

# Proton exchange membrane bearing entangled structure: Sulfonated poly(ether ether ketone)/bismaleimide hyperbranch

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## ABSTRACT

Physical cross-linking of sulfonated poly(ether ether ketones) sPEEKs with hyper-branched bismaleimide oligomer (modified bismaleimide, mBMI) leads to densely packed polymer. Different curing conditions on the two sPEEK samples containing Bismaleimide (BMI) monomer and modified Bismaleimide oligomers (mBMI) mole ratios of 70:30 (mBMI(30)) and 2:98 (mBMI(98)) are present. As the amount of BMI monomer increases, the branched structure and their degree of entanglement with sPEEK polymer matrix also increase. More rigid and more compact membrane is found in the case of mBMI(30). In contrast, relatively loose entangled network is found for mBMI(98) sample where the mBMI unit remains far apart and mostly un-connected, until high concentration of mBMI(98) is present. The branched structure and their degree of entanglement with sPEEK polymer matrix increases with longer curing time. The results shows physical cross-linking with highly branched mBMI is effective in reducing water uptake, lower methanol permeability with reduced sPEEK membrane swelling. Except for heavily entangled sample (sPEEK/mBMI(30)) annealed for 20 h, all membranes displayed fair proton conductivity above  $10^{-2}$  S/cm at room temperature. Methanol permeability is also substantially reduced to  $1.39 \times 10^{-7}$  cm<sup>2</sup>/s for sPEEK/15% mBMI(98). The DMFC single cell assembled by the sPEEK/20% mBMI(98) membrane (59  $\mu$ m thickness) displayed the highest OCV of 839 mV with a power density reaching 30 mW/cm<sup>2</sup> at 60 °C. This value is higher than that using sPEEK membrane alone.

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## 1. Introduction

The bench mark membrane materials for both PEMFC and DMFC are perfluorinated materials such as Nafion<sup>®</sup> which shows high chemical stability, long-term durability and excellent proton conductivity [1,2]. These membranes displayed unique hydrophilic percolation where high proton conductivity is established. Unfortunately, materials with percolated morphology also exhibited high methanol permeability and severe swelling in presence of methanol. For DMFC, membranes that can also resist swelling and deliver low permeability at the operating condition is highly desirable.

Proton conductivity is the most sought-after property in the development of new proton exchange membrane. However, other criteria such as chemical stability, low methanol cross-over ( $<10^{-7}$  cm<sup>2</sup>/s), low swelling and good mechanical properties should also be met. When used as PEMs, hydrophilic sulfonated

poly(ether ether ketone)s (sPEEKs) were reported to exhibit superb proton conductivity. sPEEKs are prepared by the sulfonation of commercial Victrex and Gatone PEEK, and the proton conductivity is found to increase with increasing the degree of sulfonation (Ds) [3]. However, the membranes become less resistant to water and methanol solvent and shows irreversible swelling with excessive sulfonation (Ds > 0.7). Numerous approaches are proposed to overcome the swelling and high permeation deficiency. Previous studies suggested membrane swelling can be reduced by ionic cross-linking [4–6] or covalent bond cross-linking [7–10]. However, the material is not durable during long-term operation. Several proton exchange membranes based on semi-IPN (semi-interpenetrating network) concept have also been explored for DMFC applications [11–16]. Matsuguchi [11] reported that Nafion<sup>®</sup>/DVB membrane shows low methanol permeation compared with unmodified Nafion<sup>®</sup> membrane, but proton conductivity also suffers. The poor proton conductivity was due to the interference of cross-linked DVB to the formation of ion clusters. A novel sulfonated polyimide (SPI) and poly(ethylene glycol) diacrylate (PEGDA) were developed by Lee [15]. Here poly(ethylene glycol) diacrylate (PEGDA) having flexible hydrophilic poly(ethylene

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glycol) backbone is expected to render flexible cross-linking which also displayed good proton conductivity. However the swelling is still too severe for practical purpose.

Present study described a novel membrane established by physical cross-linking the sulfonated poly(ether ether ketone) (sPEEK) with highly branched bismaleimide oligomer (mBMI). Bismaleimides (BMIs) is an important class of high performance, thermo-setting polymers that finds wide applications in composites and other related areas. It was documented previously that polymerization of BMI can produce highly branched architecture due to the dual terminal double bonds [17,18]. The interaction between sulfonated acid in sPEEK and the nitrogen or the carbonyls on BMI may provide the necessary force to induce fair degree of miscibility. It is anticipated that the highly branched BMI structure could restraint sPEEK chain to reduce swelling from water and methanol solvent. In addition, the highly branched BMI with solubility parameters ( $\delta$ ) much different from that of water and methanol could potentially reduce water uptake and deliver lowered methanol permeability. An issue of particular interest is if the membrane properties can be improved through physical cross-linking sPEEK with mBMI, and if these improved properties can be accomplished without sacrificing the proton conductivity. This design is sharply contrasted with previous approaches based on semi-IPN using linear polymers, or through covalent cross-linking of the parent polymer.

## 2. Experimental

### 2.1. Membrane preparation

In this investigation, poly(ether ether ketone) (PEEK) (Victrex 450P), *N*-methyl Pyrrolidone (NMP) [TEDIA, USA] were used as received. sPEEK polymers were prepared by dissolving 1 g of PEEK powder in 10 g of concentrated sulfuric acid at 60 °C for 5 h. The sulfonated PEEK solution was then drenched in deionized water under mechanical agitation to recover the modified polymer, followed by repeated washing with deionized water until its pH was neutral. The 10 wt% polymer solution was then prepared by dissolving sPEEK in an NMP solvent. The degree of sulfonation (DS) as determined by  $^1\text{H}$  NMR was 64%.

The BMI homopolymerization is shown in Scheme 1. This polymerization reaction has been detailed in a previous paper [17]. The reactants, *N,N'*-4,4'-diphenylmethane-bismaleimide and Barbituric acid (BTA) (molar ratio of 10:1 and 1:1), are placed in a reactor.  $\gamma$ -butyrolactone is then added to the container to make a solution with about 20 wt% of solid content. The mixture is heated to 130 °C for certain duration to yield the maleimide oligomers (mBMI).

The composite membranes were prepared by in-situ polymerization. Appropriate amounts of sPEEK (dissolved in NMP) and mBMI (dissolved in  $\gamma$ -butyrolactone) were homogeneously mixed for 1 h. The solutions were poured onto the glass plate to fabricate the film following the curing temperature program: 120 °C for 1 h, 140 °C for 1 h, and the last stage of heating occurs at 180 °C for either 6 h or 20 h. The initial heating triggers the cross-linking reaction between mBMI moieties, while the second stage of heating continues to enlarge the mBMI network thus resulting in more intimate interpenetrating network with sPEEK chain. According to previous study [17], longer curing time also leads to more complete growth of the hyper-branched mBMI at 180 °C (see Section 3.1). Therefore, the 6 h treated and 20 h treated samples represent a lower and higher degree of physically cross-linked structure with sPEEK (*vide infra*).

### 2.2. CP/MAS $^{13}\text{C}$ NMR

High-resolution solid-state  $^{13}\text{C}$  NMR is performed on a Varian 400 MHz Inova spectrometer operating at resonance frequencies of

400 and 100 MHz for  $^1\text{H}$  and  $^{13}\text{C}$ , respectively. Samples were packed in 4 mm zirconia rotors with Teflon end caps. The  $^{13}\text{C}$  chemical shift was externally referenced to adamantane at 38.3 and 29.2 ppm. The  $^{13}\text{C}$  CP/MAS spectra were measured with 2  $\mu\text{s}$   $^1\text{H}$  90° pulse angle, 2 s pulse delay time, 50 ms acquisition time, and 2048 scans. All NMR spectra were taken at 300 K with broad-band decoupling, normal cross-polarization pulse sequence, and a magic angle spinning (MAS) of 8 kHz. The variable contact time CP/MAS spectra for all samples were obtained by varying lengths of cross-polarizing contact times from 0.01 to 7.9 ms.

### 2.3. Differential scanning calorimeter

A Mettler Toledo DSC 822 differential scanning calorimetry (DSC) was employed to study the thermal transition behavior of sPEEK samples. The samples were preheated under nitrogen from room temperature to 200 °C at 20 °C/min to remove moisture, then cooled to 100 °C, and reheated from that temperature to 300 °C at 20 °C/min.

### 2.4. Water uptake

These membrane samples were subsequently immersed in deionized water, then heated at 60 °C for 1 h. The samples were dried in a vacuum oven at 100 °C for about 2 h, then weighted. The uptake was calculated using the following equation

$$\text{Uptake} = (W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}} \times 100\%$$

where  $W_{\text{wet}}$  and  $W_{\text{dry}}$  are the weight of the swollen and dry membranes, respectively.

### 2.5. Ion exchange capacity (IEC)

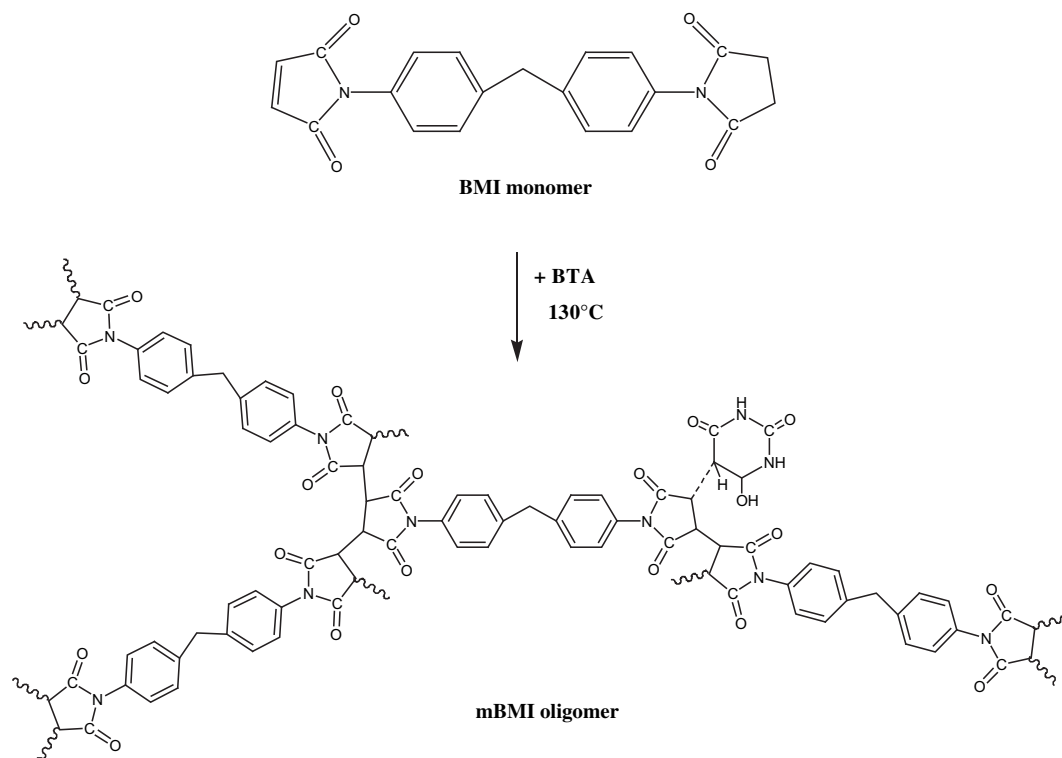
The ion exchange capacity (IEC) of the membranes was evaluated using titration method. The membranes were immersed in 1 M NaCl solution and stirred for 12 h at 40 °C. The protons released during the ion exchange process were titrated with 0.01 N NaOH solution. NaOH solution was titrated with potassium hydrogen phthalate (KHP) prior to use.

### 2.6. Proton conductivity measurement

Proton conductivity of these membranes was investigated with a cell consisting of two stainless steel electrodes over the frequency range 1 MHz to 1 Hz, using a frequency analyzer AUTOLAB/PGSTAT 30 electrochemical instrument. The bulk resistance ( $R_b$ ) was determined from the equivalent circuit analysis by using a frequency response analyzer (FRA software) of complex impedance plots. The conductivity values ( $\sigma$ ) are calculated by the equation,  $\sigma = (1/R_b)(t/A)$ , where  $t$  is the thickness and  $A$  is the area of the sample.

### 2.7. Methanol permeability measurement

The methanol permeability in the membranes was performed following the procedures described previously [19]. The membrane was inserted between vessels A and B. The volume of 40 mL methanol solution (50 vol%) and 40 mL deionized water was placed in each vessels A and B, respectively. The methanol diffusion coefficient can be derived from the amount of methanol that crossed through the membrane to vessel B (measured by the portable refractometer) with time [20].



**Scheme 1.** The polymerization of BMI monomer.

### 2.8. DMFC single cell test

Cell performance was evaluated by using a DMFC unit cell, membrane electrode assemblies (MEA) with a geometric area of 12.25 cm<sup>2</sup> were prepared using PtRu(1:1)/Vulcan XC-72 (E-Tek) and Pt/Vulcan XC-72 (E-Tek) as the anode and cathode catalysts, respectively. The catalyst loadings at the anode and the cathode were 3 mg/cm<sup>2</sup> and 4 mg/cm<sup>2</sup>, respectively. For MEA fabrication, the anode and cathode electrodes were hot-pressed onto sPEEK and sPEEK/mBMI composite membranes. Hot-pressing conditions were 139 °C, 2500 psi for 1 min and 5000 psi for 2 min, respectively.

The operating temperature of the DMFC single cell was 60 °C. 1 M methanol solution was pumped through the DMFC anode at a flow rate of 3 mL/min and humidified oxygen was fed to the cathode at 100 mL/min.

## 3. Results and discussion

The growth mechanism suggests the amount of BMI monomer that remained in the mBMI oligomer suspension can lead to different degree of hyper branching. It can be expected that high amount of BMI monomer facilitate the linkage of adjacent mBMI, therefore lead to higher degree of entanglement with sPEEK polymer when the polymerization takes place in sPEEK solution. Therefore two kinds of mBMI samples were used to composite with sPEEK. The first one contains 30 mol% mBMI oligomers with about 70 mol% of BMI monomers (code as mBMI(30)) while the second one contains 98 mol% mBMI oligomers nearly without BMI monomer (code as mBMI(98)). Membrane properties ranging from brittle to flexible have been obtained, depending on the mBMI oligomer and BMI monomer composition, as well as the curing time and temperature. The differences in the linking structure in sPEEK/mBMI(30) and sPEEK/mBMI(98) samples will also impact proton conducting properties differently, as will be examined.

### 3.1. The growth of mBMI oligomer study

BMI hyper-branched oligomer (mBMI) is formed at 130 °C, but the product can undergo further reaction through the unsaturated maleimide group at elevated temperature (>170 °C). When curing mBMI(30) at 180 °C, the double bond (7.05 ppm) signal corresponds to mBMI (and BMI monomers) decreases with curing time, as shown in the <sup>1</sup>H NMR spectra (Fig. 2). [21] The broadening of the aromatic peaks after extensive curing suggested a substantial reduction of mobility and support the formation of more complete hyper-branched structure.

Fig. 3 show the DSC thermograms for mBMI(30) samples exposed to different curing treatment. When curing the mBMI(30) sample at 160 °C, an endotherm at ~140 °C corresponds to the melting of BMI crystallite is found [22]. However, when the curing temperature is raised to 180 °C, the BMI melting peak disappears. The suppression of BMI melting peak implied a decrease of BMI concentration and support the fact that BMI is either reacted with to grow a larger mBMI, or self polymerized to form new mBMI oligomers. Notice that all samples displayed a broad exothermal peak above 180 °C corresponds to the reaction of mBMI oligomers. Both the NMR and DSC results suggested that a threshold temperature of ~180 °C is necessary to initiate the BMI polymerization or growth of mBMI oligomer.

### 3.2. sPEEK/mBMI composite membranes

When bismaleimide oligomers and bismaleimide monomers are reacted in sPEEK polymer solution, interpenetrating network structure can be established between BMI and sPEEK polymer, depicted in Fig. 1. A separate study [23] shows that mBMI molecular weight (Mw) can be as high as  $5.7 \times 10^6$  g/mol, after long period of reaction in NMP. It will be hard if not impossible to deduce the molecular weight in sPEEK matrix, but the general understanding

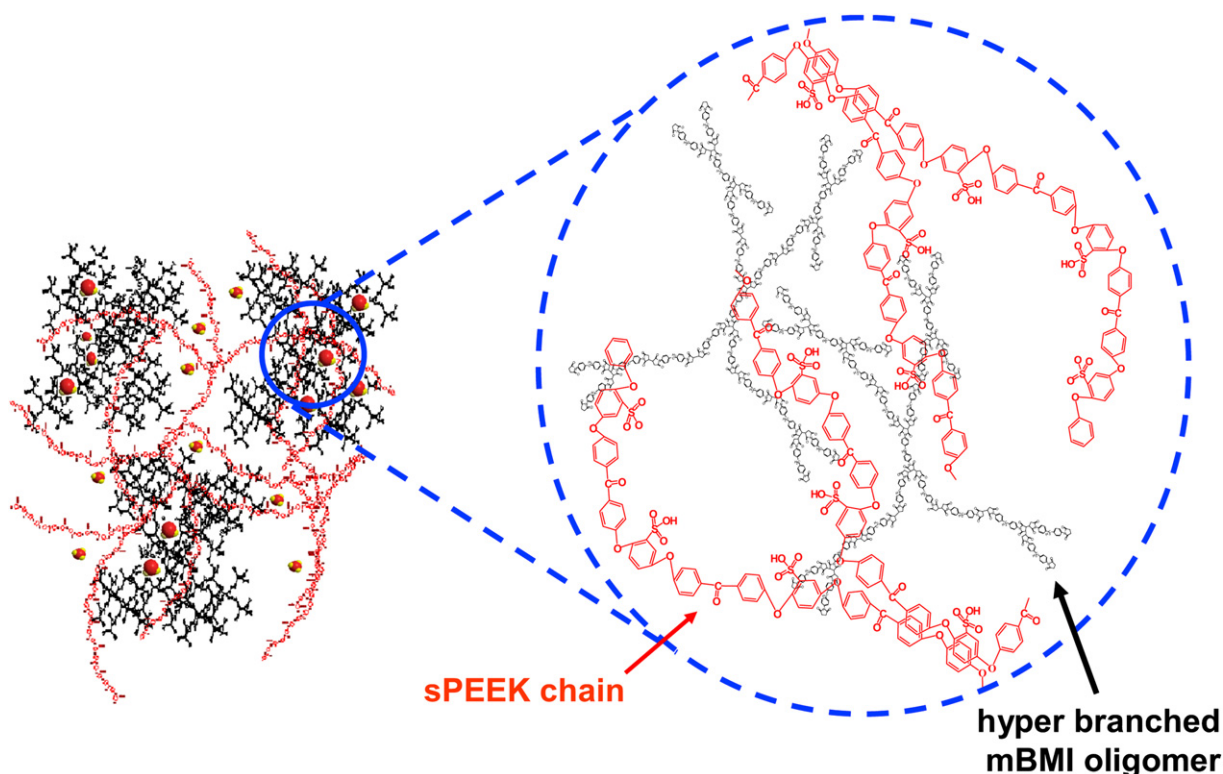


Fig. 1. Proton exchange membrane materials bearing entangled structure: sulfonated poly(ether ether ketone)/bismaleimide hyperbranch.

of mBMI growth mechanism can be applied here, although the growth rate can be substantially lower than that without sPEEK. To provide better understanding, the entangled structure and the miscibility between sPEEK and mBMI are illustrated by both the  $^{13}\text{C}$  solid-state NMR and DSC.

The  $^{13}\text{C}$  NMR spectra for sPEEK/mBMI(30) and sPEEK/mBMI(98) samples with curing at  $180^\circ\text{C}$  for 6 h are summarized in Fig. 4 with the chemical shift of each carbon on sPEEK assigned [24,25]. The broad signal near 175 ppm is attributed to the carbonyl group of mBMI oligomer. This is most pronounced for the 15% mBMI samples, but barely observable for samples with 5% mBMI. Previous study confirms the carbonyl signals from residual maleimide functions (with vinyl groups) occurs at  $\sim 170$  ppm, while the bands around 175–176 ppm correspond to the newly formed succinimide functions (without vinyl) [21]. For mBMI(30), the specie at 170 ppm is barely observable, implies that nearly all the vinyl groups are

reacted. In contrast, there are still un-reacted maleimide end group observable at  $\sim 170$  ppm region for mBMI(98).

As mentioned previously, mBMI growth, mBMI (modified Bis-maleimide oligomers) can be further polymerized to form a larger highly branched BMI architecture with increasing reaction temperature and reaction time. The suppression of  $^{13}\text{C}$  signal from maleimide functions (with vinyl groups) suggested the double bonds in mBMI(30) are consumed and a more intimate entangled structure is expected. Whereas the unsaturated double bond remains in mBMI(98) samples after extensive annealing above  $180^\circ\text{C}$  suggested the hyper-branched mBMI units are not directly connected, thus a relatively loose entangled network with sPEEK would be formed. Carbon signals of the methylene (40 ppm),

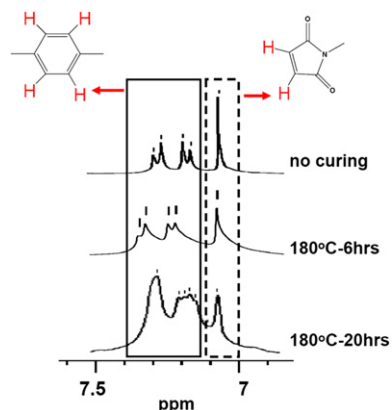


Fig. 2. The  $^1\text{H}$  NMR spectra of pure mBMI(30) sample cured at different time.

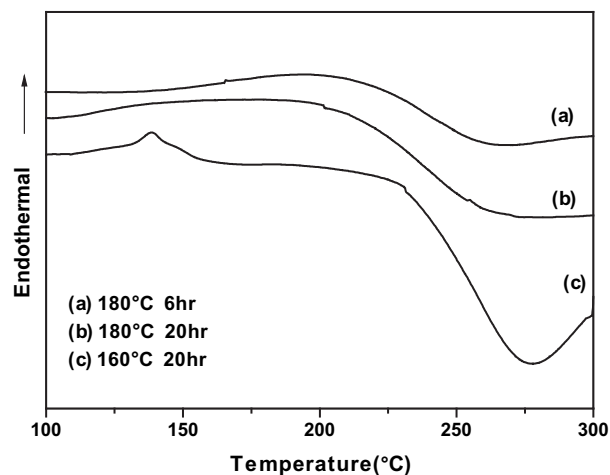
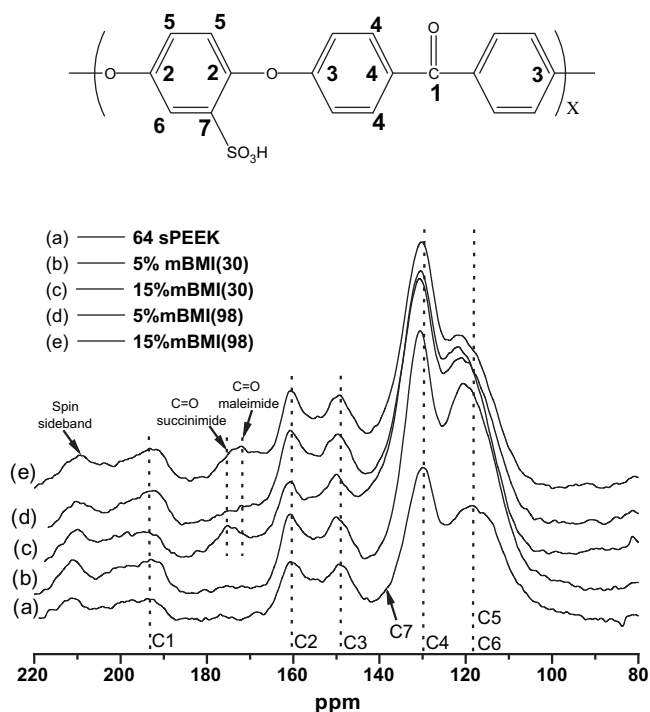


Fig. 3. The DSC thermograms of pure mBMI(30) cured at (a)  $180^\circ\text{C}$ , 6 h (b)  $180^\circ\text{C}$ , 20 h (c)  $160^\circ\text{C}$ , 20 h.





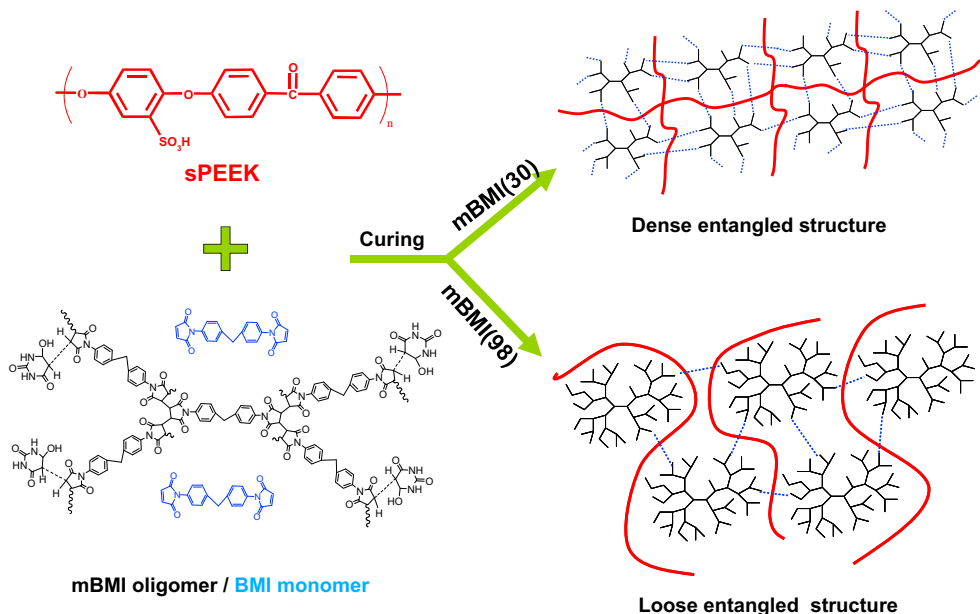
**Fig. 4.** The <sup>13</sup>C CP/MAS spectra of (a) 64%DS sPEEK; (b) 5 wt%, (c) 15 wt% mBMI(30) and (d) 5 wt%, (e) 15 wt% mBMI(98) in 64%DS sPEEK. (The samples cured at 180 °C for 6 h).

aromatic carbons (128 and 139 ppm) and ethylene double bond carbons (134 ppm) of mBMI oligomer are overlapping with the C5 of sPEEK, and not discussed Scheme 2.

In addition to higher BMI monomer content, longer reaction time also facilitates more complete growth of mBMI oligomer. With increasing reaction time from 6 h to 20 h, the unsaturated maleimide end group of mBMI oligomer continues to grow into larger mBMI domains. Therefore, the 6 h treated and 20 h treated samples represent mild and heavily entangled structure. Both the polymer physical properties, morphology as well as proton conductivity will also be affected.

The degree of physical cross-linking and miscibility between sPEEK and mBMI's are confirmed by DSC analysis. DSC studies reveals that the glass temperature of sPEEK/mBMI(30) and sPEEK/mBMI(98) differs with different degree of curing treatment (Fig. 5). For all sPEEK/mBMI samples, only single glass transition ( $T_g$ ) is observed and it increases with increasing mBMI content. The lack of multiple glass temperature suggested fair miscibility between mBMI and sPEEK in these entangled structures. The forces responsible for the miscibility can be rather complicated. The basicity of the lone-pair of N atom on the imide ring is not strong, but the IEC titration results (*vide infra*) shows neutralization of sPEEK is observed and suggested acid–base interaction in the form of hydrogen bonding can be establish between imide and the acids from sPEEK. In addition, pi–pi ring-stacking force, and the weak H-bonding between the C=O and acidic sulfonated groups are other possible sources of driving forces to induce miscibility between the two polymers.

Without a better quantification for the degree of cross-linking, the glass transition temperature can be used to gauge qualitatively the change in free volume or chain dynamics due to the formation of entanglements in the membrane. The elevation of  $T_g$  suggests that sPEEK polymer becomes more restricted due to the formation of the entangled structure formed by mBMI. With curing at 180 °C for only 6 h, the mBMI(30) sample shows gradual increase in  $T_g$  with increasing mBMI content. In contrast, the  $T_g$  elevation is less appreciable with raising mBMI content in the mBMI(98) series. The different manner observed in  $T_g$  elevation hinted the different degree of entanglement between mBMI and sPEEK. The fact that BMI monomer facilitates the formation of linkage between adjacent mBMI oligomer to form tighter network in sPEEK explains why  $T_g$  increases proportionally with increasing mBMI content in the mBMI(30) but almost dependent on BMI concentration in the mBMI(98) series at shorter curing time (6 h). As noted previously, longer reaction time (20 h) facilitates more complete growth of mBMI oligomer. As observed in Fig. 5, after curing extensively for 20 h, rapid increase of  $T_g$ s are observed for both the mBMI(30) and mBMI(98) which saturated eventually at  $T_g = 215$  °C where mBMI content reached above 5 wt%. Extensive annealing for longer than 20 h does not change  $T_g$  and suggested thermodynamic equilibrium is reached.



**Scheme 2.** The different entangled structure membranes formed from mBMI(30) and mBMI(98).

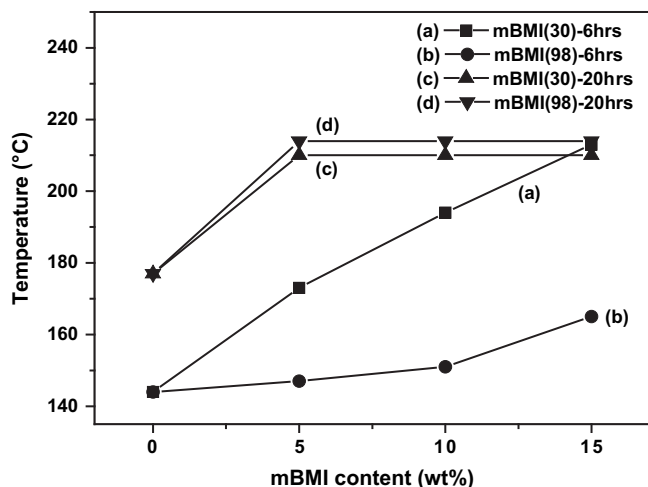


Fig. 5. The glass transition temperature ( $T_g$ ) of sPEEK/mBMI(30) and sPEEK/mBMI(98) membranes after different curing treatment.

Membrane with the entangled structure influences membrane properties such as the ion conductivity, water uptake and the degree of swelling. A general problem of homogeneous sulfonated arylene main-chain ionomer is that they begin to swell severely in water (and methanol solution) and thus lost their membrane stability above a certain degree of sulfonation (for sPEEK ion-exchange capacity is around 1.4–1.6 meq  $\text{SO}_3\text{H/g}$ ). The situation is aggravated when membrane is operated at elevated operation temperature (60–80 °C). It is interesting to find out if the physical cross-linking between sPEEK and hyper-branched mBMI could taper swelling to some degree. Water uptake (WU) of sPEEK/mBMI membranes (Fig. 6) shows a general reducing trend with increasing both the mBMI content and the curing time. It can also be seen that mBMI(30) series is more effective than mBMI(98) in this regard. At short curing time (6 h), WU decreases first with increasing mBMI, but regains when mBMI continue to increases to 20%. Hyper-branched molecule is known to exhibit stronger physical adsorption with small molecules, particular when there exist specific interactions, such as hydrogen bonding or London dispersion force. We noted that barbituric acid (BTA) is used as the initiator for the polymerization of BMI, which remains on the mBMI framework. Since hydrophilic BTA is attached, the mBMI oligomer is expected to exhibit water-absorbing property. This could explain the

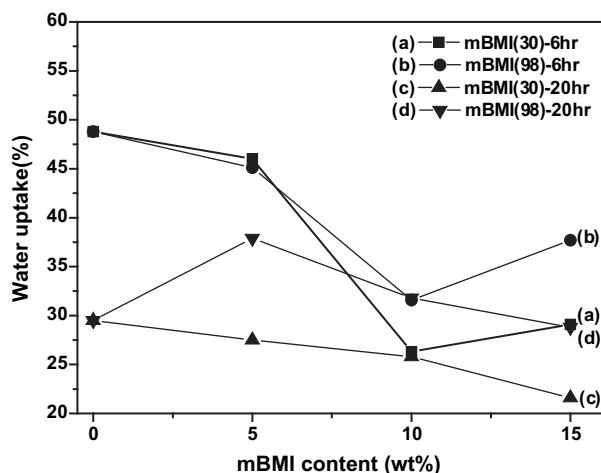
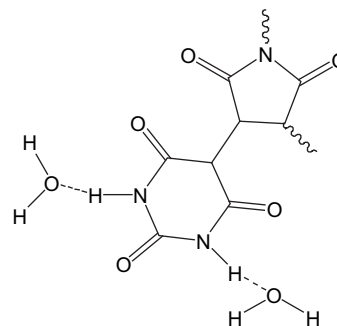


Fig. 6. The water uptake of sPEEK/mBMI(30) and sPEEK/mBMI(98) membranes cured for different time.



Scheme 3. The hydrophilic BTA molecule at the end of mBMI absorbs some waters.

observation that water uptake increases again when mBMI reached over 20 wt% level.

This finding readily implied that hyper-branched mBMI moiety can serve two important functions that it prevents membrane swelling by entanglement with sPEEK and it also retains water or methanol. The swelling and the water uptake are therefore the result of the competition between the restraint of the sPEEK and the expansion of the hyper branch itself. Unless the mBMI content reached above 30 wt% where the dry membrane becomes brittle and hard to process, these membranes with mBMI remains ductile and resilient and shows free standing character even after boiling in water for extensive period Scheme 3.

When curing the membrane extensively for 20 h, WU values drop substantially. The results further confirm the physical cross-linking with highly branched mBMI is effective in reducing sPEEK membrane swelling. The decreasing WU trend is most vivid in the case of mBMI(30) samples where WU decreases to nearly 20 wt% at the highest mBMI loading. In the case of mBMI(98), however, WU rose with initial addition of mBMI (5 wt%), followed by a later decrease with further mBMI addition. This is again accounted for by the water-adsorbing characters of the mBMI where the hyper-branched structure is not as tightly connected as that of mBMI(30). Further increasing mBMI in the mBMI(98) series leads to further connected mBMI domains and WU gradually decreases. However, the reduction is not as pronounced as that in the sPEEK/mBMI(30) membranes.

The IEC values of sPEEK/mBMI membranes are shown in Fig. 7. The parent sPEEK polymer with 64% degree of sulfonation gives rise to the IEC of 1.4 mmol/g (after heat treatment). With increasing

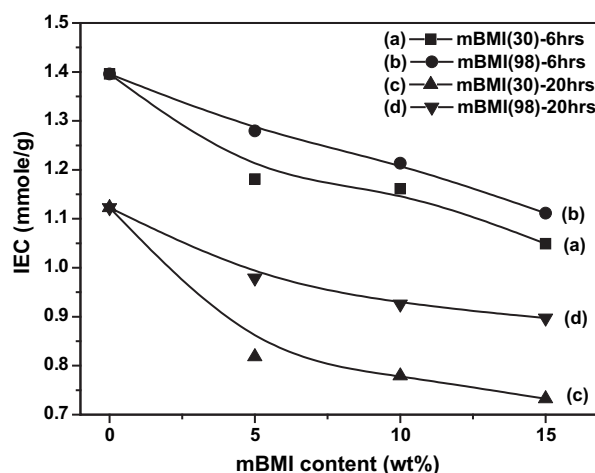


Fig. 7. The IEC of sPEEK/mBMI(30) and sPEEK/mBMI(98) membranes cured for different time.

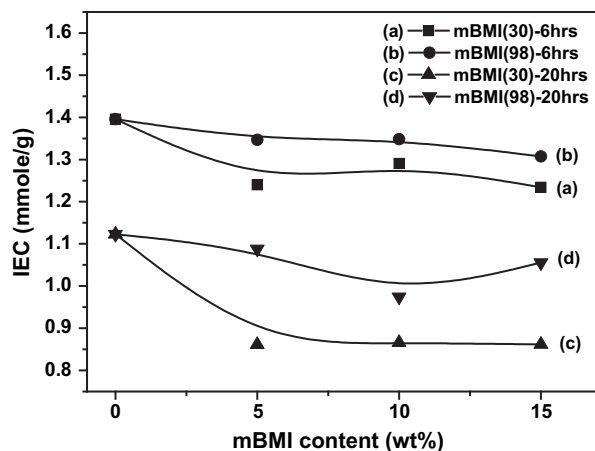


Fig. 8. The IEC of sPEEK/mBMI(30) and sPEEK/mBMI(98) membranes normalized to sPEEK weight.

mBMI(30) or mBMI(98) content, the IEC value displayed a general decrease. The IEC drop with increasing mBMI is expected as the imide contains weak base. However whether sPEEK is neutralized by mBMI will not be clear unless the IEC is recalculated on the basis of sPEEK alone. The adjusted IEC is calculated as the following:

$$IEC_{\text{adjusted}} = SO_3^- \text{ mmol}/(\text{Total membraneweight} - \text{mBMIweight})$$

The adjusted IEC value appears to be less dependent on the mBMI content in sPEEK/mBMI(98) membranes, but changed more drastically in sPEEK/mBMI(30). (Fig. 8) A plausible interpretation for such difference would be the more complete entanglement of the sPEEK chain in the case of mBMI(30). The neutralization, which reduces the IEC value, is less severe in the case of mBMI(98) since the sPEEK chain is less entangled with the branched nanostructure. The neutralization can occur between the sulfonic group of sPEEK and the imide of mBMI, which served as additional evidence for the existence of miscibility between the two.

Extensive annealing for 20 h at 180 °C also leads to reduction of IEC, even in the case without mBMI. For both mBMI(30) and mBMI(98) samples, IEC drops for about 0.4–0.5 unit. This is accounted for by the cross-linking between the adjacent sulfonate groups which produces sultone bridge. The possibility that it is due to the cleavage of the sulfonated group can be ruled out, since this will not occur until temperature rose above 250 °C. For sPEEK/mBMI(98), IEC remains roughly the same as the generic sPEEK at high mBMI content. But for sPEEK/mBMI(30), the IEC drops 0.3 unit with initial mBMI addition and leveled at ~0.85. This is the results of both the neutralization by imide and the cross-linking from adjacent sulfonate groups.

The two types of membranes with different degree of physical cross-linking impact the proton conductivity differently. Fig. 9 shows a gradual decreasing trend of proton conductivity with increasing either mBMI(30) or mBMI(98) concentration. The proton conductivity also decreases upon extensive annealing. In general, the proton conductivity of sPEEK/mBMI(98) membranes is higher than sPEEK/mBMI(30), and the conductivity shows less severe decline with mBMI content (trace (b) and (d)). In the case of mBMI(30), the drop of conductivity is more steep (trace (a) and (c)). All samples, except sPEEK/mBMI(30) annealed for 20 h, displayed fair proton conductivity above  $10^{-2}$  S/cm. Although the conductivity is somewhat lower compared with that of sPEEK, the trade-off is compensated by the improved mechanical strength and low degree of methanol swelling and water uptake in the mBMI entangled sPEEK.

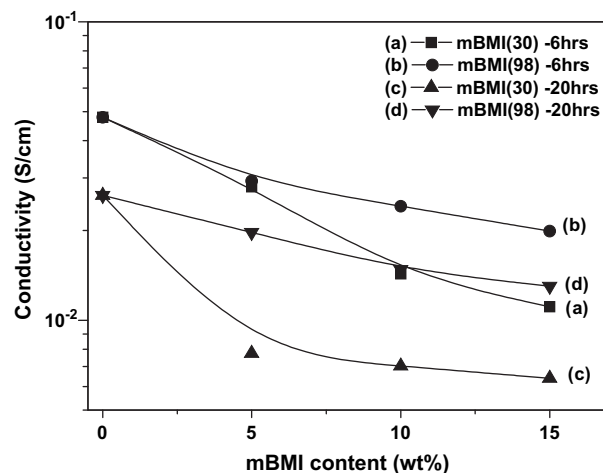


Fig. 9. The proton conductivity of sPEEK/mBMI(30) and sPEEK/mBMI(98) membranes under two different curing time.

The correlation with IEC (Fig. 10(a)) is straightforward that the conductivity of water saturated samples is almost linearly proportional to IEC in the ranges from 0.72 to 1.41, regardless of the difference in chemical composition or thermal treatments. In contrast, the conductivity correlation with water uptake is highly

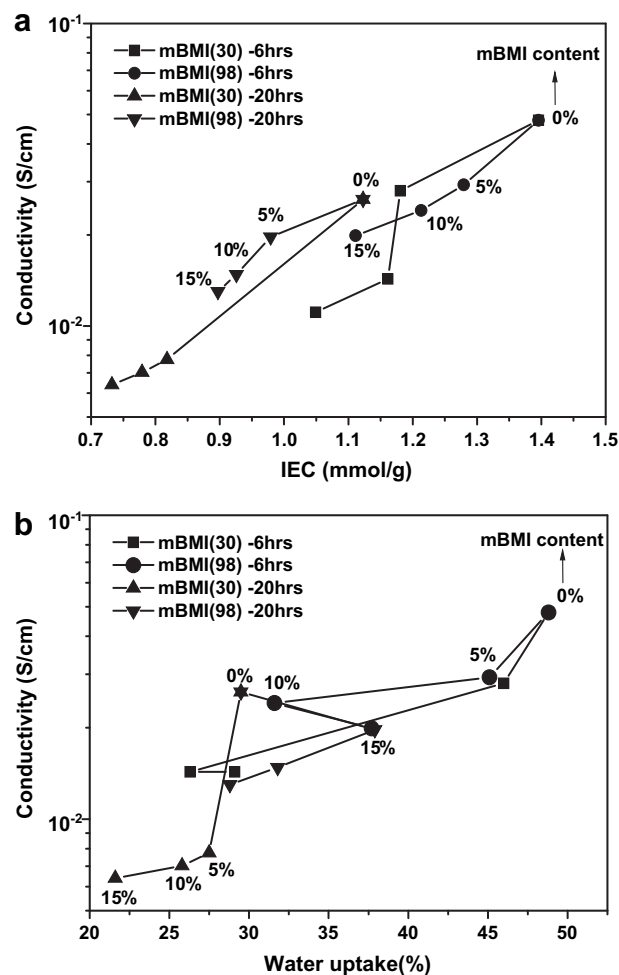


Fig. 10. Correlation between conductivity vs. (a) IEC, and (b) water uptake.

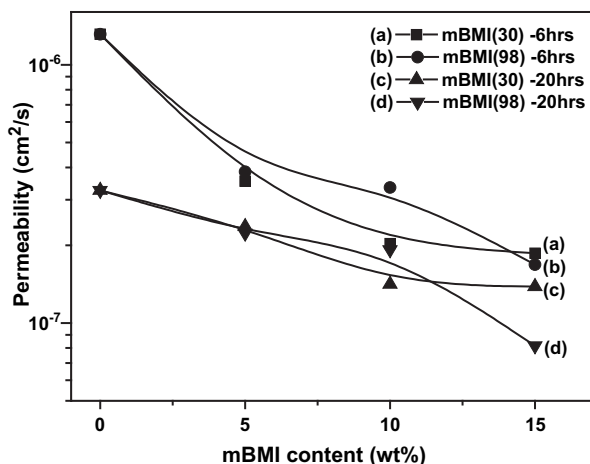


Fig. 11. The methanol permeability of sPEEK/mBMI(30) and sPEEK/mBMI(98) membranes cured at different time. (Methanol concentration: 50 vol%).

fluctuated. (Fig. 10(b)) As point out previously, water resides in both the acidic sPEEK domain as well as in the basic mBMI domain. Water resides in mBMI domain will not deliver protons with the same efficiency as those along sPEEK chain. Other factors such as channel morphology (i.e. tortuosity) may also influence conductivity. The lack of simple correlation between water uptake and ion conductivity reveals the complexity of the issue and further study of water and proton dynamic behaviors in membranes prepared with different morphology is necessary [26].

Low methanol permeability is a favorable characteristic in the application of DMFC. These membranes with entangled structure exhibited substantially lower methanol permeability in the range of  $10^{-7}$  cm²/s. The results shown in Fig. 11 indicated the permeability (with 50 vol% methanol solutions) of all membranes decreased with both increasing mBMI(30) or mBMI(98) content and with longer curing time. The lowest value is  $1.39 \times 10^{-7}$  cm²/s for sPEEK/15% mBMI(98) membrane after 20 h curing time. This is compared with that reported for sPEEK ( $1.2 \times 10^{-6}$  cm²/s) of the same degree of sulfonation, and with that of Nafion® 117 membrane ( $1.75 \times 10^{-6}$  cm²/s). The result revealed that physical cross-linking with highly branched mBMI is effective in reducing methanol permeability.

Zhong et al. shows coating the sPEEK with the cross-linked chitosan barrier layer can reduced the methanol permeability for

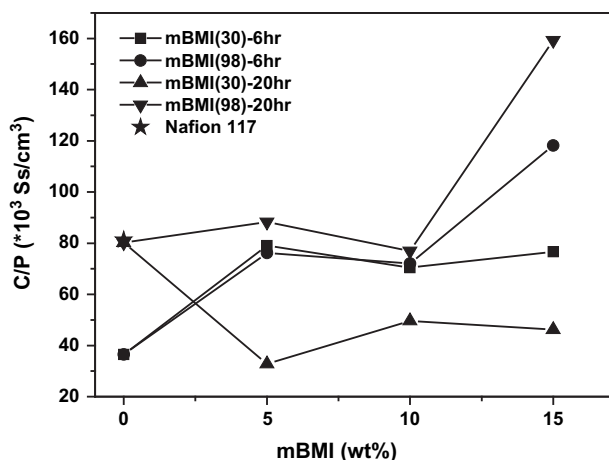


Fig. 12. Conductivity/Permeability ratio for sPEEK/mBMI(30) and sPEEK/mBMI(98).

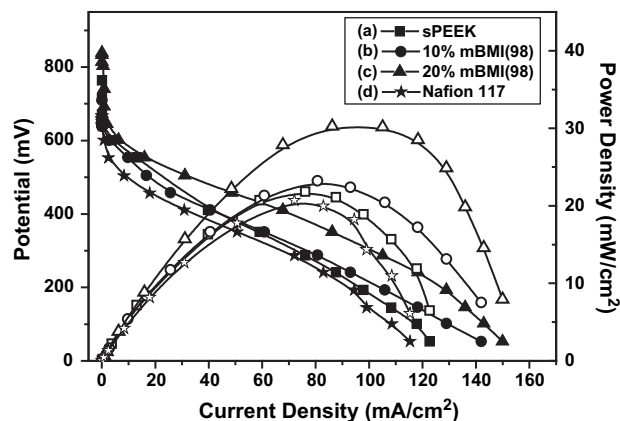


Fig. 13. Polarization curves for (a) sPEEK (DS = 63%), (b) 10% mBMI(98), (c) 20% mBMI(98), (d) Nafion 117 in DMFC. (Cell Temp.: 60 °C).

about one order [27]. Blending Poly(amide imide) with sPEEK shows the methanol permeability is reduced by a factor of three, but the proton conductivity also reduced to half [28]. Organic/inorganic composite membranes also show significantly reduced methanol permeability [29]. Except for the two-layer composite membranes, all previous efforts in reducing methanol permeability also sacrifices proton conductivity. In present paper with a single phase homogeneous membrane, we have demonstrated that methanol permeability can be successfully suppressed using hyper-branched mBMI as the barrier component without sacrificing proton conductivity.

Conductivity/Permeability ratio (C/P ratio, Fig. 12) discerns the effects resulting from the different manners by which the physical cross-linking is established. For short cross-linking time, the difference in C/P ratio is small for the two sample series until BMI content is above 15 wt%. But drastic difference is observed after longer annealing time. In the case of mBMI(98), C/P ratio is found to improve with longer curing times. However, in the case of mBMI(30), the reduction of methanol permeability with longer curing is accompanied with even greater suppression of proton conductivity. As far as C/P ratio is concern, mBMI(98) series is superior. The better C/P maybe accounted for by realizing that the methanol barrier (mBMI) function and proton conducting medium (sPEEK) are separated in mBMI(98) sample, but remains in close proximity in the mBMI(30) series of sample.

Finally the feasibility of these membranes is demonstrated by the DMFC performance. sPEEK/10% mBMI(98) and higher mBMI content (20% mBMI) are used for DMFC single cell test, due to their better C/P ratio. The polarization curves of MEAs made from the sPEEK, 10% mBMI(98) and 20% mBMI(98) membranes at 60 °C cell temperature are shown in Fig. 13. In present cases, the thickness of sPEEK, sPEEK/10% mBMI(98) and sPEEK/20% mBMI(98) are 57, 39 and 59 μm, respectively. The open circuit voltage (OCV) containing the 10% mBMI(98) membrane (710 mV) is lower than that of pure sPEEK membrane (764 mV). For thinner membranes higher methanol permeability are expected, and therefore, higher voltage losses. However the OCV in 10% mBMI(98) membrane is not much lower compared to that of pure sPEEK membrane with nearly twice the thickness. Although thinner, the 10% mBMI(98) still displayed higher power density than that in sPEEK membrane due to reduced ohmic losses. For 20% mBMI(98) membranes which bears similar thickness as pure sPEEK, higher OCV (839 mV) and lower polarization loss compared with pure sPEEK membrane are observed. Nafion with the same ~60 μm thickness is examined for comparison. However it suffered from serious methanol cross-over with poor current output. In the cell using Nafion as membrane (180 μm



thickness), the rapid potential drop at low current is characteristic of methanol cross-over effect. The thick membrane also leads to lower peak power output (peak power ca. 20 mW/cm<sup>2</sup>). These results clearly illustrated the effective methanol barrier characteristics in present membrane material originated from entangled structure between sPEEK and highly branched mBMI. A power density value of 30 mW/cm<sup>2</sup> is achieved compared to 22 mW/cm<sup>2</sup> for pure sPEEK.

#### 4. Conclusion

Physical cross-linking (via acid–base interaction) formed between hyper-branched bismaleimide oligomer and the sulfonated poly(ether ether ketones) sPEEK's lead to a more densely packed polymer which shows low water uptake and substantially reduced methanol permeability. With increasing the cross-linking time ( $T = 180\text{ }^{\circ}\text{C}$ ) BMI monomer and mBMI (modified Bismaleimide oligomers) established the larger hyper branch structure connected by the BMI monomer that entangles the sPEEK polymer chain. In the case of mBMI(30), higher BMI monomers concentration lead to more densely packed membrane. Neutralization between the sulfonic acid group of the sPEEK and the imide group of the mBMI(30), reduces the IEC value and deteriorated proton conductivity. In contrast, lower degree of entanglement between mBMI and sPEEK is found in mBMI(98). In this case, there is less neutralization and less reduction in IEC or conductivity. For both cases, lower water uptake, and lower methanol permeability are observed with increasing the degree of physical cross-linking (by increasing the mBMI content and with more extensive curing). For membranes containing mBMI(98), the proton conductivity is reduced only slightly. Except for sPEEK/mBMI(30) annealed for 20 h, all membranes displayed fair proton conductivity above  $10^{-2}\text{ S/cm}$ . Methanol permeability is also found to be substantially reduced (more than one order). The significance in the current design is that membrane properties can be balanced through physical cross-linking (via acid–base interaction) which has not found in previous approaches invoking either semi-IPN with linear polymers, or covalent cross-linking.

The membrane with best C/P ratio, 20% mBMI(98) displayed higher OCV (839 mV) and lower polarization loss compared with pure

sPEEK membrane which illustrated the effect of methanol permeation suppression attributed to the hyper-branched mBMI units in the entangled structure. A power density value of 30 mW/cm<sup>2</sup> is achieved compared to 22 mW/cm<sup>2</sup> for pure sPEEK.

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