



Preparation and characterization of an alkaline anion exchange membrane from chlorinated poly(propylene) aminated with branched poly(ethyleneimine)



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ABSTRACT

A new randomly crosslinked polymer is investigated for use as an ion-exchange membrane. The polymer was produced through amination of chlorinated poly(propylene) (PP) with poly(ethyleneimine) (PEI) and quaternized with iodoethane. The synthesis of the new polymer is confirmed by FTIR ¹H and ¹³C NMR. The microstructure of the polymer consists of aggregates on the order of 1 μm. Environmentally controlled small and wide angle X-ray analysis showed a relatively featureless amorphous morphology over length scales less than 105 nm through a full range of humidity environments. Little physical swelling of the films were observed, but very high internal water uptake was observed with λ = 50. The highest in-plane ionic conductivity with chloride as the counter ion observed was 0.29 mS cm⁻¹ at 90 °C and 95% relative humidity. Infrared spectroscopy was used to monitor the relatively rapid rate of counter-ion reaction of hydroxide with ambient CO₂ to form a mixture of carbonate and bicarbonate when exposed to air.

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1. Introduction

Anion exchange polymers have applications as ion exchange resins and as membranes for water purification [1], Li–air batteries, and in polymer exchange membrane (PEM) fuel cells [2]. PEM Fuel cells show promise as alternatives to current energy conversion devices in transportation and stationary applications as well as for use in portable devices. There is currently a large amount of interest in using anion exchange membranes (AEMs) as the electrolyte in alkali fuel cells, because of the increased power density obtained with a solid electrolyte. AEM fuel cells (AEMFCs) have advantages over proton exchange membrane fuel cells, with the potential for direct use of methanol or more complex fuels, and the potential use of non-precious metal catalysts [2]. Commercial AEMs are available from companies such as Tokuyama [3], Solvay Plastics [4], Dupont, and Fumatech [5], although many of these materials are optimized for non-fuel cell applications such as dialysis. Commercial

membranes with acceptable mechanical properties, long-term alkaline stability and higher anionic conductivity at lower RH for fuel cell applications are still needed [6,7].

In base oxidative attack of the polymer by hydroxide is less important than degradation of the cationic functionalities [2]. It is, therefore, possible to design polymer systems with methylene chain backbones. A simple approach would be to simply react an aminated polymer with a halogenated polymer to form aminated materials that could then be readily quaternized to form a potentially inexpensive AEM. In previous work, Hong et al. have synthesized similar materials by amination of chlorinated polypropylene (CPP) with ethylenediamine (EDA) [8] and amination of PPC with low molecular weight linear PEI [9,10]. It was shown that these materials exhibit good chloride ionic conductivities in water after soaking in NaCl with a maximum of 0.008 and 0.013 S cm⁻¹ for the quaternized EDA/PPC and the quaternized PEI/PPC material respectively. To extend this group of materials, we selected a branched high molecular weight polyethyleneimine (PEI) as a starting material due to the high concentration of quaternizable amine groups throughout the polymer. Polyethyleneimine (PEI) has most commonly been investigated in biological applications where it is often crosslinked and quaternized to form stable cationic polymers. Resulting products have been shown to be

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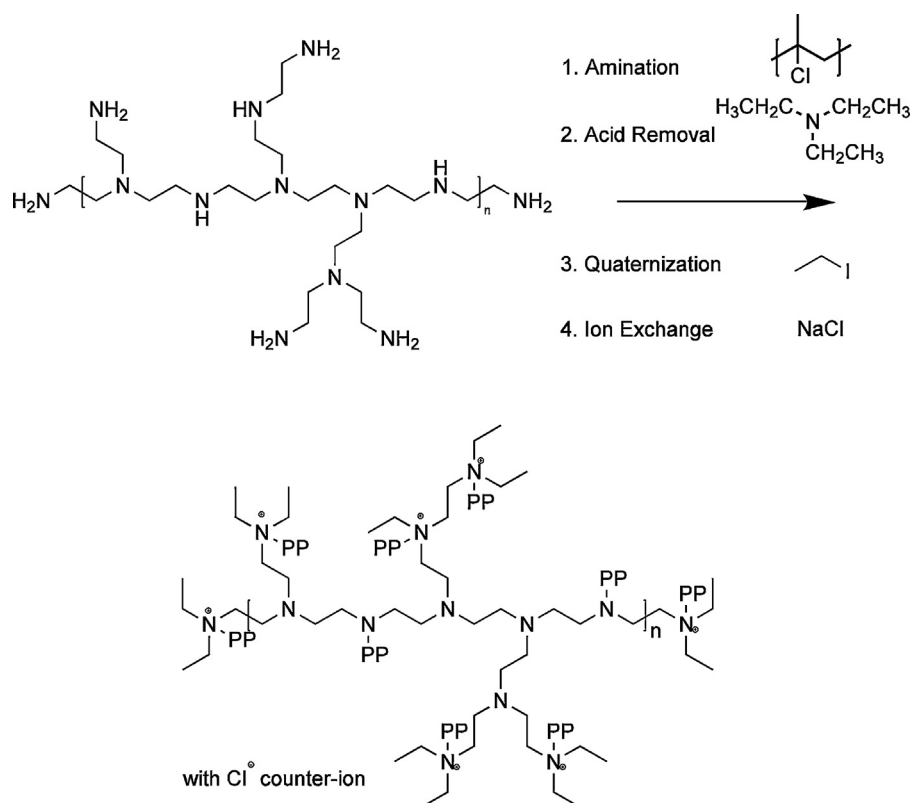


Fig. 1. Reaction sequence of quaternized PEI-PP crosslinked polymer where PP represents a chain of polypropylene.

effective in gene delivery systems and for use as antimicrobial metal surface coatings [11,12]. Its quaternized form has anti-bacterial properties [13,14].

One issue of hydroxide exchange membranes is that hydroxide reacts rapidly with the ambient CO₂ in the air, forming a mixture of carbonate and bicarbonate counter-ions [15]. The presence of bi(carbonate) ions in place of hydroxide ions is detrimental to the conductivity in the membrane due to inherently lower ion mobility. A reaction of a CO₂ molecule with a hydroxide anion in solution can produce a bicarbonate ion as shown in Eq. (1) and it may also produce a carbonate ion in the presence of two hydroxide ions as shown in Eq. (2). When CO₂ reacts with hydroxide ions located as counter anions in a polymeric membrane, the ratio of bicarbonates and carbonates can be determined by titration or FT-IR.



Suzuki et al. have observed these reactions of hydroxide with atmospheric CO₂ within the first minutes of exposure of hydroxide form Tokuyama AEMs to air [16].

Although our synthesized membrane had only a moderate IEC of 0.74(0.02) mequiv. mol⁻¹, unique water uptake and transport were observed through Dynamic Vapor Sorption (DVS) and pulsed-field gradient nuclear magnetic resonance (PFG-NMR) spectroscopy. This paper discusses the transport of anions in the context of beginning to understand the morphology of the material. Quantitative analysis of the formation of carbonates when hydroxide counter-ions in the membrane react with atmospheric CO₂ is included.

2. Experimental

2.1. Materials

Branched polyethylenimine (PEI) (solution ($M_w \sim 2000$ by LS, 50 wt% water), chlorinated polypropylene (CPP) ($M_w \sim 100,000$), trimethylamine ($\geq 99.0\%$) and iodoethane (99%) were used as received (Sigma–Aldrich). All solvents were reagent grade.

2.2. Synthesis

In preliminary studies, branched PEI solution (50 wt% water) was quaternized with a 10-fold excess of iodoethane, under flowing nitrogen at 50 °C using a condenser to minimize evaporation. The final solution was dried in vacuo to produce a highly hygroscopic white powder.

2.2.1. Quaternized PEI-polypropylene (PP-PEI)

The synthetic procedure is outlined in Fig. 1. CPP (5 g) was dissolved in toluene (50 ml) at 60 °C and added to PEI solution (10 g, 50 wt% water) at 60 °C. The amination reaction was performed at 60 °C for 48 h. The hydrochloric acid (HCl) produced during the reaction was neutralized with excess trimethylamine over 24 h. Five fold excess, based on the amine groups in the starting PEI, iodoethane was added to quaternize all the amine groups on the polymer at 60 °C for 48 h. The remaining solvent and excess trimethylamine reactants were then removed by evaporation, and the resulting polymer was washed with dionized (DI) water to extract any unreacted PEI. The resulting material was soaked in toluene, swelling considerably, and spread onto a Teflon casting block to form a membrane. The toluene was removed in vacuo at 40 °C. The resulting membrane was soaked in a 1 M NaCl solution, and again washed with DI water to guarantee that the sample was in a chloride counter-ion form for further characterization. The final

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