

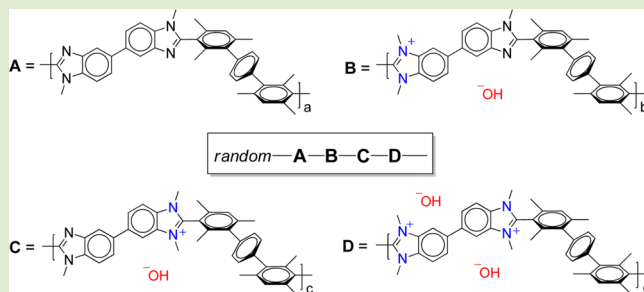
Hydroxide-Stable Ionenes

Andrew G. Wright and Steven Holdcroft*

Department of Chemistry, Simon Fraser University, Burnaby, BC V5A 1S6, Canada

Supporting Information

ABSTRACT: In the pursuit of stable, hydroxide ion-exchange ionomers and solid polymer electrolytes for fuel cells and electrolyzers, we present a novel, sterically C2-protected poly(benzimidazole) derivative incorporating a hexamethyl-*p*-terphenylene group. Using a new, scalable, and air-insensitive methylation procedure, *N*-methylation of the polymer is controlled to yield an unprecedented hydroxide-stable, methanol-soluble, and water-insoluble poly(benzimidazolium) ionene. This original polymer is also soluble in aqueous ethanol, which makes it suitable for use as a processable ionomer for catalyst layers. The water uptake and ionic conductivity is correlated to the degree of methylation. The anionic conductivity reached $9.7 \pm 0.6 \text{ mS cm}^{-1}$ for polymers with a 92% degree of methylation. Additionally, the hexamethyl-*p*-terphenylene unit shows interesting atropisomerism, which may influence their physical properties.



Alkaline anion exchange membrane (AAEM) fuel cells have received considerable interest as a high efficiency, low emission, and low cost energy converter.¹ Their use of nonprecious metal catalysts provides a potential advantage over incumbent proton exchange membrane fuel cells.² AAEMs may also find use in water electrolyzers for energy storage.³ Typical cationic functional groups for AAEMs include ammonium,⁴ sulfonium,⁵ phosphonium,⁶ pyridinium,⁷ imidazolium,⁸ benzimidazolium,⁹ and metal cations, such as ruthenium.¹⁰ However, these generally degrade when exposed to solutions of high pH and at elevated temperature.^{8,11–13} Recently, an exceptionally hydroxide-stable polymer was discovered, *mes*-PDMBI-OH[−] (Figure 1),¹⁴ which showed no observable degradation in 6 M KOH at rt or in 2 M KOH at 60 °C. Hydroxide stability is conferred by introducing steric crowding around the C2-position of the benzimidazolium units. *Mes*-PDMBI-OH[−], however, is water-soluble, requiring it to be

blended to form water-insoluble membranes. Blending reduces the ion-exchange capacity (IEC) from 4.5 mequiv g^{−1} to 1–2 mequiv g^{−1}, which limits the conductivity. Moreover, blends require the use of a high-boiling solvent, DMSO, for casting, which greatly limits processability, especially catalyst layer fabrication.

In this paper, we report novel ionenes, classically defined as polymers which contain ionic amines in the backbone,¹⁵ that are stable in hydroxide form. These ionenes are soluble in alcohol/water solvents but insoluble in water, making them candidates for ionomers in catalyst layers for fuel cells and electrolyzers. Such selective solubility of hydroxide-conducting polymers has previously proven elusive.¹⁶ Of the few ammonium-based ionomers developed, most are soluble in solvents such as NMP and DMSO, requiring higher temperatures for spray-coating and are more likely to contaminate the catalyst layer.^{17–19} A recent paper by Li et al. described an ammonium-based poly(2,6-dimethyl-phenylene oxide) with solubility in methanol and ethanol solvents; but these appear to degrade to 90% of their original conductivity after 60 h in a fuel cell and the stability in its dissolved state was not reported.²⁰

We choose 2,2'',4,4'',6,6''-hexamethyl-*p*-terphenylene (HMT) to replace the mesitylene group in *mes*-PDMBI to increase the hydrophobicity of the backbone and render the polymer water-insoluble, while maintaining steric C2-protection of the cation. This also increases the distance between the two adjacent cations, which has been shown to increase the thermal and chemical stability of this class of polymers.²¹ This

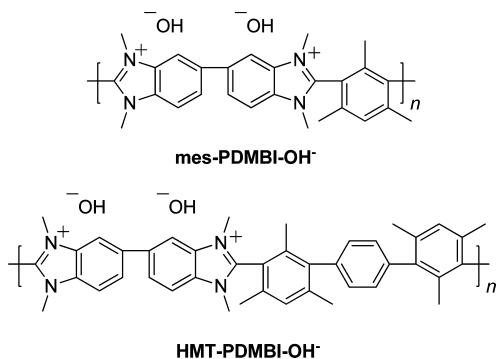
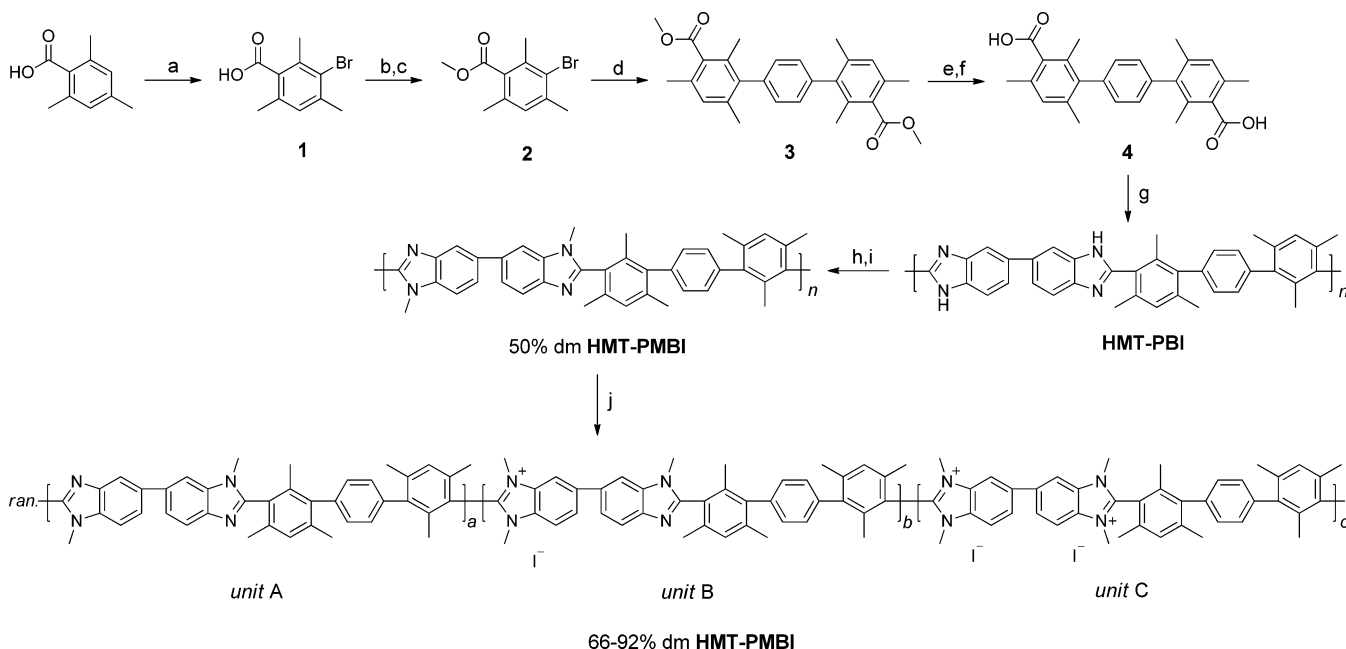


Figure 1. Chemical structures of the previously reported¹⁴ and newly reported *N*-methylated poly(benzimidazolium)s.

Received: March 20, 2014

Accepted: April 18, 2014

Published: April 22, 2014

Scheme 1^a

^aReagents and conditions: (a) bromine, AcOH, 2 h, rt, 74% yield; (b) KOH, DMSO, rt, 15 min; (c) MeI, 2 h, rt, 93% over two steps; (d) 1,4-phenylenediboric acid, 2 M K₂CO₃, 1,4-dioxane, 0.2 mol % Pd(PPh₃)₄, reflux, 22 h, 60%; (e) H₂SO₄, 30 min, rt; (f) H₂O, 15 min, 97% over two steps; (g) 3,3'-diaminobenzidine, Eaton's reagent, 120–140 °C, 1.5 h, 102%; (h) KOH, DMSO, 70 °C, 30 min; (i) MeI, rt, 3 min, 84% over two steps; (j) MeI, DCM, 30 °C, 16–18 h.

novel ionene, **HMT-PDMBI-OH⁻** (Figure 1) has an IEC_{OH⁻} of 3.14 mequiv g⁻¹ and was synthesized via the novel charge-neutral, C2-protected poly(benzimidazole), **HMT-PBI**, as shown in Scheme 1. **HMT-PBI** is insoluble in DMSO, DMF, and NMP solvents, which are often used to dissolve PBIs,²² but soluble in basic DMSO (LiH or KOH), which allowed subsequent complete methylation with iodomethane to form **HMT-PDMBI-I⁻**. However, the fully methylated polymer, after hydroxide ion-exchange, is water-soluble because of its high IEC_{OH⁻}.

Partial methylation of PBI has been shown to reduce dissolution via a reduction in IEC.^{23–25} However, methylation uses a one-pot reaction in LiH-NMP, which requires accurate stoichiometry of reagents (including volatile iodomethane) under an inert environment with heating, rendering methylation difficult to control. In order to control the degree of methylation more reproducibly, we developed a two-step, scalable, air-insensitive methylation procedure wherein the first methylation (requiring DMSO/KOH/H₂O) takes only 3 min at rt to yield the neutral polymer, 50% dm **HMT-PMBI**, as shown in Scheme 1. However, it was preferable to slightly overmethylate the polymer in order to ensure complete conversion of anionic sites. The 50% dm **HMT-PMBI** is insoluble in DMSO but soluble in chloroform and dichloromethane (DCM). Controlled, partial methylation of the remaining basic nitrogens, performed in DCM using controlled amounts of iodomethane at 30 °C over 16–18 h, led to 66, 73, 80, 89, and 92% degree of methylation (dm). The polymers are soluble in DMSO, thus aiding ¹H NMR analysis (Figure S12).

HMT-PMBI consists of four randomly distributed units: A, B, and C, where B represents two structural isomers (see Scheme 1). 50% dm **HMT-PMBI** is 100 mol % A; whereas 100% dm **HMT-PMBI** is 100 mol % C. Integration of the *N*-methyl peaks in the ¹H NMR spectra provides quantification of

dm% (eq S1). All partially methylated polymers, including 92% dm, were insoluble in water in both their iodide and hydroxide forms. Cast from DMSO solutions, they formed strong, flexible, transparent brown films. The 89% dm **HMT-PMBI** derivative was soluble in methanol in the iodide and hydroxide form, insoluble in anhydrous ethanol, but readily soluble in ethanol/water mixtures.

The iodide was exchanged for hydroxide by soaking the films in 1 M KOH for 48 h at rt, followed by soaking in deionized water for 120 h with repeated exchanges of water (see SI for details). The deionized water was exposed to air and thus carbonated. While the presence of atmospheric CO₂ is known to convert the hydroxide form to a mixed hydroxide, carbonate, and bicarbonate form²⁶ and that specialized setups are required to characterize the polymer in its hydroxide form,²⁷ the polymer is labeled **HMT-PMBI-OH⁻** for discussion.

The ionic conductivities measured by electrochemical impedance spectroscopy for **HMT-PMBI-OH⁻** derivatives are listed in Table 1 (see SI for experimental details). The conductivity exponentially increased with increasing dm%, as shown in Figure S13, from 0.10 ± 0.03 mS cm⁻¹ for 66% dm to 9.7 ± 0.6 mS cm⁻¹ for 92% dm. These are likely to be much higher in the absence of CO₂.^{26–28} For example, Yan and Hickner found that the majority of hydroxide is converted to bicarbonate in air,²⁷ and Disabb-Miller et al. found that the bicarbonate diffusion coefficient of the mobile ion approached that of the dilute solution limit at hydration numbers (λ) above 20.²⁹ With dilute solutions, the diffusion coefficients of hydroxide and bicarbonate are 5.3 × 10⁻⁵ and 1.2 × 10⁻⁵ cm² s⁻¹, respectively.³⁰ Assuming that the 92% dm **HMT-PMBI-OH⁻** was in bicarbonate form, the hydroxide conductivity would be 4.4 times larger, that is, 43 mS cm⁻¹, which is of the same order of magnitude as for other imidazolium- and benzimidazolium-based polymers.^{8,14,31,32}

Table 1. Properties of HMT-PMBI-OH⁻ at Varying Degrees of Methylation

| dm (%) ^a | IEC (mequiv g ⁻¹) ^b | water uptake (wt %) | λ^c | σ (mS cm ⁻¹) ^d |
|---------------------|--|---------------------|------------------|--|
| ~50 | 0.0 | n/a ^e | n/a ^e | n/a ^e |
| 66 | 1.1 | 29 ± 4 | 15 | 0.10 ± 0.03 |
| 73 | 1.5 | 36 ± 3 | 13 | 0.45 ± 0.06 |
| 80 | 2.0 | 42 ± 3 | 12 | 1.4 ± 0.2 |
| 89 | 2.5 | 80 ± 20 | 18 | 6.1 ± 1.2 |
| 92 | 2.7 | 180 ± 50 | 37 | 9.7 ± 0.6 |
| ~100 | 3.1 | n/a ^f | n/a ^f | n/a ^f |

^aDegree of methylation as determined by ¹H NMR. ^bHydroxide ion-exchange capacity as calculated from ¹H NMR. ^cH₂O/OH⁻ mole ratio. ^dIonic conductivity at 22 °C when fully hydrated. ^eCould not be cast from DMSO due to its insolubility. ^fWater-soluble material.

The hydroxide stability of 92% dm HMT-PMBI dissolved in 2 M KOD/CD₃OD/D₂O at 60 °C over 7 days (see SI) was monitored; these conditions are known to strongly accelerate degradation.³¹ The stability test was carried out in polypropylene tubes as silica glass leads to precipitates in strongly basic conditions.³² Samples were extracted periodically and analyzed by ¹H NMR (Figure S14). The chemical shifts of the peaks associated with the polymer were unchanged over the 7 days. However, several of the aromatic peaks slowly vanished after 63 h, suggestive of deuterium exchange, as opposed to degradation. This was proved by carrying out the same experiment for 4 days in KOD/CD₃OD/D₂O followed by 4 days in KOH/CH₃OH/H₂O. The spectra of 92% dm HMT-PMBI (Figure 2) show the disappearance of two aromatic peaks due to deuterium-exchange, which are fully recovered after hydrogen-exchange.

It is important to note that several new peaks appeared in all of the degradation test spectra and continued to grow over time at 1.27 ppm (broad singlet), 1.23 ppm (sharp singlet), and 0.83 ppm (multiplet). These peaks were found to arise from the polypropylene tube, as observed in a control experiment shown

in Figure S15, an observation that does not appear to have been reported by others.

Since no new NMR peaks were formed from 92% dm HMT-PMBI over 7 days, it can be assumed that steric C2-protection of the cationic group has been successful at negating ring-opening degradation. As the 92% dm HMT-PMBI-OH⁻ is not fully methylated, the uncharged *N*-methyl groups were used as an internal standard for ¹H NMR integration relative to the cationic *N*-methyl groups. Integration of these peaks indicates the dm% varies by <1% over the 7 day degradation experiment and 8 day deuterium-exchange experiment, thus providing evidence that there is also negligible nucleophilic displacement occurring, which showcases the remarkable hydroxide stability of this polymer.

An interesting aspect of the HMT group is the atropisomerization it exhibits in solution at rt, as shown in Figure 3. With a concentration of 50 mg of **4** per 1.0 mL of DMSO-*d*₆ (50 g/L), the NMR peaks at 1.98 ppm appear as a quartet but in fact are two overlapping sets of two singlets derived from the inner 2, 2'', 6, and 6'' methyl groups from hindered rotation around the central phenyl ring. The chemical shifts are further influenced by concentration, suggestive of aggregation. Likewise, this effect is also observed using variable-temperature ¹H NMR of **4** (50 g/L) between 25 and 148 °C, as shown in Figure S16. At 25 °C, isomerization is slower than the 500 MHz ¹H NMR time-scale but faster at 50 °C, going from an apparent quartet to two peaks. Upon increasing the temperature, the two peaks coalesce at 101 °C and continue to move apart at 148 °C, explained by the average angle of preference around the central phenyl ring. Atropisomerization may be important in choosing the temperature used to cast or spray-coat HMT-PMBI-OH⁻ as this may influence the solid state conformation of the polymer, free volume, and various physical properties. In this work, membranes were cast only from DMSO at 86 °C.

In summary, novel alkaline anion exchange ionenes were synthesized, which showed exceptionally high stability in accelerated degradation conditions as well as possessing

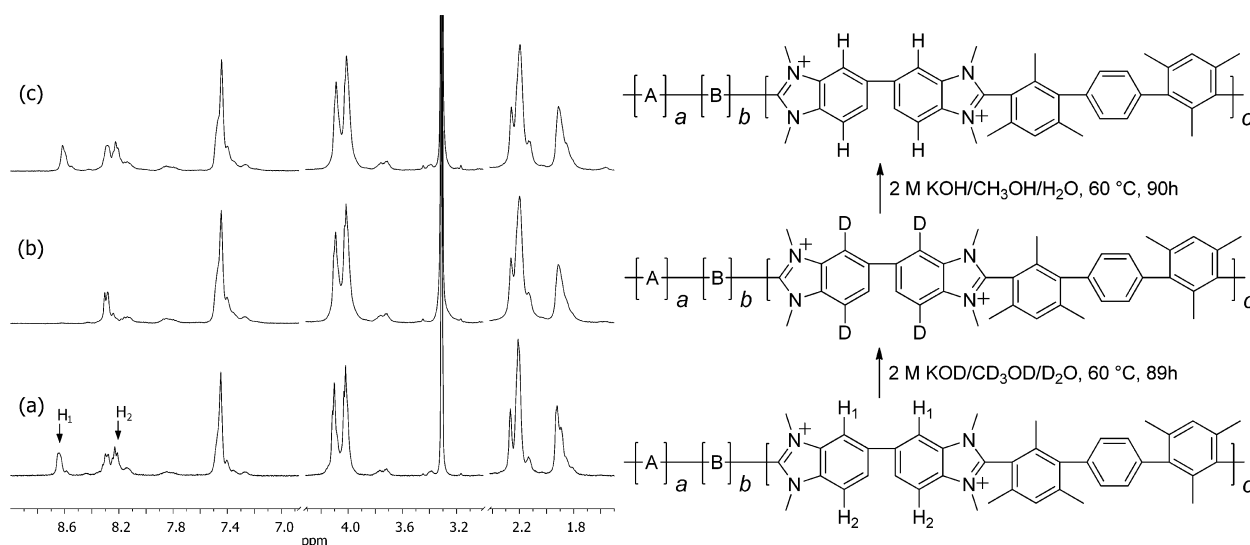


Figure 2. Stacked ¹H NMR spectra regions and corresponding chemical structures of 92% dm HMT-PMBI (a) initially in its cast, iodide form, (b) after 89 h in 2 M KOD/CD₃OD/D₂O at 60 °C to exchange the polymer to the deuterium form, and (c) after 90 h of the deuterium-exchanged polymer being subjected to 2 M KOH/CH₃OH/H₂O at 60 °C conditions to return the polymer to its original hydrogen-based form. The anions are not shown for clarity.

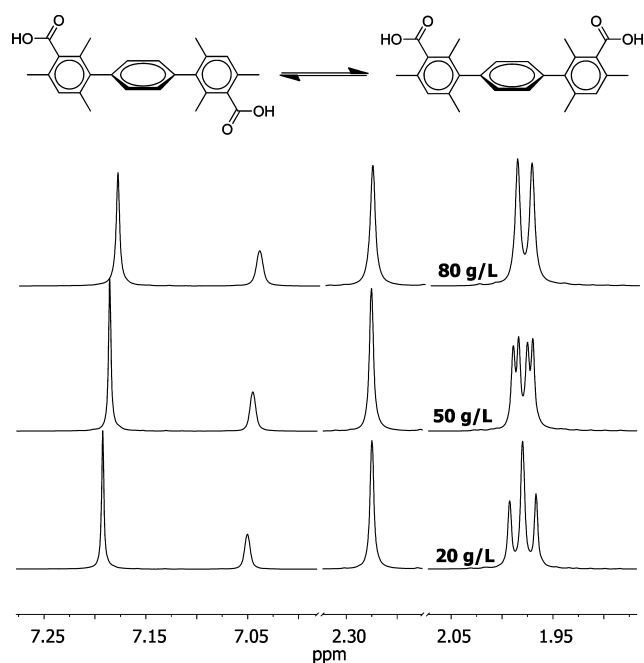


Figure 3. Racemization of compound **4** in solution as observed by the ^1H NMR (500 MHz) in $\text{DMSO-}d_6$ at 20, 50, and 80 g/L concentrations.

solubility in alcohol-based solvents, giving them potential application in fuel cells and water electrolyzers. These materials have also been shown to comprise of an atropisomeric unit, which can be further investigated, as can the possibility of cross-linking via the remaining basic nitrogens. Incorporation and analysis of these materials in electrochemical conversion devices is currently under investigation.

■ ASSOCIATED CONTENT

● Supporting Information

Includes synthetic conditions, experimental details, membrane preparation, and characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: holdcrof@sfu.ca.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by the Natural Sciences and Engineering Research Council of Canada (NSERC). We thank Dr. Andrew Lewis for his technical assistance with variable-temperature ^1H NMR spectroscopy.

■ REFERENCES

- (1) Varcoe, J. R.; Slade, R. C. T. *Fuel Cells* **2005**, *5*, 187–200.
- (2) Pan, J.; Chen, C.; Zhuang, L.; Lu, J. *Acc. Chem. Res.* **2012**, *45*, 473–481.
- (3) Kreuter, W.; Hofmann, H. *Int. J. Hydrogen Energy* **1998**, *23*, 661–666.
- (4) Wang, J.; Wang, J.; Zhang, S. *J. Membr. Sci.* **2012**, *415–416*, 205–212.
- (5) Zhang, B.; Gu, S.; Wang, J.; Liu, Y.; Herring, A. M.; Yan, Y. *RSC Adv.* **2012**, *2*, 12683–12685.

- (6) Noonan, K. J. T.; Hugar, K. M.; Kostalik, H. A.; Lobkovsky, E. B.; Abruña, H. D.; Coates, G. W. *J. Am. Chem. Soc.* **2012**, *134*, 18161–18164.
- (7) Huang, A.; Xia, C.; Xiao, C.; Zhuang, L. *J. Appl. Polym. Sci.* **2006**, *100*, 2248–2251.
- (8) Chen, D.; Hickner, M. A. *ACS Appl. Mater. Interfaces* **2012**, *4*, 5775–5781.
- (9) Thomas, O. D.; Soo, K. J. W. Y.; Peckham, T. J.; Kulkarni, M. P.; Holdcroft, S. *Polym. Chem.* **2011**, *2*, 1641–1643.
- (10) Zha, Y.; Disabb-Miller, M. L.; Johnson, Z. D.; Hickner, M. A.; Tew, G. N. *J. Am. Chem. Soc.* **2012**, *134*, 4493–4496.
- (11) Arges, C. G.; Ramani, V. *Proc. Natl. Acad. Sci. U.S.A.* **2013**, *110*, 2490–2495.
- (12) Long, H.; Kim, K.; Pivovar, B. S. *J. Phys. Chem. C* **2012**, *116*, 9419–9426.
- (13) Ye, Y.; Elabd, Y. A. *Macromolecules* **2011**, *44*, 8494–8503.
- (14) Thomas, O. D.; Soo, K. J. W. Y.; Peckham, T. J.; Kulkarni, M. P.; Holdcroft, S. *J. Am. Chem. Soc.* **2012**, *134*, 10753–10756.
- (15) Rembaum, A.; Baumgartner, W.; Eisenberg, A. *J. Polym. Sci., Part B: Polym. Lett.* **1968**, *6*, 159–171.
- (16) Wang, Y.-J.; Qiao, J.; Baker, R.; Zhang, J. *Chem. Soc. Rev.* **2013**, *42*, 5768–5787.
- (17) Carmo, M.; Doubek, G.; Sekol, R. C.; Linardi, M.; Taylor, A. D. *J. Power Sources* **2013**, *230*, 169–175.
- (18) Tanaka, M.; Koike, M.; Miyatake, K.; Watanabe, M. *Polym. Chem.* **2011**, *2*, 99–106.
- (19) Holdcroft, S. *Chem. Mater.* **2014**, *26*, 381–393.
- (20) Li, N.; Leng, Y.; Hickner, M. A.; Wang, C.-Y. *J. Am. Chem. Soc.* **2013**, *135*, 10124–10133.
- (21) Henkensmeier, D.; Cho, H.; Brela, M.; Michalak, A.; Dyck, A.; Germer, W.; Duong, N. M. H.; Jang, J. H.; Kim, H.-J.; Woo, N.-S.; Lim, T.-H. *Int. J. Hydrogen Energy* **2014**, *39*, 2842–2853.
- (22) Pu, H.; Liu, G. *Polym. Int.* **2005**, *54*, 175–179.
- (23) Hu, M.; Pearce, E. M.; Kwei, T. K. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 553–561.
- (24) Henkensmeier, D.; Kim, H.-J.; Lee, H.-J.; Lee, D. H.; Oh, I.-H.; Hong, S.-A.; Nam, S.-W.; Lim, T.-H. *Macromol. Mater. Eng.* **2011**, *296*, 899–908.
- (25) Henkensmeier, D.; Cho, H.-R.; Kim, H.-J.; Nunes Kirchner, C.; Leppin, J.; Dyck, A.; Jang, J. H.; Cho, E.; Nam, S.-W.; Lim, T.-H. *Polym. Degrad. Stab.* **2012**, *97*, 264–272.
- (26) Yanagi, H.; Fukuta, K. *ECS Trans.* **2008**, *16*, 257–262.
- (27) Yan, J.; Hickner, M. A. *Macromolecules* **2010**, *43*, 2349–2356.
- (28) Hickner, M. A.; Herring, A. M.; Coughlin, E. B. *J. Polym. Sci., Part B: Polym. Phys.* **2013**, *51*, 1727–1735.
- (29) Disabb-Miller, M. L.; Zha, Y.; DeCarlo, A. J.; Pawar, M.; Tew, G. N.; Hickner, M. A. *Macromolecules* **2013**, *46*, 9279–9287.
- (30) Vanýsek, P. *Ionic Conductivity and Diffusion at Infinite Dilution*. In *CRC Handbook of Chemistry and Physics*, 94th ed.; Haynes, W. M., Bruno, T. J., Lide, D. R., Eds.; Taylor & Francis Limited: New York, 2013; pp 5–78; <http://www.hbcpnetbase.com> (accessed February 24, 2014).
- (31) Gu, F.; Dong, H.; Li, Y.; Si, Z.; Yan, F. *Macromolecules* **2014**, *47*, 208–216.
- (32) Lin, B.; Dong, H.; Li, Y.; Si, Z.; Gu, F.; Yan, F. *Chem. Mater.* **2013**, *25*, 1858–1867.