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A Ring-Opening Metathesis Polymerization Route to Alkaline Anion Exchange Membranes: Development of Hydroxide-Conducting Thin Films from an Ammonium-Functionalized Monomer

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A critical component of a fuel cell is the electrolyte membrane, which acts as a barrier between the fuel and oxidant streams and simultaneously transports ions.[1] Nafion, a proton exchange membrane, has dominated the field due its processability, chemical and thermal stability, and high proton conductivity (when properly hydrated).[1b,2] However, Nafion also has some significant drawbacks including high cost[3] along with considerable methanol crossover when used in direct methanol fuel cells, resulting in decreased efficiency.[4] Despite being relatively underdeveloped, alkaline anion exchange membranes (AAEMs), materials that conduct hydroxide ions, offer important benefits such as reduced methanol crossover and greatly enhanced kinetics for the oxygen reduction reaction.[5] This increases fuel cell efficiency and also permits the use of cheaper non-noble metal catalysts making this technology financially more viable.

Some recent important developments in the field of AAEMs come from Varcoe, Slade and co-workers who reported that γ-irradiation-induced functionalization of mixed fluorocarbon/hydrocarbon membranes followed by attachment of tetraalkylammonium ions yield mechanically strong AAEMs with promising hydroxide conductivities and low methanol permeability.[6] Others have shown that polysulfones can act as scaffolds for postpolymerization modification reactions again yielding robust, conductive AAEMs.[7] Both of these examples not only illustrate the remarkable progress made in this area but also reveal limitations in the synthetic approaches employed. Herein we present our work on the facile synthesis and ring-opening metathesis polymerization (ROMP) of a tetraalkylammonium-functionalized norbornene with dicyclopentadiene (**DCPD**) as a cross-linkable comonomer to yield strong, hydroxide-conducting thin films that exhibit negligible swelling in hot aqueous methanol.

We targeted a ROMP route, as olefin metathesis is an extraordinarily powerful C−C bond forming reaction, and the use of air-stable Grubbs' second generation catalyst ([Ru]) enables functionalized monomers to be polymerized due to its exceptional tolerance.[8] By employing monomers with the tetraalkylammonium moiety already present, AAEM synthesis is greatly simplified because postpolymerization modifications are unnecessary. Monomer **1** was prepared in three straightforward steps in 62% overall isolated yield as a crystalline solid (Figure 1). The lack of β-hydrogen atoms in **1** prevents degradation by Hofmann elimination and increases ammonium group stability.[9,10] Additionally, trimethylammonium groups exhibit good stability under alkaline conditions at elevated temperatures.[11]

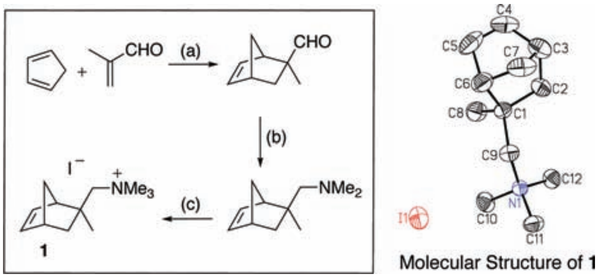

Figure 1. Synthetic procedure for monomer *rac*-**1**: (a) 10 mol % BCl_3, CH_2Cl_2, −50 °C, 1.5 h, 92%. (b) Me_2NH, $Na[BH(OAc)_3]$, 20 °C, 16 h, 83%. (c) MeI, acetone, 20 °C, 16 h, 80%.

Hillmyer and co-workers have recently shown that robust nanoporous composites can be constructed by the [Ru]-catalyzed copolymerization/cross-linking of **DCPD** with block copolymers containing pendant norbornene groups.[12] We hypothesized that this cross-linking reaction would benefit our AAEM synthesis by making film casting easier and film properties more tunable and would also render the ionomer less likely to swell and dissolve in aqueous solutions. Additionally, Holdcroft and DeSimone have independently described liquid polymer electrolytes that can be readily cross-linked to yield membranes with high proton conductivity.[13] They attribute this to increased incorporation of acidic sulfonate groups made possible by the cross-linking route without any solubility or swelling issues.

In the present work, thin copolymer films were synthesized by combining [Ru] with a chloroform solution of **1** and **DCPD** at room temperature (Figure 2). After 1 min of vigorous stirring, the homogeneous solution was transferred to a flat, preheated glass dish where the polymerization continued, followed by solvent evaporation yielding the clear, thin film.

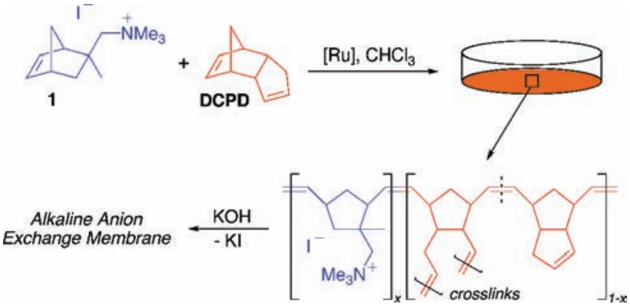

Figure 2. Procedure for AAEM synthesis.

The thickness and properties of the films could be easily controlled by simply varying the amount and molar ratios, respectively, of **1** to **DCPD**. Upon conversion to the hydroxide form, it became clear that films with **1** as the major component (e.g., a molar ratio of **1**:**DCPD** greater than 1:1) could not be quantitatively evaluated due to significant swelling and hydrogel formation.

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Table 1. Characterization Data for AAEMs Synthesized by the ROMP of **1** and **DCPD**

measurement	2:1 **DCPD:1**	1:1 **DCPD:1**
IEC (mmol OH^-/g)[a]	1.0	1.4
% swelling in methanol[b]	1.7	n.d.[c]
tensile stress at break (MPa)[d]	16 ± 6	2.3 ± 0.5
% tensile strain at break[d]	7.2 ± 3	26 ± 3
σ_{20} (mS/cm)[e]	14 ± 2	18 ± 2
σ_{50} (mS/cm)[e]	21 ± 4	28 ± 3

[a] Ion exchange capacity determined by titration, average of two trials. [b] Three-dimensional swelling of AAEM after sitting in 2 M aqueous methanol at 60 °C for 2 h, average of two trials. [c] Not determined due to uncontrollable curling of the film. [d] Mechanical testing of the films, average of four trials. [e] Hydroxide conductivities of the AAEMs fully immersed in water, average of four trials. σ_{20} and σ_{50} are measurements at 20 and 50 °C, respectively.

Similarly, AAEMs comprised of considerable amounts of **DCPD** (e.g., a ratio of **DCPD:1** greater than 2:1) were exceptionally strong but were not sufficiently conductive due to decreased ionicity.

Overall, our studies indicated that the optimal AAEMs, with respect to mechanical integrity and hydroxide conductivity, had a **DCPD:1** molar ratio of either 2:1 or 1:1. Detailed characterization data are provided in Table 1. The average ion exchange capacities (IECs) for the 2:1 and 1:1 samples are 1.0 and 1.4 mmol OH^-/g, respectively, and fall into the range observed for Nafion-117 (0.91 mmol H^+/g)[13b] as well as AAEMs reported by other groups.[6,7] The theoretical IECs for the 2:1 and 1:1 films are 1.75 and 2.28 mmol OH^-/g, respectively; such variations are commonly observed.[6,7a]

We also evaluated the dimensional swelling of the 2:1 sample. An ideal membrane will not swell appreciably in length, width, or thickness upon exposure to solvents contained within a fuel cell at typical operating temperatures (50−80 °C). Encouragingly, our results indicate that negligible swelling occurs in 2 M aqueous methanol after 2 h at 60 °C. To further test the methanol tolerance of this material, we performed the same measurements using more concentrated aqueous methanol solutions. Indeed significant swelling (e.g., >10%) was not observed until immersion into methanol solutions greater than 8 M. This exceptional methanol tolerance is likely attributable to the presence of the hydrocarbon **DCPD** cross-linker as the major component.

The mechanical properties of both samples were evaluated using tensile stress−strain measurements. The 2:1 sample exhibited considerable tensile strength with an average 16 MPa of stress resulting in 7.2% strain. This compares favorably to the non-cross-linked films reported by Varcoe and Slade which range from 45 to 70% strain at 13−18 MPa.[6] The toughness of the 2:1 film can also be accounted for by the cross-linked **DCPD** regions. Further supporting this is the dramatic decrease in toughness observed with lower **DCPD** loadings; only 2.3 MPa were required to break the 1:1 sample.

The in-plane hydroxide conductivity was determined for each film composition at both 20 and 50 °C. The 2:1 sample had a conductivity of 14 mS/cm at room temperature that increased to 21 mS/cm at 50 °C. Moreover, increasing the ionicity with higher loadings of **1** in the 1:1 sample led to higher conductivities. At 20 °C, this membrane exhibited conductivity at 18 mS/cm that rose to 28 mS/cm at 50 °C. This places the 1:1 film among the highest conducting AAEMs reported to date. For example, Cornelius and co-workers' optimized system conducts at 35 mS/cm at 30 °C[7a] while that of Varcoe and Slade has a conductivity of 34 mS/cm at 50 °C.[6]

In summary, we have developed a ROMP route to AAEMs *via* the copolymerization of **1** with **DCPD**. The thin films generated are mechanically strong and exhibit high hydroxide ion conductivities and exceptional methanol tolerance. Future work will focus on studying their efficacy under operating conditions and investigating AAEMs with saturated polymer backbones, as they may be oxidatively more stable than their unsaturated counterparts. We are also generating new materials that retain excellent mechanical properties but display increased hydroxide conductivity.

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Supporting Information Available: Complete experimental procedures, characterization data, and crystallographic details. This information is available free of charge via the Internet at http://pubs.acs.org.

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