

# Synthesis and characterisation of alkaline anionic-exchange membranes for direct alcohol fuel cells

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## INTRODUCTION

Great effort in research and development has been made over the years to improve and commercialize new systems (e.g. Fuel Cells) of generating electricity. The use of polymer electrolytes represents an interesting path to pursue for these systems, the most important being proton exchange membrane fuel cell (PEMFC), which uses an acidic membrane like Nafion (sulfonated fluorocarbon polymers) as an electrolyte [1]. However, when Nafion membranes are applied to direct alcohol fuel cells (DAFCs), several obstacles emerge, i.e. methanol crossover and relative low activity [2]. Therefore, there is a need for the development of novel anion exchange membranes (AEMs) that can be applied in these systems. In alkaline fuel cells, the OH anions are produced at the cathode and then transported through the membrane to the anode where they are consumed (opposite to the movement of protons in acidic membranes). The pathway of the OH anions opposes the direction of methanol flux through the membrane leading to an intrinsic reduction in methanol crossover (Figure 1) [3].

Poly(arylene ether sulfones) are engineering thermoplastic materials that display a variety of desirable properties. They have a high shear modulus, and are usually amorphous, tough thermoplastic materials that display relatively high glass transition temperatures in the range of 180 – 250°C depending on the structure of the backbone. Common backbone characteristics include the rigid phenylene groups that are connected by flexible ether and sulfone linkages. The general rigidity associated with this class of polymers is usually associated with the inflexible phenyl groups, while the toughness is usually associated with the mobility of the ether linkages even below T<sub>g</sub> [4]. These polymers are good candidates for high temperature molding and/or chemically aggressive applications due to their excellent thermal, chemical and oxidative stabilities.

The work presented here involves the preparation of anion exchange membranes from poly(arylene ether), by the conventional aromatic nucleophilic displacement route via chloromethylation and quaternary amination. The primary objective was to acquire basic information on structure-property relationships to permit the design of a membrane with good overall properties for potential use in fuel cell applications.

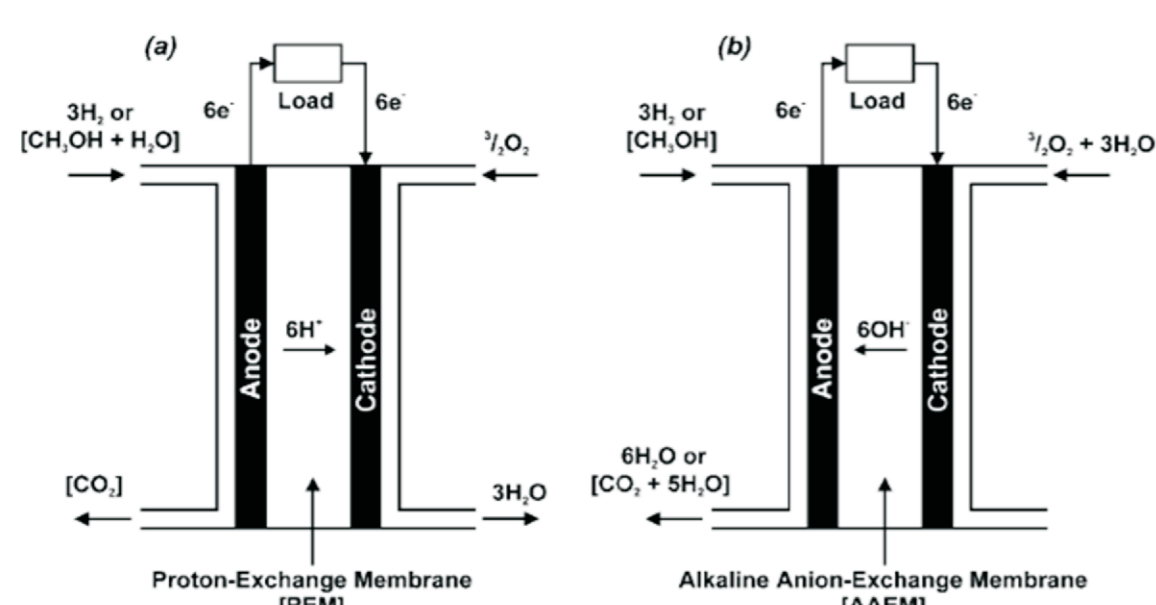
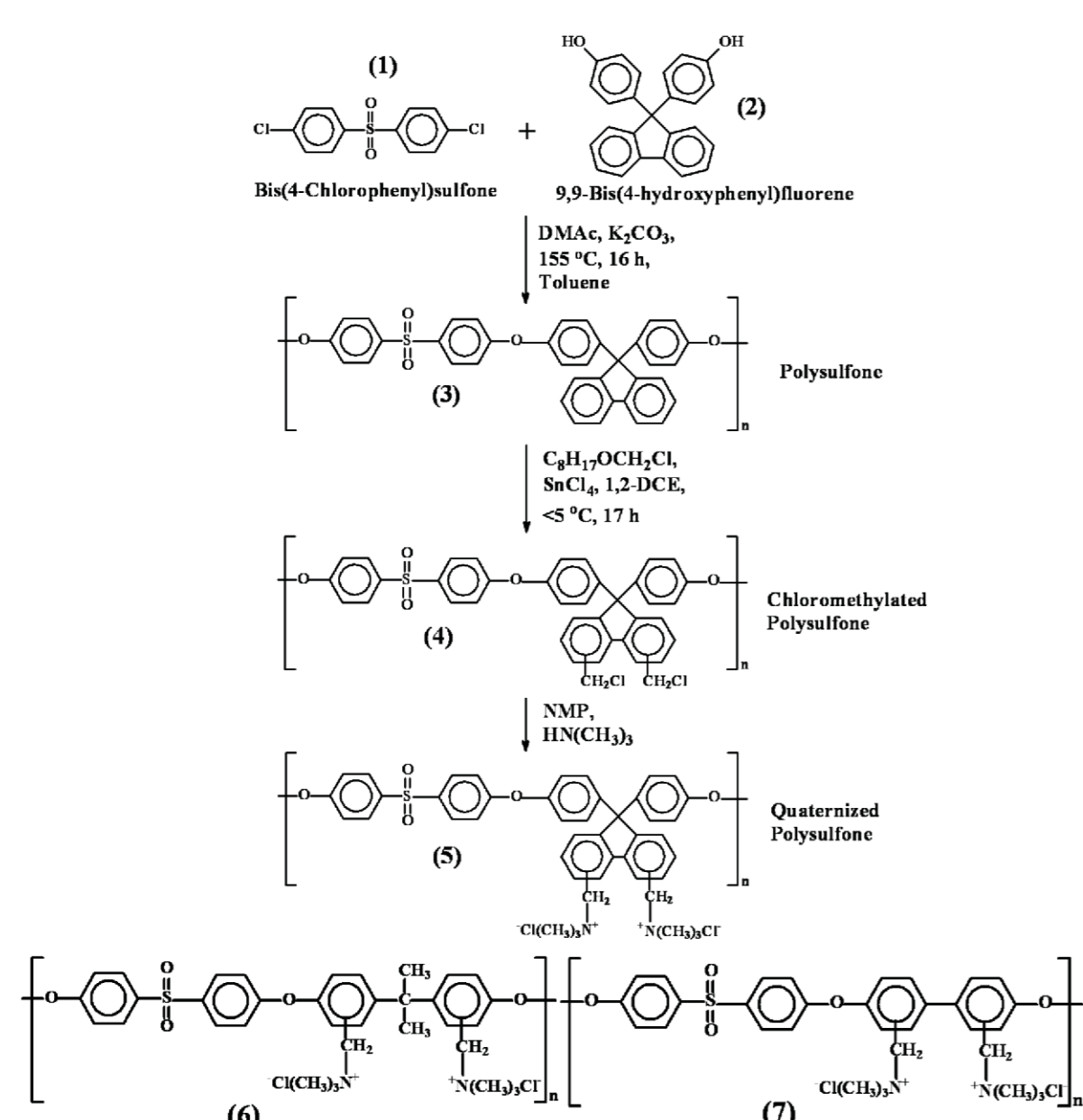


Figure 1: Schematic diagrams of a typical (a) proton exchange membrane and (b) an alkaline exchange membrane fuel cells [3].

## EXPERIMENT

### PREPARATION OF ALKALINE EXCHANGE MEMBRANE



Membranes (6) and (7) were modified from commercially available polyether sulfones and polyphenylsulfone respectively following the procedure above.

Scheme 1: Multi-step synthesis of quaternized polysulfones.

## RESULTS AND DISCUSSIONS

### 1. <sup>1</sup>H-NMR SPECTRA

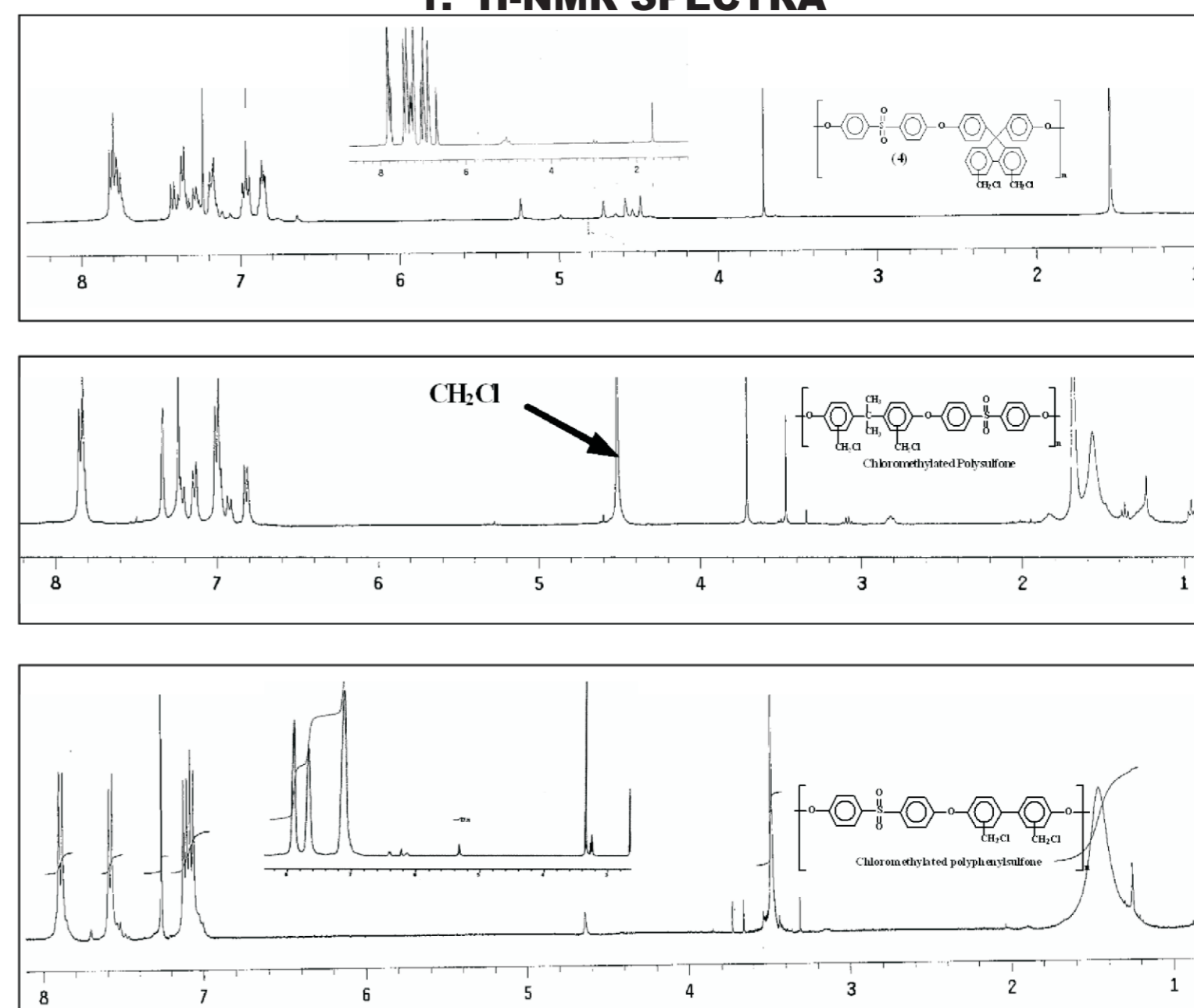
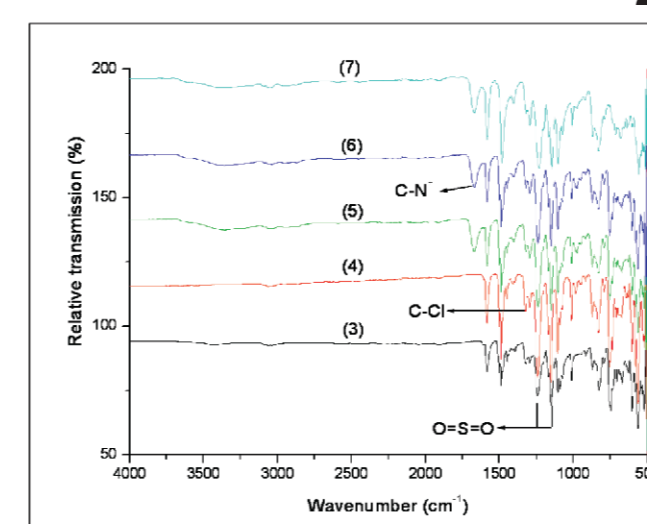


Figure 2: <sup>1</sup>H-NMR spectra of chloromethylated intermediates. All spectra were recorded on a Gemini 300 MHz spectrometer using CDCl<sub>3</sub> as solvent. Insert spectra are polymers.

### 2. FT-IR SPECTRA

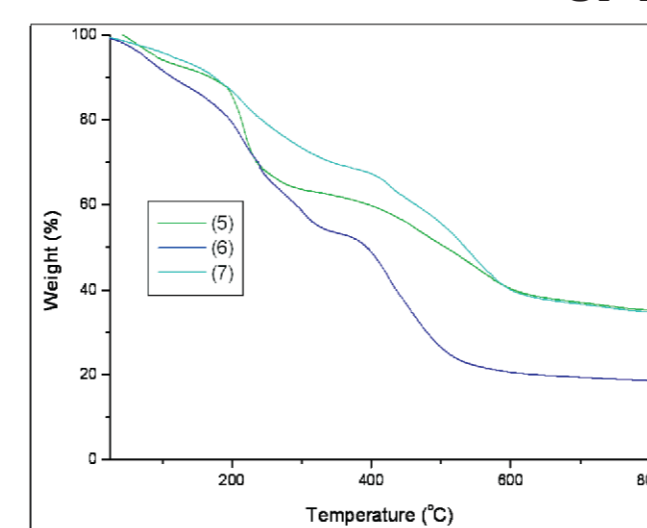


Functional group	Frequency (cm <sup>-1</sup> )
C-N (CH <sub>3</sub> )	1667
O=S-O	1240, 1152
C-Cl	1321

Table 1: Summarized stretching frequencies

Figure 3: FT-IR spectra of (3), (4), (5), (6) and (7) respectively were recorded on a diamond plate.

### 3. THERMAL ANALYSIS



Polymers	Weight Loss (%)	Temperature (°C)
5	29.68	216
6	25.17	215
7	55.07	240
	34.75	425
	28.86	215
	31.97	217

Table 2: Summarized thermal stability

Figure 4: TG curves of compounds (5), (6) & (7). All samples were heated at 10 °C/min under N<sub>2</sub>.

- Incorporation of CH<sub>2</sub>Cl group was quantitative as shown by <sup>1</sup>H-NMR peak ca. 4.5 ppm with respect to the parent polymer (insert spectra) **Figure 3**.
- As the quaternized polymers were not soluble in CDCl<sub>3</sub>, no NMR spectra are presented.
- FT-IR spectra displayed additional absorbance at 1667 cm<sup>-1</sup> for all quaternized polymers, indicated that the reaction proceeded as expected.
- TGA profile also showed the weight loss between 200 and 240 °C is due to the removal of quaternary ammonium groups and the second loss at higher temperatures above 400 °C is due to polymer backbone degradation.

## CONCLUSIONS AND FUTURE WORK

- All anionic membranes were successfully synthesized with minor impurities.
- FT-IR confirmed the formation of the anionic membranes while <sup>1</sup>H-NMR results confirmed the formation of the chloromethylated intermediates.
- Thermal studies demonstrated that the quaternized polymers have good thermal and higher degradation temperatures which are comparable to Nafion ~280 °C [5].
- Future studies will be conducted to compare, ionic conductivities of all quaternized membranes at different NaOH concentrations over a temperature range of 25 – 70 °C.
- Methanol permeability of all the membranes as a function of temperature will also be determined. From these results, it will be determined if the membranes are suitable for use in direct alcohol alkaline fuel cells.

## REFERENCES

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