

# Preparation of a Functional Poly(ether imide) Membrane for Potential Alkaline Fuel Cell Applications: Chloromethylation

Guigui Wang, Yiming Weng, Jun Zhao, Rongrong Chen, Dong Xie

Richard G. Lugar Center for Renewable Energy, Purdue School of Engineering and Technology,  
Indiana University/Purdue University at Indianapolis, 723 West Michigan Street, SL-220E, Indianapolis, IN 46202

Received 25 June 2008; accepted 8 October 2008

DOI 10.1002/app.29471

Published online 13 January 2009 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** We have developed a novel poly(ether imide)-based alkaline anion-exchange membrane. The effects of several important parameters on the chloromethylation of the membrane have been investigated. These parameters include the reaction temperature, reaction time, concentration of the chloromethylation agent, concentration of the polymer, and amount of the catalyst. The results show that all the studied parameters have significant impacts on chloromethylation. Among them, the concentration of the chloromethylation agent plays a

key role in increasing the attachment of chloromethyl functional groups onto the polymer. It has been found that gelation can be avoided if these reaction parameters are controlled. This study also provides useful information for the successful chloromethylation of other membrane-related polymers. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 721–727, 2009

**Key words:** anion exchange membrane; ionic conductivity; chloromethylation

## INTRODUCTION

Fuel cells are electrochemical devices that convert chemical energy directly into electrical energy. Recently, fuel cell research has become even more important because of the energy crisis. One of the key components of fuel cells is the electrolyte. The use of solid polymer electrolytes represents an interesting path to pursue for these electrochemical devices.<sup>1</sup> Two types of solid polymer electrolytes exist in fuel cell research: proton-exchange polymer membranes and anion-exchange polymer membranes. The former are used for proton-exchange membrane (PEM) fuel cells, and the latter are used for anion-exchange membrane fuel cells. Over the past few decades, much effort has been focused on PEM development.<sup>1,2</sup> Although PEMs exhibit excellent chemical, mechanical, and thermal stability as well as high ionic conductivity, several significant disadvantages have limited their further development

when they are applied to fuel cells.<sup>2</sup> The disadvantages of PEM-constructed fuel cells include slow electrode kinetics, carbon monoxide poisoning of nonreusable and expensive Pt and Pt-based electrocatalysts at low temperatures, high membrane costs, and high methanol permeability.<sup>1</sup> To overcome these hurdles, alkaline anion-exchange membranes (AAEMs) were created. AAEMs are designed to provide sufficient hydroxyl ions for ion exchange during electrochemical reactions in alkaline fuel cells. Alkaline fuel cells have numerous advantages over PEM fuel cells with respect to both cathode kinetics and ohmic polarization. The inherently faster kinetics of the oxygen reduction reaction in an alkaline fuel cell allow the use of non-noble and low-cost metal electrocatalysts such as silver and nickel. Furthermore, the anodic oxidation of methanol in alkaline media is more feasible than that in acidic media. Currently, there is growing interest in AAEM research.<sup>1</sup> So far, only a few AAEMs have been evaluated for use as solid polymer electrolytes for alkaline fuel cells.<sup>1,3–8</sup> These membranes were constructed mainly from poly(sulfone ether)s and polystyrenes. Crosslinked polystyrenes have been widely used as building matrices for cation and anion-exchange resins.<sup>9</sup> Polysulfones are high-performance polymers that are thermally and chemically stable.<sup>10</sup> Aromatic polyimides are other well-established high-performance materials originally developed for the aerospace industry.<sup>11</sup> High

Correspondence to: D. Xie (dxie@iupui.edu).

Contract grant sponsor: Army Research Laboratory; contract grant number: W911NF-07-2-0036.

Contract grant sponsor: Richard G. Lugar Center for Renewable Energy at Indiana University/Purdue University at Indianapolis.

thermal stability combined with chemical resistance and excellent mechanical properties make polyimides attractive for a variety of applications such as electronics, coatings, composite materials, and membranes.<sup>11,12</sup> However, this type of outstanding material has not been explored in AAEM research. In this article, we discuss functionalizing poly(ether imide) from the high-performance polyimide family for potential fuel cell applications.

The preparation of AAEMs involves several chemical reactions: chloromethylation, quaternization, and alkalization.<sup>1</sup> Among them, chloromethylation is the first and most important reaction. Without it, the next steps would not be possible. During this study, we found that chloromethylation was not easily controllable and that the number of chloromethyl groups attached to the polymer could be very low, thus affecting the ultimate conductivity. The reaction often caused gelation if it was not sufficiently controlled. Therefore, in this article, we also demonstrate how we improved chloromethylation by tuning several important parameters that often affect the chloromethylation of a polymer.

The objective of this study was to synthesize a novel functionalized poly(ether imide) and investigate the effects of several important parameters on chloromethylation. The conductivity of the formed AAEM was also evaluated.

## EXPERIMENTAL

### Materials

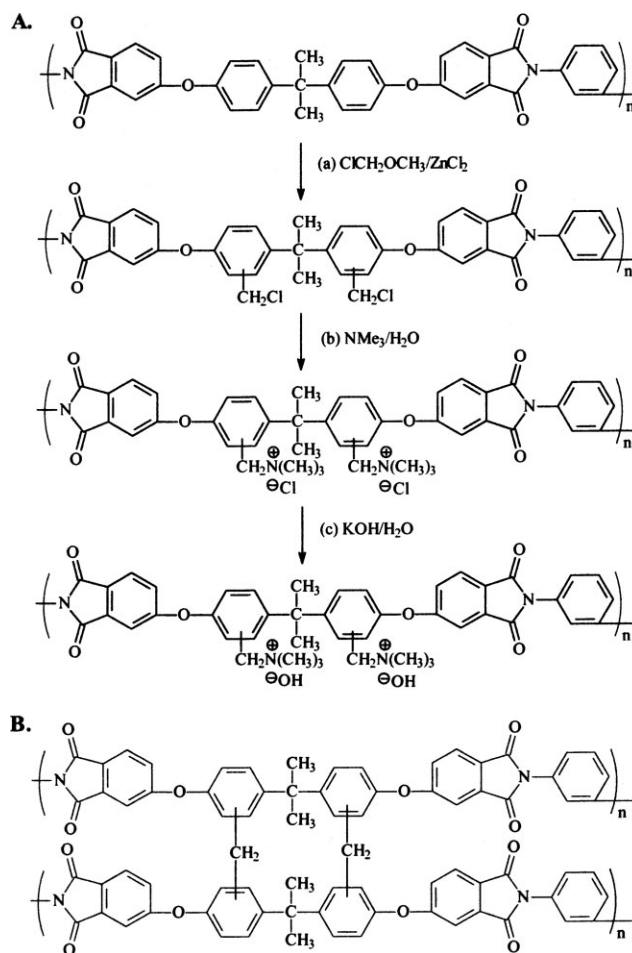
Poly(ether imide), 1,2-dichloroethane, zinc chloride, chloromethyl ether (CME), methanol, *N,N*-dimethylformamide, a 45% trimethylamine aqueous solution, potassium hydroxide, and deuterated chloroform were used as received from Fisher Scientific, Inc. (Pittsburgh, PA), without further purification.

### AAEM preparation

The preparation of the AAEM was conducted in three steps: (1) chloromethylation, (2) quaternization, and (3) alkalization. A schematic diagram of the preparation of the AAEM is shown in Figure 1(A).

#### Chloromethylation of poly(ether imide)

Briefly, to a reactor charged with 15 mL of 1,2-dichloroethane, 2.0 g of poly(ether imide), and 0.1 g of zinc chloride, 1.3 mL of chloromethyl ether was added dropwise with stirring at 70°C. The reaction was allowed for 4.5 h. After that, the polymer was precipitated into methanol to remove the catalyst, excess chemicals, and solvent, and this was followed by washing with methanol and deionized water several times before drying.



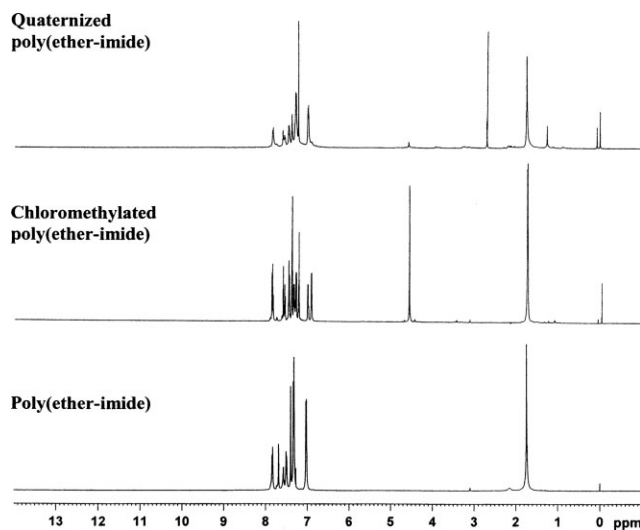
**Figure 1** Schematic diagram of synthesis and crosslinking: (A-a) chloromethylation, (A-b) quaternization, (A-c) alkalization, and (B) side reaction (crosslinking for gel formation).

#### Quaternization of poly(ether imide)

The purified chloromethylated polymer was dissolved in *N,N*-dimethylformamide and then poured into a Petri dish. The polymer in the Petri dish was dried in an oven overnight at 70°C and then at 150°C for an additional 2 h. The formed membrane was then treated overnight with a 30% trimethylamine solution, and this was followed by washing with deionized water several times. The thickness of the formed membranes was in the range of 25–30  $\mu\text{m}$ .

#### Alkalization of poly(ether imide)

The quaternized membrane was soaked in a 1M potassium hydroxide aqueous solution at room temperature for 24 h before testing. The alkalinized membrane was then washed with deionized water several times and soaked in deionized water with numerous washings within 24 h before evaluation.



**Figure 2**  $^1\text{H-NMR}$  spectra of poly(ether imide), chloromethylated poly(ether imide), and quaternized poly(ether imide).

### Characterization and ionic conductivity measurements

#### Characterization

The functionalized polymers and the degree of chloromethylation were characterized with NMR spectroscopy.  $^1\text{H-NMR}$  spectra were obtained on a Varian 500 NMR spectrometer (Varian, Palo Alto, CA) with deuterated chloroform as a solvent. The thermal decomposition history of both poly(ether imide) and quaternized poly(ether imide) membranes was determined on a thermogravimetric analyzer (TGA 7, PerkinElmer, Shelton, CT) at a heating rate of  $10^\circ\text{C}/\text{min}$  under a nitrogen flow.

#### Ionic conductivity measurements

The  $\text{OH}^-$  ionic conductivity of the formed membranes was measured by alternating-current impedance spectroscopy with a Solartron 1250 frequency response analyzer (Solartron Analytical, Farnborough, Hampshire, UK) interfaced with a 1287 potentiostat/galvanostat. The measurement was conducted in the galvanostatic mode over frequencies ranging from 0.1 Hz to 60 kHz with a galvanostatically controlled alternating current of 5 mA. A standard four-probe conductivity cell (BekkTech LLC, Loveland, CO) was used to assemble the membrane test sample. The area resistance of the membrane was determined in deionized water at  $24^\circ\text{C}$ . Ionic conductivity [ $\sigma$  (S/cm)] was calculated according to the following equation:<sup>13</sup>

$$\sigma = l/(RTW)$$

where  $l$  is the length of the membrane between two potential-sensing platinum wires (cm),  $R$  is the mem-

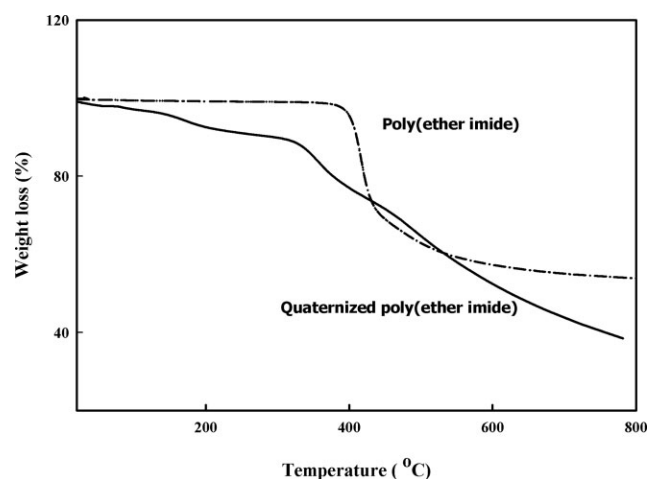
brane resistance ( $\Omega$ ),  $T$  is the thickness of the membrane (cm), and  $W$  is the width of the membrane (cm).

## RESULTS AND DISCUSSION

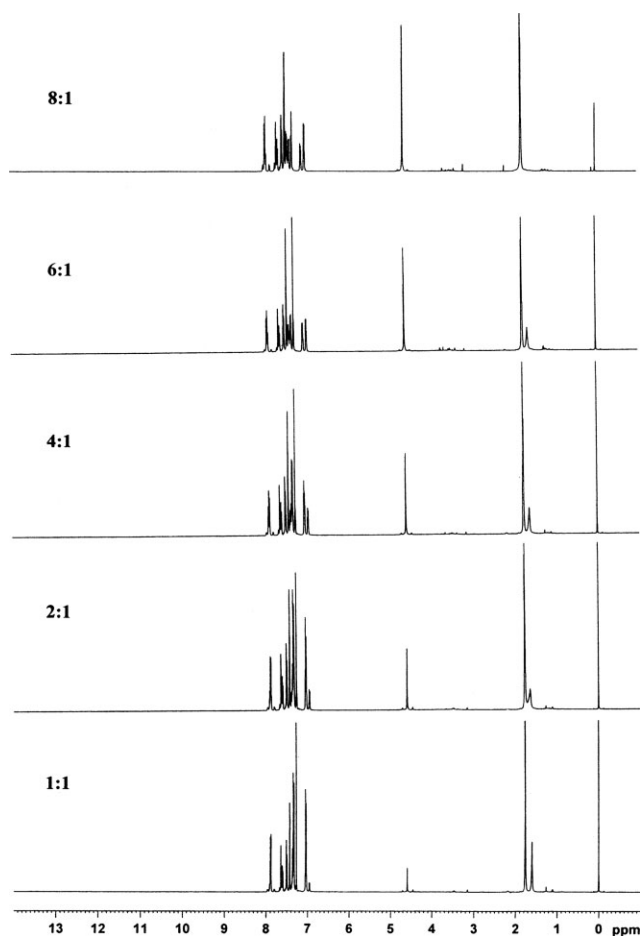
### Characterization

Figure 2 shows the  $^1\text{H-NMR}$  spectra for the poly(ether imide), chloromethylated poly(ether imide), and quaternized poly(ether imide). The chemical shifts (ppm) of the poly(ether imide) were found to be (a) 7.26–7.9 (multi Hs on phenyl groups) and (b) 1.72 ( $\text{CH}_3$ ). The chemical shifts (ppm) of the chloromethylated poly(ether imide) were (a) 7.26–7.9 (multi Hs on phenyl groups), (b) 4.64 ( $\text{CH}_2\text{Cl}$ ), and (c) 1.72 ( $\text{CH}_3$ ). The chemical shifts (ppm) for the quaternized poly(ether imide) were (a) 7.26–7.9 (multi Hs on phenyl groups), (b) 2.70 ( $\text{CH}_3$  linked to N), and (c) 1.72 ( $\text{CH}_3$  on bisphenol A). The characteristic chemical shift at 4.64 confirmed the formation of the chloromethylated poly(ether imide). The disappearance of the chemical shift at 4.64 and the appearance at 2.70 confirmed the formation of the quaternized poly(ether imide).

Figure 3 shows the TGA weight-loss curves for the poly(ether imide) and quaternized poly(ether imide). For the poly(ether imide), the weight loss was observed between 400 and  $550^\circ\text{C}$ . This loss was approximately 55%, suggesting that the polymer was very stable and only partially degraded at such a high temperature. For the quaternized poly(ether imide), two significant weight-loss transition traces were noticed: (1) a weight loss between 140 and  $270^\circ\text{C}$ , which was probably due to the removal of the quaternary ammonium groups,<sup>4</sup> and (2) a weight loss above  $325^\circ\text{C}$ , which was probably due to partial degradation of poly(ether imide). Both weight-loss



**Figure 3** TGA traces of poly(ether imide) and quaternized poly(ether imide).



**Figure 4**  $^1\text{H-NMR}$  spectra for showing the effect of the CME/polymer ratio on chloromethyl tethering. The values in Figure 7 were obtained from this figure by peak integrations.

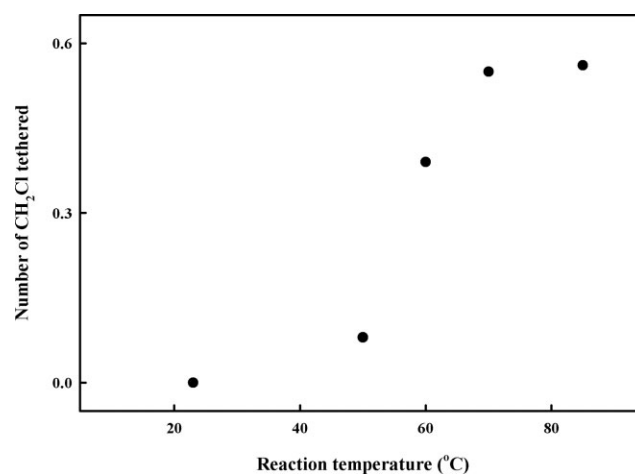
curves indicate that this poly(ether imide) was a very thermally stable polymer.

#### Effects of several parameters on chloromethylation

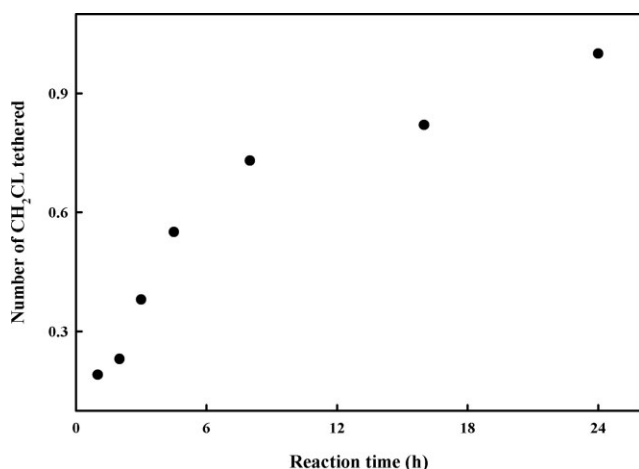
The most important step in preparing AAEMs is chloromethylation because the chloromethylated polymer is readily chemically modified on account of the high reactivity of the tethered chloromethyl group.<sup>14</sup> The degree of chloromethylation also determines how many conductive hydroxyl groups can be loaded onto the polymer chain, which in turn determines the conductivity. On the one hand, we found that several parameters could affect the chloromethylation reaction and the number of tethered chloromethyl groups. On the other hand, we noticed that the chloromethylation could easily cause gelation, leading to a lower yield of the chloromethylated polymer. It has been reported that crosslinking often takes place rapidly during the chloromethylation of a polystyrene resin as the active aromatic ring attacks the chloromethyl group in a Friedel-

Crafts alkylation fashion, and this in turn causes interpolymer or intrapolymer crosslinking or gel formation,<sup>15</sup> as shown in Figure 1(B). To improve chloromethylation without gelation or with less gelation, we studied the effects of the reaction temperature, reaction time, concentration of the chloromethylation agent, polymer concentration, and amount of the catalyst on the number of tethered reactive chloromethyl groups. The  $^1\text{H-NMR}$  spectrum was used as a tool to investigate these effects. Figure 4 presents a representative diagram containing a set of  $^1\text{H-NMR}$  spectra for the effect of the CME/polymer ratio on the number of tethered chloromethyl groups. All the numbers of the chloromethyl groups shown in the following figures were obtained by the integration of chemical shifts exhibited by chloromethyl and phenyl groups. The following discussion provides details on the effects of several parameters.

The reaction temperature is very critical to most chemical reactions. As we know, increasing the temperature can either accelerate a reaction by providing sufficient energy to the reactants or initiate some unnecessary side reactions, which can often be avoided at normal or low temperatures. Figure 5 shows the effect of the reaction temperature on the number of tethered chloromethyl groups. It is apparent that increasing the temperature increased the number of tethered chloromethyl groups. No reaction was observed at 23°C, and this suggests that this reaction requires heat to activate even in the presence of the catalyst. It was also found that after 70°C, the number of tethered chloromethyl groups did not increase (see 85°C), and this indicates that 70°C might be the best temperature for the chloromethylation of this specific poly(ether imide).



**Figure 5** Effect of the reaction temperature on the number of tethered chloromethyl groups (time = 4.5 h, CME = 2/1, polymer concentration = 15%,  $\text{ZnCl}_2$  = 5%). The number of chloromethyl groups was determined by  $^1\text{H-NMR}$ .



**Figure 6** Effect of the reaction time on the number of tethered chloromethyl groups (temperature = 70°C, CME = 2/1, polymer concentration = 15%, ZnCl<sub>2</sub> = 5%).

Figure 6 shows the effect of the reaction time. With increasing reaction time, the number of tethered chloromethyl groups increased linearly, and this indicated that the longer the reaction was, the more the chloromethyl group was tethered. This is consistent with the behavior of most chemical reactions. However, a longer reaction time can also increase the probability of side reactions. We found in this study that about 10% of the polymers became gels when the reaction time reached 24 h (see Table I).

It is known that during the reaction, adding excessive amounts of one reactant can often lead to a high conversion. As shown in Figure 7, increasing the ratio of CME to the polymer significantly increased the number of tethered chloromethyl groups. The role of the CME/polymer ratio was enormous because it increased the number of tethered chloromethyl groups from 0.25 to 1.52 per repeating unit of poly(ether imide). Theoretically,

the maximum number of tethered chloromethyl groups should be 2 if one considers the chemical structure of the repeating unit of poly(ether imide) shown in Figure 1. On the basis of the results shown in Figure 7, however, the chloromethyl group seems less likely to become attached. The maximum number of tethered chloromethyl groups was 1.52 at CME/polymer = 8. This may be partially attributed to the size and steric hindrance of the bulky polymer. On the other hand, 78% of the polymers became gelled during the reaction when 1.52 was reached (see Table I), and this indicated that CME/polymer = 8 might be too high to obtain a high yield.

Figure 8 shows the effect of the polymer concentration on chloromethylation. It is clear that increasing the polymer concentration increased the number of tethered chloromethyl groups. This can be attributed to the fact that the higher the concentration was of the reactants, the higher the probability was of the reactants reacting with each other and thus the higher the yield was of the product. However, the impact of the polymer concentration on increasing the number of tethered chloromethyl groups was not as significant as that from the CME/polymer ratio. The number of tethered chloromethyl groups was only 0.83 at a polymer concentration of 25% versus 1.52 at CME/polymer = 8.1. Furthermore, we were unable to increase the polymer concentration any higher because the probability of gelation was significantly increased. At a polymer concentration of 25%, 30% of the polymer became a gel (see Table I).

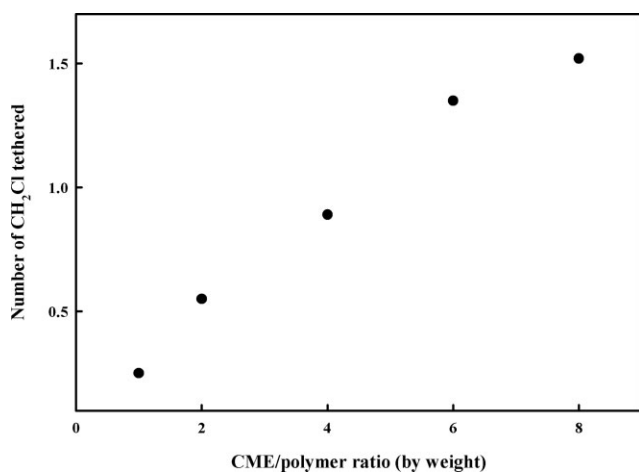
The catalyst is another parameter crucial to the reaction because its role is to lower the activation energy of the reaction, thus leading to an accelerated reaction rate.<sup>16</sup> Increasing the catalyst in this study increased the number of tethered chloromethyl groups (Fig. 9). The catalyst also shortened the reaction duration. We found that when the catalyst level reached 15%, 16% of the polymer became gelled.

**TABLE I**  
Gel Formation Corresponding to the Parameters Affecting Chloromethylation

Temperature (°C)	Time (h)	CME/polymer (wt/wt)	Polymer concentration (wt %)	Catalyst added (wt %)	Gelation <sup>a</sup>	Tethered CH <sub>2</sub> Cl <sup>b</sup>
70	4.5	2/1	15	5	No	0.55
85	4.5	2/1	15	5	No	0.56
70	16	2/1	15	5	No	0.82
70	24	2/1	15	5	10%	1.00
70	4.5	6/1	15	5	22%	1.35
70	4.5	8/1	15	5	78%	1.52
70	4.5	2/1	20	5	No	0.74
70	4.5	2/1	25	5	30%	0.83
70	4.5	2/1	15	10	No	0.80
70	4.5	2/1	15	15	16%	1.05

<sup>a</sup> Gelation was determined by simple weighing.

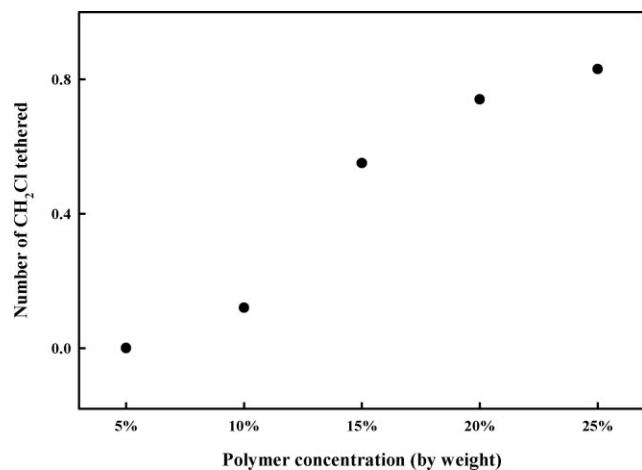
<sup>b</sup> The number of chloromethyl groups was determined by <sup>1</sup>H-NMR.



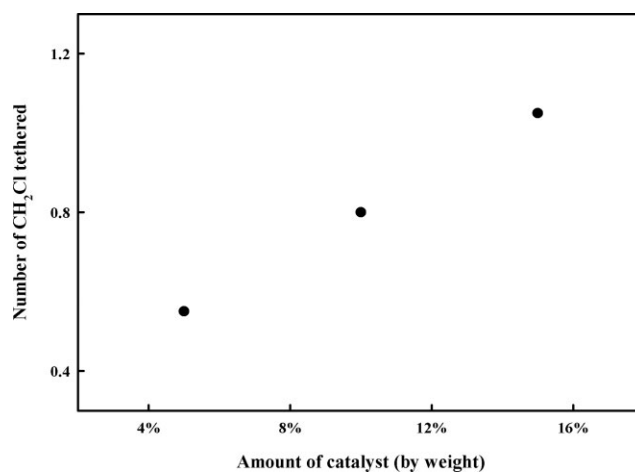
**Figure 7** Effect of the CME/polymer ratio on the number of tethered chloromethyl groups (temperature = 70°C, time = 4.5 h, polymer concentration = 15%, ZnCl<sub>2</sub> = 5%).

This occurred only at 2 h (see Table I). Apparently, too much catalyst causes an out-of-control reaction.

According to this discussion, it appears that all the parameters investigated in this study affect chloromethylation. In general, a higher temperature, a longer reaction time, a higher CME/polymer ratio, a higher polymer concentration, and a suitable amount of a catalyst are all favorable to the reaction. Under the same conditions, we could obtain only up to 0.56, 1.0, 0.83, and 1.05 chloromethyl groups per repeating unit in the poly(ether imide) by increasing the reaction temperature, time, polymer concentration, and catalyst, respectively. On the other hand, we could obtain up to 1.52 chloromethyl groups when we increased the CME/polymer ratio to 8/1. Therefore, the CME/polymer ratio seems to be the most critical parameter for attaching the maximum



**Figure 8** Effect of the polymer concentration on the number of tethered chloromethyl groups (temperature = 70°C, time = 4.5 h, CME = 2/1, ZnCl<sub>2</sub> = 5%).

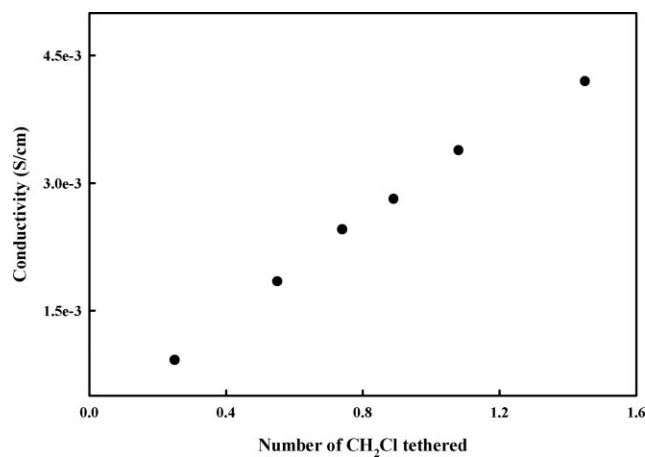


**Figure 9** Effect of the amount of the catalyst used on the number of tethered chloromethyl groups (temperature = 70°C, time = 4.5 h, CME = 2/1, polymer concentration = 15%).

number of chloromethyl groups to the poly(ether imide).

### Conductivity

To test the conductivity of the newly functionalized poly(ether imide), we selected several polymers with different numbers of tethered functional groups per unit. After they were converted to tertiary amines that could carry hydroxyl ions, we measured the conductivity of the formed membrane. Figure 10 shows the effect of the number of tethered chloromethyl groups on the ionic conductivities of the formed AAEMs. As we know, the ionic conductivity is proportional to the number of ions that can be exchanged or transported through the membrane



**Figure 10** Effect of the number of chloromethyl groups on the ionic conductivity of the formed AAEM. The membranes were conditioned in a 1M KOH aqueous solution for 24 h before testing. The conductivity was measured at 24°C.

under an electrical potential. The ions for conductivity are actually hydroxyl anions ( $\text{OH}^-$ ). Thus, when more chloromethyl groups are tethered onto the poly(ether imide), more  $\text{OH}^-$  anions will be available, and the expected ionic conductivity will be higher. As shown in Figure 10, increasing the number of tethered chloromethyl groups increased the ionic conductivity. The conductivity ranged from  $9.21 \times 10^{-4}$  to  $4.20 \times 10^{-3}$ , corresponding to the number of tethered chloromethyl groups per unit of poly(ether imide), which ranged from 0.25 to 1.45.

### CONCLUSIONS

This study investigated the effects of several important parameters on the chloromethylation of a novel poly(ether imide)-based AAEM. The results show that all the parameters exhibited significant impacts on chloromethylation. Among them, the chloromethylation agent CME played a key role in increasing the attachment of chloromethyl functional group onto the poly(ether imide). Gel formation could be avoided if these reaction parameters were controlled. This study also provides useful information for the successful chloromethylation of other membrane-related polymers. Future studies will include evaluating the other properties of this novel AAEM, fur-

ther improving its conductivity, and applying it to fuel cells.

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