Anionic multiblock copolymer membrane based on vinyl addition polymerization of norbornenes: Applications in anion-exchange membrane fuel cells

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ABSTRACT

Stable, non-hydrolysable, hydroxide-conducting polymers are of interest for electrochemical devices such as fuel cells, electrolyzers and flow-batteries. In this study, a series of tetrablock copolymers containing an all-hydrocarbon backbone were synthesized. The synthesis is based on vinyl addition polymerization of norbornene using (η^3-allyl)Pd(P₃Cl) as the catalyst and lithium tetrakis(pentafluorophenyl)-borate(2.5Et₂O) (Li[FBABA]) as the activator. The tetrablock polymers were cast into membranes with an ion-exchange capacity (IEC) between 1.55 and 2.60 milliequivalents per gram (meq/g). The number of bound and unbound water molecules per ion pair was measured and correlated with conductivity. The membrane with the highest IEC (2.60 meq/g) had 10.6 unbound (i.e. free) and 17.9 bound water molecules per ion pair within the polymer. The presence of excess unbound water has led to flooding of the ion conductive channels and low hydroxide ion conductivity. The optimal anion conductivity was found with about 6.7 unbound and 11.9 bound water molecules per ion pair. Excellent hydroxide conductivity (> 120 mS/cm at 80 °C) was obtained at an ion-exchange capacity of 1.88 meq/g. The results show that hydroxide mobility is aided by phase segregation within the copolymer. The ion conducting polymer was stable in 1 M NaOH solution at 80 °C, showing essentially no loss in ion conductivity in 1200 h. Thermogravimetric analysis showed that the membrane backbone was stable up to 400 °C, consistent with previous polynorbornene-based materials. The peak power density of a H₂/O₂, hydroxide conducting fuel cell containing one of these membranes was 542.57 mW/cm² at 0.43 V and current density of 1.26 A/cm² at 60 °C.

1. Introduction

Anion-exchange membranes (AEM) are of interest for a number of electrochemical devices (i.e. fuel cells, electrolyzers, redox flow battery) [1,2]. The development of AEMs with long-term alkaline stability and high hydroxide ion conductivity is of current interest [3–6]. The operation of fuel cells and electrolyzers at high pH allows the use of non-precious metal catalysts, especially for oxygen reduction and evolution, and reduced fuel crossover compared to proton-exchange membranes (PEM) devices [7–11]. Early AEMs have had low ionic conductivity, poor stability at high pH, and high water uptake [12–14]. However, recent studies have shown that the tethered, long-chain trimethyl ammonium (TMA) cation is stable in alkaline environments at elevated temperature [15–18].

High hydroxide conductivity is critical in membranes for fuel cells, batteries and electrolyzers. The use of multiblock copolymers can improve the hydroxide mobility compared to random copolymers [19]. This is due to the high degree of phase segregation in block copolymers leading to efficient ion-channel formation, compared to random copolymers. In addition, water management within the membrane can play an important role in controlling the mechanical deformation (i.e. water swelling) and ionic conductivity. Water is needed in the membrane to form the ionic hydration shell for the mobile hydroxide ion and stationary cation. However, excessive water uptake can lead to swelling of the ion conduction channels resulting in lower ionic conductivity (i.e. lower ion mobility) and softening of the membrane [19]. Thus, it is necessary to optimize the ion conducting channel size so that the amount of free, unbound (unproductive) water is minimized.

The long-term stability of AEMs largely depends on the chemical nature of the polymer backbone, position of the cation within the polymer architecture, and chemical nature of the fixed cation. In the past, polymers based on poly(arylene ether sulfone)s [20–22] and poly(arylene ether ketone)s [23,24] were investigated as AEMs. Significant degradation was observed at high pH. Polysulfone and polyketone groups in the polymer backbone were susceptible to nucleophilic attack by hydroxide. The poly(aryl ether) backbone undergoes cleavage of the C–O bonds at high pH which limits the long-term use [25–27].

In addition to the polymer backbones, nucleophilic attack of the fixed cation headgroups results in degradation. The mechanisms for degradation of quaternary ammonium headgroups include β-hydrogen Hofmann elimination, direct nucleophilic substitution (S_N2) and elimination via ylide formation [27–29]. Hibbs et al. found that a hexamethylene spacer between the trimethylammonium (TMA) cation and the polymer backbone results in better stability than the...
polynorbornene was shown to have excellent stability \[39\]. In this paper, it was observed that the polymers with the combination of an all-hydrocarbon backbone and tethered quaternary ammonium group on a long alkyl chain have the best long-term alkaline stability \[32–34\].

Price et al. synthesized hydrogenated poly(norbornene) as an anion-exchange membrane via ring-opening metathesis polymerization (ROMP) with high ionic conductivity, 177 mS/cm at 80 °C. Although the conductivity was high, the membranes were mechanically weak and not stable under alkaline condition \[35\]. Register et al. described the synthesis of block copolymers by vinyl addition polymerization of substituted norbornenes in a living polymerization and their use as a pervaporation membrane \[36–38\]. In a previous study, high T<sub>f</sub> (385 °C) polynorbornene was shown to have excellent stability \[39\]. In this paper, a facile synthetic strategy was used to prepare a series of tetra-block AEM copolymers based on vinyl addition polymerization of norbornenes, Scheme 1. The AEMs were cast from solution and the impact of bound and unbound water on conductivity was evaluated. High thermal stability, excellent mechanical properties and negligible long-term degradation at high pH (1 M NaOH solution at 80 °C) were demonstrated. The AEMs were used as membranes in an all-alkaline fuel cell.

2. Experimental

2.1. Materials

1-hexene, 5-bromo-1-pentene and dicyclopentadiene were purchased from Alfa Aesar and used as-received. The monomers, butyl norbornene (BuNB) and bromopropyl norbornene (BPNB), were synthesized via a Diels-Alder reaction at high-temperature according to a published procedure \[40\]. Prior to polymerization, the monomers were purified by distillation over sodium and degassed by three freeze-pump-thaw cycles. All polymerization reactions were performed under a dry argon atmosphere in a glove box with rigorous care to avoid moisture and air. Toluene was dried by heating under reflux for 6 h over sodium and benzophenone. Toluene was freshly distilled prior to use. Trisopropylphosphine and ([\(\eta^3\)-allyl]Pd(Cl))<sub>2</sub> were purchased from Sigma-Aldrich and used as-received. The catalyst, ([\(\eta^3\)-allyl]palladium(triisopropylphosphine)chloride ([\(\eta^3\)-allyl]Pd([Pr<sub>3</sub>P]Cl)), was prepared according to a previously published report \[41\]. Lithium tetrakis(pentafluorophenyl)borate(2.5Et<sub>2</sub>O) (Li[FABA]) was purchased from Boulder Scientific Co. and used as-received. a,a,a-trifluorotoluene (TFT), anhydrous, ≥ 99% and tetrahydrofuran (THF) were purchased from Sigma-Aldrich and used as-received.

2.2. Synthesis of tetrablock copolymer \([\text{Poly(BuNB-b-BPNB-b-BuNB-b-BPNB)}]\)

The tetrablock copolymer, consisting of alternating butyl norbornene (BuNB) and bromopropyl norbornene (BPNB) blocks (two blocks each), was synthesized by the sequential addition of the monomers (one after the other) at room temperature in an inert atmosphere glove box. The monomers were divided into four round-bottomed flask (two for each monomer) and toluene was added to make a 5 wt% solution in each flask. The catalyst solution was prepared separately in a vial by dissolving ([\(\eta^3\)-allyl]Pd([Pr<sub>3</sub>P]Cl)) (12 mg, 0.03 mmol) and Li[FABA]) (28 mg, 0.03 mmol) in a solution composed of 0.5 g toluene and 0.5 g TFT. The catalyst solution was stirred for 20 min. BuNB (0.45 g, 3.00 mmol) and toluene (10 mL) were added to the 100 mL round-bottomed flask fitted with a magnetic stir bar. The catalyst solution was injected into the flask under vigorous stirring. After 20 min the BuNB polymerization was complete. A small aliquot was removed and quenched with CH<sub>3</sub>CN for gel permeation chromatography (GPC) analysis. Then, a mixture of BPNB (0.64 g, 3.00 mmol) and toluene (12 mL) was added to the reaction flask, still containing the catalyst, and stirred for 3 h to incorporate the BPNB block onto the BuNB polymer. After the 3 h reaction time (complete consumption of BPNB), a small aliquot was taken out and quenched with CH<sub>3</sub>CN for GPC analysis. Next, BuNB (0.45 g, 3.00 mmol) and toluene (10 mL) were added to the reaction flask and allowed to react for 20 min for incorporation of the third block. A small aliquot was again taken out and quenched with CH<sub>3</sub>CN for GPC analysis. Finally, a mixture of BPNB (0.64 g, 3.00 mmol) and toluene (12 mL) was added to the flask and stirred for 3 h to incorporate the fourth block onto the polymer. After completion, the reaction mixture was quenched and the polymer precipitated by addition of methanol. The resulting polymer was dissolved in THF and stirred over activated charcoal. The solution was passed through an alumina filter to remove any palladium residue. The resulting product was precipitated from THF by addition of methanol. The polymer product was dried under vacuum at 60 °C. Tetrablock copolymers with different hydrophobic and hydrophilic chain lengths were synthesized by changing the monomer to catalyst feed ratio.

2.3. Nuclear magnetic resonance (NMR) spectra and GPC

The polymer samples were analyzed by \(^1\)H NMR using Bruker Avance 400 MHz NMR instrument using. CDCl<sub>3</sub> was the solvent. The number average molecular weight (M<sub>n</sub>) and polydispersity index (M<sub>d</sub>/M<sub>n</sub>) of the polymer samples were determined by GPC (Shimadzu) equipped with an LC-20 CE HPLC pump and a refractive index detector (RID-20 A, 120 V). Measurements were performed in THF with the
eluent flow rate of 1.0 mL/min at 30 °C. A polystyrene standard was used.

2.4. Membrane casting and ion-exchange

The tetrablock copolymer (0.20 g) was dissolved in 5 mL chloroform and the resulting solution was filtered through a 0.2 µm poly(tetrafluoroethylene) (PTFE) membrane syringe filter into a 4 cm diameter aluminum dish. The solvent was evaporated at room temperature in a nitrogen gas stream. The membrane was dried overnight under vacuum. The membranes were colorless, flexible and free-standing with a thickness of ca. 50 µm. Next, the bromobutyl headgroup was quaternized by immersion of the membrane in 45 wt% aqueous trimethylamine solution for 48 h at room temperature. The quaternized membrane with bromide counter-ion was removed from solution and washed thoroughly with DI water. The membranes were then soaked in 1 M NaOH solution under nitrogen for 24 h to exchange the bromide ions for hydroxide ions. The membranes were stored in DI water after being washed with DI water three times.

2.5. Morphological characterization

Small angle X-ray scattering (SAXS) was used to analyze the morphology of AEMs. Hydrated membranes in bromide form were tested in air using either a Malvern Analytical Empyrean XRD (Netherlands) instrument with a Pixel 3D detector or the NSLS-II beamline at the Center for Functional Nanomaterials (Brookhaven National Laboratory, Upton, NY). The wave vector ($q$) was calculated using Eq. (1), where $2\theta$ is the scattering angle.

$$q = \frac{4\pi \sin \theta}{2\lambda}$$

The characteristic separation length, or inter-domain spacing ($d$) (i.e. the Bragg spacing) was calculated using Eq. (2).

$$d = \frac{2\pi}{q}$$

Transmission electron microscopy (TEM) was also used to analyze the morphology of membranes. TEM was performed with a JEOL JEM-1400 Transmission Electron Microscope. Dry membranes with a bromide counter ion were stained by fuming with osmium tetroxide at room temperature prior to TEM examination. The stained membranes were embedded within an epoxy resin, sectioned into ca. 50 nm thick samples with a Leica UC6rt Ultramicrotome, and placed on a copper grid for observation.

2.6. Hydroxide conductivity and alkaline stability

The ionic resistance of the membranes was measured using a four-point, in-plane probe and electrochemical impedance spectrometry (1 Hz to 1 MHz) with a PAR 2273 potentiostat. All samples were tested in HPLC-grade water under a nitrogen purge to minimize the detrimental effects of CO$_2$. The samples were allowed to equilibrate for 30 min prior to each measurement. The in-plane ionic conductivity was calculated using Eq. (3).

$$\sigma = \frac{L}{WTR}$$
was also measured by titration [42]. The membrane in Br- form was discussed in detail in the next section. In addition, the membrane IEC (N_{bound}) molecules (2.7. Ion exchange capacity (IEC), water uptake (WU), hydration number \(\lambda\), number of freezable water (\(N_{free}\)) and bound, nonfreezable water (\(N_{bound}\)) molecules)

The ion exchange capacity was calculated using NMR data which is discussed in detail in the next section. In addition, the membrane IEC was also measured by titration [42]. The membrane in Br form was first immersed in 0.1 M NaCl solution for 24 h to exchange the bromide ions for chloride ions. Next, the membrane in chloride form was thoroughly washed with DI water and dried under vacuum for 24 h to obtain the dry weight. The dried membrane was immersed in a fixed volume of 0.5 M aqueous NaN_3 solution for 24 h. The Cl^- ions released from the membrane were titrated with 0.05 M AgNO_3 using K_2CrO_4 (10 wt%) as the indicator. The IEC was calculated using Eq. (4).

\[
IEC = \frac{C_{AgNO_3} \times V_{AgNO_3}}{M_d}
\]  

In Eq. (4), \(C_{AgNO_3}\) (mL) is the volume of AgNO_3 solution, \(C_{AgNO_3}\) (0.05 mol L^-1) is the concentration of AgNO_3 solution, and \(M_d\) (g) is the weight of the dried membrane sample.

The water uptake of the membranes was calculated using Eq. (5).

\[
WU(\%) = \frac{M_d - M_w}{M_d} \times 100
\]

In Eq. (5), \(M_d\) is the dry mass of the membrane and \(M_w\) is the wet mass of the membrane after removing excess surface water. The membranes were in OH form and measured at room temperature. The hydration number (\(\lambda\), number of water molecules per ionic group, was calculated using Eq. (6).

\[
\lambda = \frac{1000 \times WU(\%)}{IEC \times 18}
\]

The number of freezable water (\(N_{free}\)) and bound water (or non-freezable water) (\(N_{bound}\)) were determined by differential scanning calorimetry (DSC). DSC measurements were carried out on a Discovery DSC with autosampler (TA Instruments). The membrane samples were fully hydrated by soaking in deionized water for one week. After the water on the membrane surface was dabbed off, a 5–10 mg sample was quickly sealed in an aluminum pan. The sample was cooled to −50 °C and then heated to 30 °C at a rate of 5 °C/min under N_2 (20 mL/min). The quantity of freezable and non-freezable water was determined by Eqs. (7) – (9) [43–45].

\[N_{free} = \frac{M_{free}}{M_{tot}} \times \lambda
\]

\[M_{free} = \frac{H_t/H_{free}}{(M_{tot} - M_d)/M_d}
\]

\[H_t\] is the enthalpy obtained by the integration of the DSC freezing

<table>
<thead>
<tr>
<th>Block copolymer</th>
<th>Molecular Weight (kg/mol)</th>
<th>M_x/M_y</th>
<th>IEC (Ion Exchange Capacity) (meq./g)</th>
<th>OH Conductivity (mS/cm)</th>
<th>(\sigma/\text{IEC})</th>
<th>Water Uptake (%)</th>
<th>Hydration number (\lambda)</th>
<th>(N_{free})</th>
<th>(N_{bound})</th>
<th>Inter-domain spacing, d (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNB-X_{74}Y_{26}</td>
<td>39.58</td>
<td>1.42</td>
<td>1.55</td>
<td>23.4</td>
<td>61.3</td>
<td>26.2</td>
<td>9.41</td>
<td>0.91</td>
<td>8.50</td>
<td>ND</td>
</tr>
<tr>
<td>PNB-X_{70}Y_{30}</td>
<td>37.97</td>
<td>1.29</td>
<td>1.77</td>
<td>27.0</td>
<td>67.4</td>
<td>38.1</td>
<td>59.6</td>
<td>18.71</td>
<td>5.42</td>
<td>37.2</td>
</tr>
<tr>
<td>PNB-X_{67}Y_{33}</td>
<td>38.86</td>
<td>1.28</td>
<td>1.92</td>
<td>32.2</td>
<td>71.8</td>
<td>37.4</td>
<td>68.8</td>
<td>19.91</td>
<td>7.81</td>
<td>12.10</td>
</tr>
<tr>
<td>PNB-X_{70}Y_{32}</td>
<td>50.77</td>
<td>1.54</td>
<td>2.21</td>
<td>50.9</td>
<td>101.9</td>
<td>46.1</td>
<td>71.0</td>
<td>17.85</td>
<td>7.61</td>
<td>10.24</td>
</tr>
<tr>
<td>PNB-X_{68}Y_{32}</td>
<td>45.33</td>
<td>1.55</td>
<td>2.60</td>
<td>44.9</td>
<td>80.0</td>
<td>30.8</td>
<td>133.6</td>
<td>28.55</td>
<td>10.65</td>
<td>17.90</td>
</tr>
<tr>
<td>PNB-X_{70}Y_{32}</td>
<td>114.9</td>
<td>1.42</td>
<td>1.88</td>
<td>62.0</td>
<td>122.7</td>
<td>65.2</td>
<td>63.0</td>
<td>18.62</td>
<td>6.74</td>
<td>11.88</td>
</tr>
</tbody>
</table>

\[a\] Measured in bromopropyl form by gel permeation chromatography at RT in THF relative to polystyrene standards.

\[b\] IEC (Ion Exchange Capacity) was calculated via ^1H NMR results in bromopropyl form.

\[c\] OH- conductivity was measured by four-probe conductivity cell.

\[d\] Ionic conductivity at 80 °C/IEC.

\[e\] Water uptake was measured at room temperature.

\[f\] Inter-domain spacing measured using small angle X-ray scattering (SAXS) in bromide form; ND = not determined. PNB = polynorbornene; X = hydrophobic block; Y= hydrophilic block; numbers in the subscript indicate the molar ratio of each block.

2.7. Ion exchange capacity (IEC), water uptake (WU), hydration number \(\lambda\), number of freezable water (\(N_{free}\)) and bound, nonfreezable water (\(N_{bound}\)) molecules

The ion exchange capacity was calculated using NMR data which is discussed in detail in the next section. In addition, the membrane IEC was also measured by titration [42]. The membrane in Br form was first immersed in 0.1 M NaCl solution for 24 h to exchange the bromide ions for chloride ions. Next, the membrane in chloride form was thoroughly washed with DI water and dried under vacuum for 24 h to obtain the dry weight. The dried membrane was immersed in a fixed volume of 0.5 M aqueous NaN_3 solution for 24 h. The Cl^- ions released from the membrane were titrated with 0.05 M AgNO_3 using K_2CrO_4 (10 wt%) as the indicator. The IEC was calculated using Eq. (4).

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\lambda = \frac{1000 \times WU(\%)}{IEC \times 18}
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The number of freezable water (\(N_{free}\)) and bound water (or non-freezable water) (\(N_{bound}\)) were determined by differential scanning calorimetry (DSC). DSC measurements were carried out on a Discovery DSC with autosampler (TA Instruments). The membrane samples were fully hydrated by soaking in deionized water for one week. After the water on the membrane surface was dabbed off, a 5–10 mg sample was quickly sealed in an aluminum pan. The sample was cooled to −50 °C and then heated to 30 °C at a rate of 5 °C/min under N_2 (20 mL/min). The quantity of freezable and non-freezable water was determined by Eqs. (7) – (9) [43–45].

\[N_{free} = \frac{M_{free}}{M_{tot}} \times \lambda
\]

\[M_{free} = \frac{H_t/H_{free}}{(M_{tot} - M_d)/M_d}
\]

\[H_t\] is the enthalpy obtained by the integration of the DSC freezing
peak and $H_{\text{Ice}}$ is enthalpy of fusion for water, corrected for the subzero freezing point according to Eq. (9).

$$H_{\text{Ice}} = H_{\text{fus}} - \Delta C_p \Delta T_f$$  

(9)

$\Delta C_p$ is the difference between the specific heat capacity of liquid water and ice. $\Delta T_f$ is the freezing point depression.

The thermal stability of the dried membranes in bromide ion form was studied using thermogravimetric analysis (TGA) on a TA Instruments Q50 analyzer. The temperature was ramped at 10 °C/min up to 800 °C in a nitrogen atmosphere.

### 2.8. Membrane electrode assembly (MEA) fabrication and single-cell testing

One of the best performing membrane in this study (PNB-X62-Y38) was selected for testing in an alkaline exchange membrane fuel cell (AEMFC). The AEM anode and cathode were fabricated via the slurry method and were identical. A lower molecular weight (20.5 kg/mol) version of the poly(BuNB-b-BPNB-b-BuNB-b-BPNB) tetrablock...
The alkaline stability of polynorbornene AEMs at 1 M NaOH solution at 80 °C.

Prior to MEA testing, the electrodes and membranes were soaked in 1 M NaOH for 1 h (replacing the solution every 20 min) in a nitrogen atmosphere to convert the membrane and ionomer to hydroxide form. The MEA was placed into Fuel Cell Technologies hardware between single-pass serpentine graphite plates with 6 mil PTFE gaskets. The MEAs were tested in a Scribner 850e Fuel Cell Test Station at a cell temperature of 60 °C. Humidified H₂ and O₂ gas feeds were supplied at the anode and cathode, respectively, at 0.5 L/min. The dew points of the anode and cathode streams were adjusted throughout the course of testing in order to optimize the water balance within the AEMFC.

3. Results and discussion

3.1. Synthesis and characterization of tetrablock copolymer

The monomers (BuNB and BPNB) were synthesized by a previously described procedure [40]. The catalyst, (η⁵-allyl)Pd(Pr₃P)Cl, was prepared in high yield and purity following a previous report [41].

The reactivity of the BuNB monomer ([M]₀/[Pd] = 100:1) was higher than that of the BPNB monomer. The reaction time for each block varied (20 min for BuNB and 3 h for BPNB) in order to achieve complete conversion for each block. A one-to-one mole ratio of Li[FABA] to the catalyst was sufficient to generate the cationic Pd complex for the polymerization initiation. The absence of olefinic protons in the ¹H NMR spectra of the polymer produced shows that the polymerization reaction proceeded through the vinyl addition pathway, eliminating the occurrence of ring-opening metathesis polymerization (ROMP), Scheme 1. A representative GPC trace of the polymer produced shows that the polymerization reaction proceeded through the vinyl addition pathway, eliminating the occurrence of ring-opening metathesis polymerization (ROMP), Scheme 1. 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of 1.28–1.55. The IEC value was determined by $^1$H NMR spectroscopy and found to be 1.55–2.60 meq/g, as discussed later. The methyl protons of the hydrophilic block resonate at 0.89 ppm. The methylene protons adjacent to the bromine atom in the hydrophobic block appear at 3.41 ppm. The X and Y values within poly(BuNB-b-BPNB-b-BuNB-b-BPNB) was analyzed via NMR by comparing the integration ratio of $H_x$ and $H_y$, Fig. 1. The mol% and wt% of the combined hydrophilic and hydrophobic blocks in the tetrablock copolymer were calculated via the NMR spectra.

3.2. Morphology and characterization

SAXS and/or TEM were used to investigate the microstructure of the polyboronene membranes synthesized here. The inter-domain spacing ($d$), or the average separation length between inhomogeneities in the membranes, was determined from the Bragg spacing of the primary scattering peak in the SAXS spectra, as shown in Fig. 3. The inter-domain spacing values are listed in Table 1. The domain size range was 37.2–86.4 nm, which directly correlated with water uptake. More specifically, it can be seen that the number of unbound waters tracks with the domain size. Larger domains provide regions where free (unbound) water can populate. For example, PNB-X$_{67}$Y$_{33}$ showed a very high water uptake, 133.6%, and a d-spacing, 86.4 nm. By comparison, these values are about twice as large as the ones for PNB-X$_{67}$Y$_{33}$, which had a water uptake of 68.8% and a d-spacing of 44.2 nm.

PNB-X$_{67}$Y$_{33}$ was examined using transmission electron microscopy (TEM) because the X-ray scattering was not as definitive as with other samples. TEM analysis was performed in bromide form rather than in hydroxide form to avoid inadvertent degradation of the membranes due to concentrated hydroxide in dry membranes. It was observed that the size of the phases increased with the hydrophilicity of the membranes. This is consistent with the increasing inter-domain spacing observed by SAXS. The ion channels also appear to lose their definition and well-defined structure as the channel size became larger. Fig. 4 shows TEM micrographs for five of the membranes. The dark regions correspond to the hydrophilic domains with bromide counter ions and the bright regions correspond to hydrophobic domains. Membranes with higher hydrophilicity also contain more dark regions in the TEM micrographs. It should be noted that trends observed using TEM in the dry state would likely be more pronounced if the membranes could be observed swollen with water as in the SAXS measurements.

3.3. Ion Exchange Capacity (IEC), hydroxide conductivity

The IEC is an important parameter in determining the membrane ionic conductivity and water uptake. The IEC was evaluated from $^1$H NMR spectroscopy and found to be between 1.55 and 2.60 meq/g. Taking PNB-X$_{64}$Y$_{46}$ as the representative sample, the IEC was calculated by comparing the integration ratio of the methylene protons adjacent to the bromine atom of the hydrophobic block at 3.41 ppm and methyl protons of the hydrophobic block at 0.89 ppm, Fig. 1. From Fig. 1, the integration ratio of $H_x$ to $H_y$ was 3.46:2 which is equal to 1.153:1 (for 1 proton). To further confirm the extent of the quaternization reaction, the IEC was measured by titration. The titration procedure involved converting the counter anion in the membrane to chloride, followed by titration of the amount of chloride present in the membrane, as described in the Experimental Section. An excellent correlation for IEC was found between the two methods, titration and NMR. For PNB-X$_{67}$Y$_{33}$, the measured IECs by titration and NMR were found to be 1.90 meq/g and 1.92 meq/g, respectively.

High hydroxide conductivity ($\sigma$) is desired in membranes used in electrochemical devices [14]. Fig. 5 shows that the hydroxide conductivity increased with temperature from 25°C to 80°C and followed an Arrhenius relationship. In the case of PNB-X$_{68}$Y$_{32}$, the conductivity was 122.7 mS/cm at 80°C. Membrane (PNB-X$_{68}$Y$_{32}$) had the highest IEC, 2.60 meq/g, but a modest conductivity, 80 mS/cm at 80°C, in comparison to PNB-X$_{67}$Y$_{32}$ (IEC = 1.88 meq/g). Fig. 6 shows the plot of $\ln$ vs. 1000/T for all the membranes. The hydroxide transport activation energy ($E_a$) was calculated from the slope in Fig. 6 and was found to be 9.33–15.28 kJ mol$^{-1}$. These $E_a$ values are close to that of Nafion-117, 12.75 kJ mol$^{-1}$ [47].

The $\sigma$/IEC ratio is a measure of the hydroxide mobility. By this metric, PNB-X$_{66}$Y$_{32}$ had the highest hydroxide mobility, despite having a more modest IEC (Table 1). Conversely, the hydroxide mobility in PNB-X$_{54}$Y$_{46}$ was the lowest among the membranes even though the IEC was the highest (Table 1). A higher IEC may be expected to have higher mobility because there would be a greater tendency for phase segregation. A possible explanation for the high anion mobility with PNB-X$_{68}$Y$_{32}$ is its molecular weight. The higher molecular weight of PNB-X$_{68}$Y$_{32}$, compared to the other samples, contributed to its lower water uptake and greater chain entanglement, compared to the other samples. The effect of molecular weight is particularly clear when comparing the PNB-X$_{68}$Y$_{32}$ (last line of Table 1) to the third and fourth lines (-Y$_{33}$ and -Y$_{38}$, respectively). The number of blocks is the same and the IEC values are close (ca. 1.88–2.21). However, the $\sigma$/IEC is almost double for PNB-X$_{68}$Y$_{32}$ due to its longer block length which enables better ion channel formation. Further investigation of the effect of molecular weight is underway.

3.4. Water uptake (WU), hydration number ($\lambda$), number of freezable water molecules ($N_{\text{bound}}$) and bound, non-freezable water molecules ($N_{\text{bound}}$)

Water uptake is a key parameter in determining the conductivity and mechanical stability of the AEMs. An adequate amount of water is necessary for ion hydration and conduction. However, excess water in the form of free water can lead to swelling and poor performance of the membrane electrode assembly (MEA) due to membrane softening and channel flooding. Hence, an optimum amount of bound water in the membrane is required to form the ion solvent shell [16,17,48]. As shown in Table 1, the water uptake of the membranes increased with increasing IEC, reaching up to 133.6%. The best performing membrane, PNB-X$_{68}$Y$_{32}$ had 63% WU and conductivity of 122.7 mS/cm at 80°C. PNB-X$_{67}$Y$_{32}$ had the highest IEC and consequently the highest WU of 133.6% but lower ionic conductivity (80 mS/cm at 80°C) compared to PNB-X$_{68}$Y$_{32}$. The hydration number ($\lambda$) is the number of water molecules per ionic head-groups. The high hydration number of PNB-X$_{64}$-Y$_{46}$ was the result of the presence of unproductive water and larger channel size. The inter-domain spacing was 86.4 nm, as measured by SAXS. The free water content increased with domain size, as shown in Table 1. More specifically, it can be seen that the number of unbound waters tracks with the domain size. This shows that the unproductive, free-water can populate ion channels when they are larger than the optimum size [19]. Previously, it was shown that ion channels that are too small had low water uptake resulting in poor ion mobility and conductivity.

Differential scanning calorimetry was used to measure the number of freezable water molecules ($N_{\text{free}}$) and bound, non-freezable water molecules ($N_{\text{bound}}$) in the membrane. In the DSC thermogram, free water freezes just below 0°C. Using the hydration number, the number of free water $N_{\text{free}}$ can be obtained by subtracting the number of bound waters. The results of all the membranes are shown in Table 1. In the case of PNB-X$_{68}$Y$_{32}$, the amount of $N_{\text{free}}$ and $N_{\text{bound}}$ in the membrane was 6.7 and 11.9, respectively. This was close to the optimum number of bound waters (9–10 per ionic pair), as previously reported [16]. Consequently, this membrane also showed the highest conductivity, 122.7 mS/cm at 80°C. The presence of higher free (10.6) and bound (17.9) water for PNB-X$_{64}$-Y$_{46}$ resulted in a decrease in the conductivity, 80 mS/cm at 80°C, although the IEC (2.60 vs. 1.88) was higher than PNB-X$_{68}$Y$_{32}$. This can be attributed to the formation of overly large ion conducting channels flooded with unproductive water. The lower free water content (0.9) for PNB-X$_{68}$Y$_{32}$ was not sufficient to support
effective ion transport. Hence, the conductivity was lower (61.3 mS/cm at 80 °C). In case of PNB-X67-Y33, even though the free water (7.8) was acceptable, the higher bound water (12.1) resulted in lower conductivity due to the larger number of waters of hydration. The lower free water (5.4) and higher bound water (13.3) for PNB-X62-Y30 was the reason for lower ionic conductivity in the membrane.

3.5. Alkaline and thermal stability

Membrane durability is essential for long operational life in electrochemical devices. The alkaline stability assessment of the current AEMs was performed by soaking the membranes in 1 M NaOH solution at 80 °C. The loss of ionic conductivity was measured vs. time for 1200 h. No detectable (< 1%) loss was observed in the ionic conductivity over 1200 h, Fig. 7. Hence, it can be concluded that the non-hydrolysable polymer backbone with cations tethered via long side chains displays adequate alkaline stability compared to hydrolysable polymer backbones (e.g. polysulfone, polyketone, polyethers) and the benzyl attachment of cations to the polymer chains.

The thermal stability of the membranes was investigated by thermogravimetric analysis (TGA), Fig. 8. Four degradation stages were observed. The first stage of decomposition, below 100 °C, was due to water loss from the membrane. The second stage around 250 °C was due to the decomposition of the quaternary ammonium group. The third stage from 300 °C to 400 °C resulted from the degradation of the alkyl side chains in the polymer. The fourth stage, above 400 °C, was due to the decomposition of polymer backbone [17,37]. Our results suggest that the membranes were sufficiently stable at the operating conditions for low temperature AEM fuel cells or electrolyzers, which typically operate below 80 °C.

3.6. Fuel cell testing

PNB-X62-Y38 was selected for single-cell alkaline exchange membrane fuel cell testing because of its high ionic conductivity and excellent alkaline stability. The free-standing membrane was also mechanically robust and withstood compression in the fuel cell hardware without damage.

The fuel cell was operated at 60 °C to be comparable to many other AEMFCs found in literature. The MEA underwent a break-in startup procedure, where the cell was discharged at 0.5 V for one hour followed by an additional hour at 0.2 V. The anode and cathode dew point were set to 50 °C (69.5% RH) to avoid flooding of the catalyst layer. The open circuit voltage (OCV) was found to be 1.028 V after break-in.

After the initial conditioning period, water balance within the cell was optimized by adjusting the dew point of the humidified H2 and O2 streams at a constant cell voltage of 0.2 V. After each dew point adjustment, a discharge curve from open circuit to 0.2 V was recorded. Omasta et al. previously found that proper water management was important for both stability and performance in AEMFCs [49]. Because the hydrogen oxidation reaction at the anode produces water and some of it diffuses through the AEM to hydrate the cathode, excess water content (< 100% RH) in the H2 input stream should be avoided. After adjusting the anode and cathode dew points, it was found that both anode and cathode dew points of 46 °C (59.83% RH) provided the optimal stability and power output. As seen in Fig. 9, a peak power density of 542.57 mW/cm² was obtained at 0.43 V and 1.26 A/cm². When corrected for IR loss across the membrane (HFR = 123 mΩ cm²), the IR-corrected peak power density of the AEMFC was 713.04 mW/cm². This ohmic resistance is higher than that reported by Omasta et al. (ca. HFR = 50 mΩ cm²) and can also be attributed to other factors such as membrane thickness (t = 115 μm) and interfacial contact resistance due to a non-optimized ionomer and catalyst layer. Nonetheless, these results are promising and refinements to the MEA could lead to even higher performance.

4. Conclusion

A series of tetabrach copolymers containing all-hydrocarbon backbone based on vinyl addition polymerization of norbornene were synthesized for anion-exchange membranes. To the authors’ knowledge, this is the first anion exchange membrane based on vinyl addition-type polyboronnorene. These membranes displayed high thermal stability up to 400 °C. For PNB-X68-Y38, the ionic conductivity was 122.7 mS/cm at 80 °C with an IEC (1.88 meq/g), which was less than PNB-X54-Y36 (2.6 meq/g). This shows the importance of optimizing the bound and unbound water content in the membrane. Water content in PNB-X68-Y38 was measured by DSC analysis and it was found that 6.7 unbound water molecules and 11.9 bound water molecules in the membrane leading to the best ionic conductivity among the synthesized samples. The long-term alkaline stability test in 1 M NaOH solution at 80 °C showed exceptional chemical stability with no detectable degradation (< 1%) over a 1200 h period. PNB-X62-Y38 was used to fabricate an MEA for an alkaline fuel cell test which achieved excellent performance with a peak power density of 542.57 mW/cm² at 0.43 V and 1.26 A/cm².

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Appendix A. Supplementary material

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References


