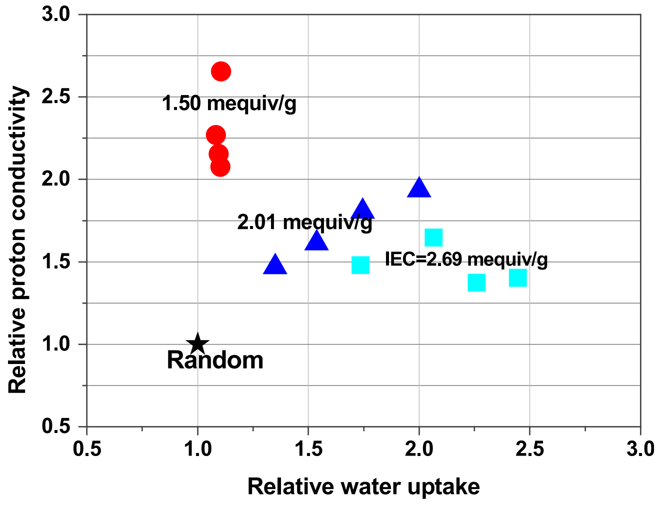


Fig. 8. The relative water uptake as a function of the relative proton conductivity.

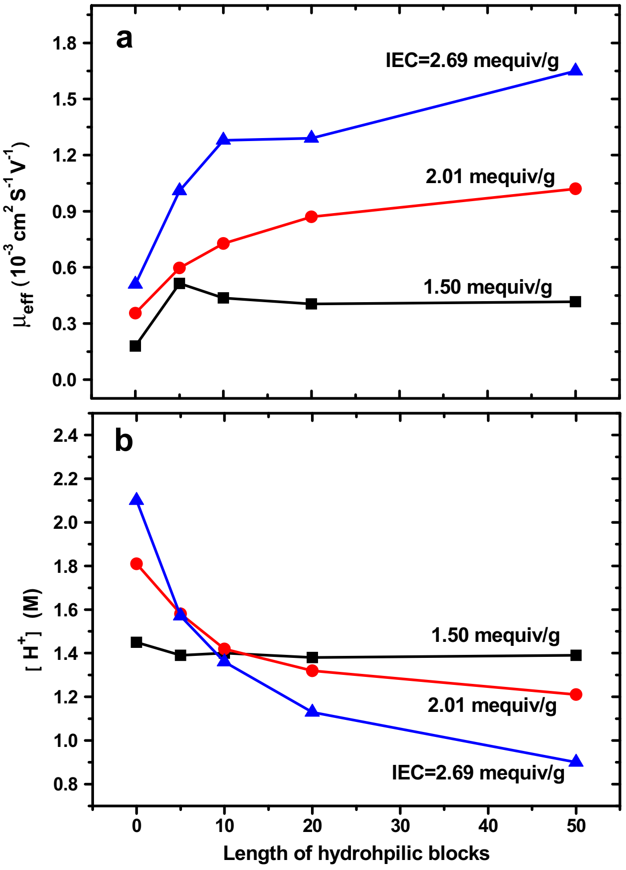


Fig. 7. Plots of (a) the *effective* proton mobility *vs* the length of hydrophilic blocks, (b) [H^+] *vs* the length of hydrophilic blocks.

3.4. Hydrolytic stability

The hydrolytic stability of SPIs is significantly influenced by the chemical structure of the polymer chain. As has been reported, polyimides with flexible structures [48] and high basicity of diamine moieties [23,49] tend to have a good hydrolytic stability. Recently, we have reported that SPIs based on a dianhydride with lower electron affinity showed a considerably improved hydrolytic stability as opposed to SPIs based on a dianhydride with a high electron affinity [41]. In order to verify the hydrolytic stability under accelerated conditions, the sulfonated polyimide membranes were treated at 140 °C in water for 24 h, and Fig. 9

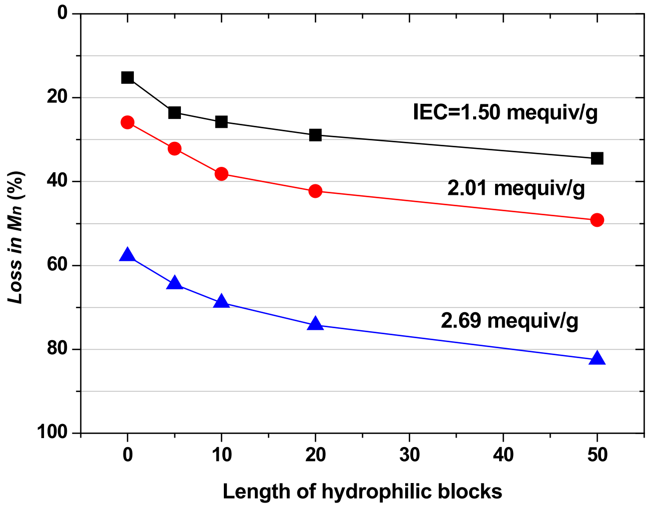


Fig. 9. The hydrolytic stability of SPI membranes as a function of length of hydrophilic blocks.

displayed a plot of the molecular weight change of the membranes as a function of block lengths. The molecular weight loss of the copolyimide membranes was dependent on the IEC and the general trend consisted in a higher molecular weight loss for membranes with higher IECs. Additionally, the block copolyimides displaying a significant water uptake displayed a higher molecular weight loss due to the higher water uptake of block membranes resulting in the imide ring being more easily attacked by water molecules. The membranes became brittle when the molecular weight loss was higher than ca. 35%.

4. Conclusions

Novel hydrophilic–hydrophobic multiblock copolymers based on polyimide were developed by two-pot procedure and characterized. The hydrophilic blocks of the novel block copolyimides were composed of sulfonated dianhydride and sulfonated diamines. The sulfonic acid groups were present on every aromatic ring (fully sulfonated), and the distance between them was thus minimized. As a result, the block copolyimides demonstrated a higher water uptake and superior proton conductivities than their random counterparts. Consequently, almost constant values of water uptake and proton conductivity were observed for these multiblock copolyimides. The results confirmed that both the distribution of the sulfonic acid groups and the length of the blocks played a critical role on the morphological structures of the membranes, and thereby also on their water uptakes and proton conductivities.

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