

Metal-Cation-Based Anion Exchange Membranes

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S Supporting Information

ABSTRACT: Here we present the first metal-cation-based anion exchange membranes (AEMs), which were synthesized by copolymerization and cross-linking of a norbornene monomer functionalized with a water-soluble bis(terpyridine)ruthenium(II) complex and dicyclopentadiene. Each ruthenium complex has two associated counteranions, unlike most ammonium- and phosphonium-based membranes with single cation–anion pairs. The resulting AEMs show anion conductivities and mechanical properties comparable to those of traditional quaternary-ammonium-based AEMs as well as good alkaline stability and methanol tolerance. These results suggest that metal-cation-based polymers hold promise as a new class of materials for anion-conducting applications.

Herein we report for the first time the synthesis of metal-cation-based anion exchange membranes (AEMs) via ring-opening metathesis polymerization (ROMP) of a bis(terpyridine)ruthenium(II) complex-functionalized norbornene and a cross-linkable comonomer, dicyclopentadiene (DCPD). AEMs are used in a variety of applications such as electro dialysis and ion exchange processes.^{1,2} As a critical component of fuel cells, AEMs overcome many of the hurdles faced in liquid-electrolyte alkaline fuel cells, including electrolyte leakage and carbon dioxide poisoning, by employing a solid-polymer electrolyte.³ In comparison to proton exchange membranes such as Nafion, AEMs that conduct anions and maintain a high pH in the membrane electrode assembly have the potential to reduce the costs of fuel cell technology while achieving high power output and energy density. These advantages are mainly due to nonprecious metal catalyst stability in a basic environment and reduction of the cathode oxygen reduction overpotential.⁴ Furthermore, oxygenated hydrocarbon fuels such as methanol and ethanol can be effectively employed in AEM fuel cells because of the low oxidation overpotential of these fuels at high pH and reduced fuel crossover.³

To date, most AEMs are based on polymers containing monovalent benzyltrimethyl quaternary ammonium groups, such as quaternized poly(arylene ether sulfone),^{5–7} poly(arylene ether ketone),⁸ poly(phenylene oxide),⁹ poly(phenylene),¹⁰ poly(ether–imide),¹¹ and radiation-grafted fluorinated polymers,¹² as well as olefin-based cross-linked networks.^{13,14} Poor membrane stability in alkaline solutions is a

widely quoted concern with quaternary-ammonium-based AEMs, especially at elevated temperatures (e.g., 80 °C).^{15,16} To circumvent this obstacle and to achieve higher ionic conductivity, researchers continue to explore alternatives to quaternary ammonium groups. Recently, Yan and co-workers synthesized a quaternary phosphonium-based ionomer, tris-(2,4,6-trimethoxyphenyl)polysulfone–methylene quaternary phosphonium hydroxide, which had high hydroxide conductivity (27 mS/cm at 20 °C).⁴ Additionally, Zhang and co-workers reported the synthesis of AEMs based on benzyl quaternary guanidinium hydroxide groups with high conductivity (45 mS/cm at 20 °C) and good alkaline stability.¹⁷ However, these systems are all based on monovalent organic cations and can carry only one anion per cationic group. On the other hand, multivalent charged metal cations have the capacity to associate more than one anion per cationic center. Multivalent cations have the potential to increase the ion exchange capacity of the membrane, leading to higher ion conductivity. To the best of our knowledge, mechanically stable multivalent metal-cation-based AEMs have not yet been synthesized or investigated.

Among the potential metal species, ruthenium was chosen because bis(terpyridine)Ru(II) complexes are well-known for their temperature and pH stabilities.^{18,19} In an AEM fuel cell, the oxidation potential of hydrogen at the anode at pH 14 is +0.83 V (vs SHE for all the potentials reported here), and the reduction potential of oxygen at the cathode is +0.40 V.³ In comparison, almost all of the bis(terpyridine)Ru(II) complexes have more negative redox potentials, which fall outside of the operational potentials of a fuel cell.^{20–22} For example, the oxidation potentials of the first oxidation wave of Ru(terpyridine)₂²⁺ complexes ranges between –0.98 and –1.08 V (pH 14 for all of the potentials reported here), and the reduction potential of the first reduction wave is –1.41 V.^{21,22} Therefore, the Ru complexes in the AEM are unlikely to be destabilized significantly by the redox processes in the fuel cell.

The Ru ion in the complex was also selected because it has a +2 charge and two associated anions per metal center.¹⁸ To date, most polymer-containing Ru complexes have non-coordinating counterions such as PF₆[–] or BF₄[–],²³ which make the complexes insoluble in water and thus unable to undergo the necessary ion exchange to make bicarbonate- or hydroxide-conducting AEMs. Additionally, high water uptake

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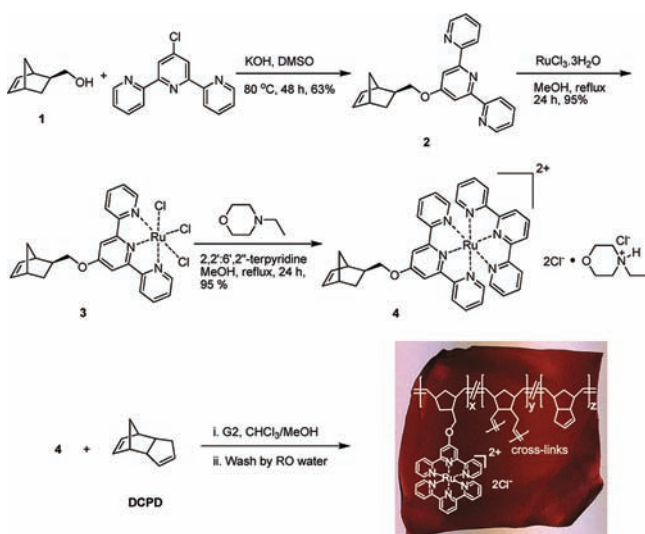


Figure 1. Synthesis of monomer **4** and the corresponding AEM. A photograph of a representative membrane is also shown.

by the hydrophilic structure of the membrane is a key facet for inducing high ionic conductivity. Here we developed hydrophilic cross-linked AEMs based on a novel water-soluble heteroleptic bis(terpyridine)Ru(II) complex and investigated their properties as a function of the amount of DCPD cross-linker.

The bis(terpyridine)Ru(II) complex-functionalized norbornene monomer, **4**, was synthesized in three straightforward, high-yielding steps (Figure 1). The monomer was isolated as a cosalt, which was not surprising considering that the purification of previously reported Ru complexes has often used the noncoordinating counterion salts to precipitate those complexes from water.^{18,19,24} Although the *N*-ethylmorpholinium chloride byproduct was difficult to separate from the monomer, it was easily removed from the polymer or the cross-linked network, as explained later. Employing a monomer with the metal cation already present enabled the synthesis of the AEM without postpolymerization functionalization. DCPD was used as a cross-linkable comonomer, and the Grubbs' second-generation catalyst (G2) was used for the ROMP because of its high air stability and exceptional functional group tolerance. Coates and co-workers recently showed that robust, conductive AEMs can be synthesized by G2-catalyzed cross-linking of quaternary-ammonium-functionalized norbornene and DCPD.¹³

In the present work, the polymer was synthesized by cross-linking **4** and DCPD using G2 in a chloroform/methanol solvent mixture at room temperature. The homogeneous solution was stirred vigorously for 1 min and then transferred to a flat, preheated (ca. 40 °C) aluminum pan, where the polymerization continued. Subsequent solvent evaporation yielded a translucent, thin membrane. The *N*-ethylmorpholinium chloride byproduct was then removed by soaking the membrane in excess deionized water overnight. The removal of *N*-ethylmorpholinium chloride was confirmed by ¹H NMR and IR analysis of the homopolymer and membrane, respectively, before and after dialysis [Figures S1 and S2 in the Supporting Information (SI)]. After dialysis, the *N*-ethylmorpholinium chloride quartet at 3.23 ppm and triplet at 1.38 ppm were absent, indicating successful removal of the byproduct from the homopolymer. The band observed at 1110 cm⁻¹, attributed to

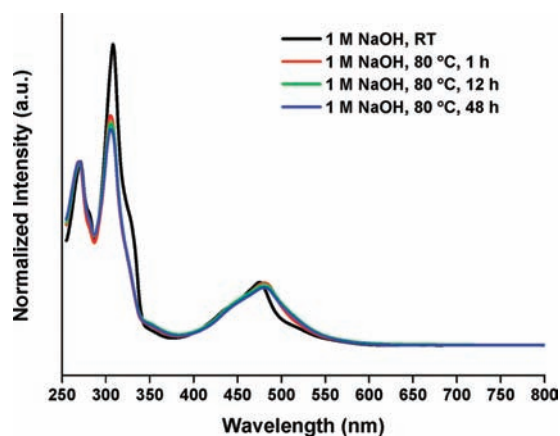


Figure 2. UV-vis spectra of monomer **4** in 1 M NaOH solution at 80 °C at various times. The ligand-centered absorption peak at 270 nm was used to normalize the intensity.

the C–O–C ring stretching vibration,²⁵ was also absent for both the homopolymer and membrane after dialysis.

Stability of these AEMs in an alkaline environment is important, as their tetraalkylammonium counterparts are known to degrade under basic conditions.^{3,14,26} The alkaline stability of these AEMs was investigated by UV-vis spectroscopy using the three representative absorption peaks for the Ru complex in the UV-vis region. The Ru complex exhibited excellent stability in 1 M NaOH solution at room temperature over 6 months (Figure S3). As shown in Figure 2, when the metal complex was heated to 80 °C in 1 M NaOH, some minor changes in the spectra were observed after 1 h. Upon continued heating for extended times, no further changes were observed. To examine the cross-linked membrane, UV-vis spectra were collected for the bicarbonate form before and after exposure to 1 M NaOH at 80 °C, and essentially no changes were observed (Figure S4). The stability of the membrane was also confirmed by tracking the mass changes and conductivity upon exposure to alkaline solutions. Figure S5 shows some minor weight loss initially (~3% at 2 h) that stabilized at longer times (12–24 h). The mass loss may be related to chemical changes in the membrane, but removal of more sol fraction (non-cross-linked chains) cannot be ruled out. The membranes showed stable hydroxide conductivity, with only the most highly cross-linked membrane demonstrating a few mS/cm decrease upon exposure to 1 M KOH for 2 h (Figure S6).

The properties of the AEMs were tuned by varying the molar ratio of **4** to DCPD. The thickness was maintained at 103 ± 5 μm. Membranes were characterized in both their OH⁻ and HCO₃⁻ forms. The OH⁻ conductivity was measured in water under an active argon gas purge in an attempt to limit the exposure of the OH⁻-form membranes to CO₂ (Figure S7). The rapid uptake of CO₂ was recently documented by Yanagi and Fukuta, who reported that OH⁻ was neutralized quickly upon exposure to air because of the rapid absorption of CO₂.²⁷ Hickner and co-workers confirmed the conversion of AEMs from the OH⁻ to the HCO₃⁻ form, causing a corresponding decrease in ionic conductivity due to the lower mobility of HCO₃⁻ ions in dilute solution.²⁸

As shown in Table 1, the molar ratio of **4** to DCPD was changed from 1:2 to 1:10 to investigate how increasing the hydrophobic content and cross-linking density would impact the membrane properties. As expected, increasing the DCPD content reduced the theoretical ion exchange capacity (IEC),

Table 1. Membrane Properties at Various 4:DCPD Ratios

4:DCPD ratio	1:2	1:5	1:10
theoretical IEC (mequiv/g) ^a	2.0	1.4	1.0
liquid water uptake (wt %) ^b	432	126	30
E_a (kJ/mol) ^c	14	16	22
$\sigma_{30^\circ\text{C}}$ (mS/cm) ^d	19.6	28.6	14.1
tensile stress at break (MPa) ^e	0.6 ± 0.1	6.2 ± 0.4	27.0 ± 0.5
tensile strain at break (%) ^e	53 ± 2	80 ± 11	87 ± 16

^aIon exchange capacity calculated on the basis of the chemical structure. ^bIn the OH⁻-form at 30 °C. Liquid water uptake = $[(m_{\text{wet}} - m_{\text{dry}})/m_{\text{dry}}] \times 100\%$. ^cActivation energy for HCO₃⁻ conduction. ^dOH⁻ conductivity at 30 °C. ^eDetermined by mechanical testing of the membranes using dynamic mechanical analysis. Standard errors were calculated from three samples.

which was calculated from the chemical composition of the membrane, resulting in a decrease in the water uptake. The activation energy for HCO₃⁻ conduction (E_a) increased from 14 to 22 kJ/mol with decreasing water uptake, which was coupled with a decrease in OH⁻ conductivity from 28.6 to 14.1 mS/cm as a result of the lower IEC and water uptake. As shown in Figure S8, both the water uptake and ionic conductivity increased with increasing humidity (over the range from 22 to 95% relative humidity), in agreement with results for other reported membranes.^{29,30} These membranes exhibited mechanical properties comparable to those of other cross-linked systems. The tensile stress at break increased from 0.6 to 27.0 MPa as the AEM cross-linking density increased, while Coates and co-workers reported cross-linked membranes with tensile stress at break from 2.3 to 16 MPa.^{13,31} The tensile strain at break (53–87%) also fell into the range observed for those cross-linked membranes (7.2–170%).^{13,31} Generally, the properties of our Ru-complex-based AEMs followed the same trends as more traditional quaternary-ammonium-based AEMs and exhibited the mechanical properties necessary for use as fuel cell membranes.^{5,6,28}

Figure 3 shows that the HCO₃⁻ conductivity increased linearly with temperature for all three AEMs when they were fully hydrated.^{7,14} The AEMs with 4:DCPD = 1:2 and 1:5 had similar conductivities over the entire temperature range investigated, while the conductivity of the AEM with 4:DCPD = 1:10 was lower. This is most likely due to its high DCPD loading and subsequent low water uptake. At 50 °C, the HCO₃⁻ conductivities of the AEMs with 4:DCPD = 1:2 and 1:5 were both ca. 9.8 mS/cm, which is comparable to the values reported for quaternary ammonium AEMs in the HCO₃⁻ form (10.1–25.7 mS/cm).^{14,28} In addition, the cross-linked AEMs with a quaternary ammonium monomer and DCPD reported by Coates and co-workers exhibited a OH⁻ conductivity of 28 mS/cm at 50 °C,¹³ and the quaternary phosphonium AEM reported by Yan and co-workers had a OH⁻ conductivity of 27 mS/cm at 20 °C.⁴ Overall, these Ru-complex-based AEMs possess conductivity comparable to those of traditional organic-cation-based counterparts.

The OH⁻/HCO₃⁻ and Cl⁻/HCO₃⁻ conductivity ratios for the samples are reported in Figure 4. From the dilute-solution mobilities of the anions, the OH⁻/HCO₃⁻ conductivity ratio should be 4.4 and the Cl⁻/HCO₃⁻ conductivity ratio should be 1.7, assuming that the activities of the ions remain constant (see the SI for HCO₃⁻-form and Cl⁻-form water uptake values).^{32,33} The low water uptake of the membrane with 4:DCPD = 1:10 was likely the cause of the low conductivity ratios, while the membrane with 4:DCPD = 1:5 with high water uptake had

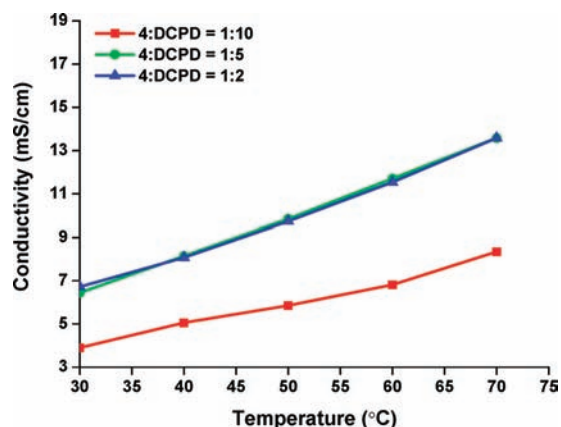


Figure 3. Impact of temperature on the conductivity for the AEMs in the HCO₃⁻ form. Conductivities were measured with samples exposed to liquid water.

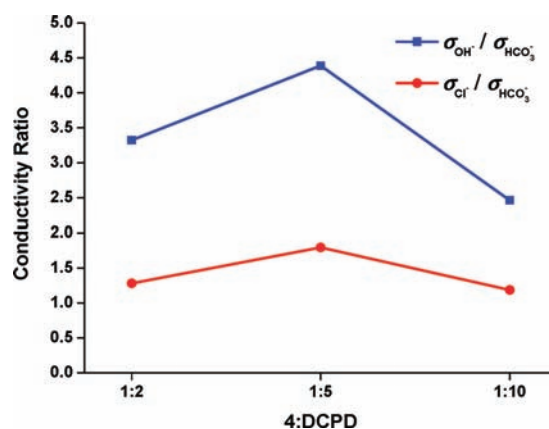


Figure 4. The OH⁻/HCO₃⁻ (blue) and Cl⁻/HCO₃⁻ (red) conductivity ratios for all three AEMs. Conductivities were measured with samples exposed to liquid water at 30 °C.

ratios of 4.4 and 1.8, as could be expected. The membrane with 4:DCPD = 1:2, which had the largest water uptake, showed a lower conductivity than the 1:5 sample, most likely as a result of ion dilution and a decrease in the charge carrier density.

Direct methanol fuel cells (DMFCs) and other liquid-fed fuel cells are of great interest, as many liquid fuels have higher volumetric energy density than hydrogen. With the potential of liquid fuels in mind, the dimensional swelling of the membranes in the bicarbonate form was studied to evaluate their methanol tolerance. Ideally, relative to pure water, DMFC membranes should not swell appreciably upon exposure to aqueous methanol solutions at typical device operating temperatures (50–80 °C). Figure 5 shows the volume swelling ratio (Q) of the membranes in aqueous methanol solutions of different concentrations normalized by the volume swelling ratio in pure water. No significant increase in swelling was observed for any of the membranes in 2 M aqueous methanol solution after 2 h at 80 °C relative to their swelling in liquid water. Even when the concentration of the methanol solution was increased to 10 M the AEMs with 4:DCPD = 1:5 and 1:10 still showed only minor differential swelling. This exceptional methanol tolerance is likely due to the high loading of the DCPD cross-linker and is important for future applications because it could allow for the use of more concentrated fuel in the cell, resulting in higher energy density.

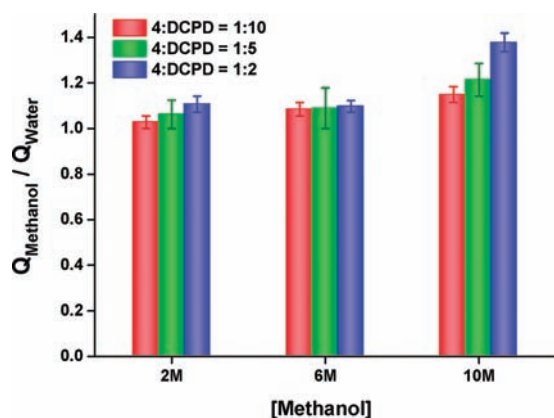


Figure 5. Methanol tolerance as evaluated by the volume swelling ratio (Q) in aqueous methanol solutions of different concentrations normalized to the Q value in pure water. Standard errors were calculated from three samples.

In summary, novel multivalent metal-cation-based AEMs have been synthesized by cross-linking a bis(terpyridine)Ru(II) complex-functionalized norbornene and a hydrocarbon comonomer. These AEMs show conductivity and mechanical strength comparable to those of traditional quaternary-ammonium-based AEMs. The present system also exhibits the potential for applications in direct methanol fuel cells because of its excellent methanol tolerance. Studies are underway to investigate the use of other metals in these metal-cation-based AEMs, which could further improve the stability and reduce the cost of these already promising materials.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures and characterization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Sata, T. *J. Membr. Sci.* **2000**, *167*, 1.
- (2) Xu, T. W. *J. Membr. Sci.* **2005**, *263*, 1.
- (3) Varcoe, J. R.; Slade, R. C. T. *Fuel Cells* **2005**, *5*, 187.
- (4) Gu, S.; Cai, R.; Luo, T.; Chen, Z. W.; Sun, M. W.; Liu, Y.; He, G. H.; Yan, Y. S. *Angew. Chem., Int. Ed.* **2009**, *48*, 6499.
- (5) Hibbs, M. R.; Hickner, M. A.; Alam, T. M.; McIntyre, S. K.; Fujimoto, C. H.; Cornelius, C. J. *Chem. Mater.* **2008**, *20*, 2566.

- (6) Wang, J. H.; Zhao, Z.; Gong, F. X.; Li, S. H.; Zhang, S. B. *Macromolecules* **2009**, *42*, 8711.
- (7) Pan, J.; Lu, S. F.; Li, Y.; Huang, A. B.; Zhuang, L.; Lu, J. T. *Adv. Funct. Mater.* **2010**, *20*, 312.
- (8) Tanaka, M.; Koike, M.; Miyatake, K.; Watanabe, M. *Macromolecules* **2010**, *43*, 2657.
- (9) Wu, L.; Xu, T. W.; Wu, D.; Zheng, X. *J. Membr. Sci.* **2008**, *310*, 577.
- (10) Hibbs, M. R.; Fujimoto, C. H.; Cornelius, C. J. *Macromolecules* **2009**, *42*, 8316.
- (11) Wang, G. G.; Weng, Y. M.; Chu, D.; Xie, D.; Chen, R. R. *J. Membr. Sci.* **2009**, *326*, 4.
- (12) Varcoe, J. R.; Slade, R. C. T.; Yee, E. L. H.; Poynton, S. D.; Driscoll, D. J.; Apperley, D. C. *Chem. Mater.* **2007**, *19*, 2686.
- (13) Clark, T. J.; Robertson, N. J.; Kostalik, H. A.; Lobkovsky, E. B.; Mutolo, P. F.; Abruna, H. D.; Coates, G. W. *J. Am. Chem. Soc.* **2009**, *131*, 12888.
- (14) Robertson, N. J.; Kostalik, H. A.; Clark, T. J.; Mutolo, P. F.; Abruna, H. D.; Coates, G. W. *J. Am. Chem. Soc.* **2010**, *132*, 3400.
- (15) Zagorodni, A. A.; Kotova, D. L.; Selemenev, V. F. *React. Funct. Polym.* **2002**, *53*, 157.
- (16) Neagu, V.; Bunia, I.; Plesca, I. *Polym. Degrad. Stab.* **2000**, *70*, 463.
- (17) Wang, J. H.; Li, S. H.; Zhang, S. B. *Macromolecules* **2010**, *43*, 3890.
- (18) Aamer, K. A.; Tew, G. N. *Macromolecules* **2007**, *40*, 2737.
- (19) Gohy, J. F.; Lohmeijer, B. G. G.; Varshney, S. K.; Schubert, U. S. *Macromolecules* **2002**, *35*, 7427.
- (20) Maestri, M.; Armaroli, N.; Balzani, V.; Constable, E. C.; Thompson, A. M. W. C. *Inorg. Chem.* **1995**, *34*, 2759.
- (21) Hutchison, K.; Morris, J. C.; Nile, T. A.; Walsh, J. L.; Thompson, D. W.; Petersen, J. D.; Schoonover, J. R. *Inorg. Chem.* **1999**, *38*, 2516.
- (22) Collin, J. P.; Guillerez, S.; Sauvage, J. P.; Barigelletti, F.; DeCola, L.; Flamigni, L.; Balzani, V. *Inorg. Chem.* **1991**, *30*, 4230.
- (23) Schubert, U.; Hofmeier, H.; Newkome, G. R. *Modern Terpyridine Chemistry*; Wiley-VCH: Weinheim, Germany, 2006.
- (24) Aamer, K. A.; De Jeu, W. H.; Tew, G. N. *Macromolecules* **2008**, *41*, 2022.
- (25) Malherbe, F. E.; Bernstein, H. J. *J. Am. Chem. Soc.* **1952**, *74*, 4408.
- (26) Mürner, H. R.; Chassat, E.; Thummel, R. P.; Bünzli, J. C. G. *J. Chem. Soc., Dalton Trans.* **2000**, 2809.
- (27) Yanagi, H.; Fukuta, K. *ECS Trans.* **2008**, *16*, 257.
- (28) Yan, J. L.; Hickner, M. A. *Macromolecules* **2010**, *43*, 2349.
- (29) Xu, K.; Oh, H.; Hickner, M. A.; Wang, Q. *Macromolecules* **2011**, *44*, 4605.
- (30) Zhou, Z.; Dominey, R. N.; Rolland, J. P.; Maynor, B. W.; Pandya, A. A.; DeSimone, J. M. *J. Am. Chem. Soc.* **2006**, *128*, 12963.
- (31) Kostalik, H. A.; Clark, T. J.; Robertson, N. J.; Mutolo, P. F.; Longo, J. M.; Abruna, H. D.; Coates, G. W. *Macromolecules* **2010**, *43*, 7147.
- (32) Dean, J. A. *Lange's Handbook of Chemistry*, 15th ed.; McGraw-Hill: New York, 1999.
- (33) Vanysek, P. In *CRC Handbook of Chemistry and Physics*, 83rd ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 2002.