our future through science

Chemical modification and characterization of quaternized polysulfones

P. Nonjola[1]*, M. Mathe[1], S. Hietkamp[1]

[1]Council for Scientific and Industrial Research, Materials Science and Manufacturing, PO Box 395, Pretoria 0001, RSA

*snonjola@csir.co.za

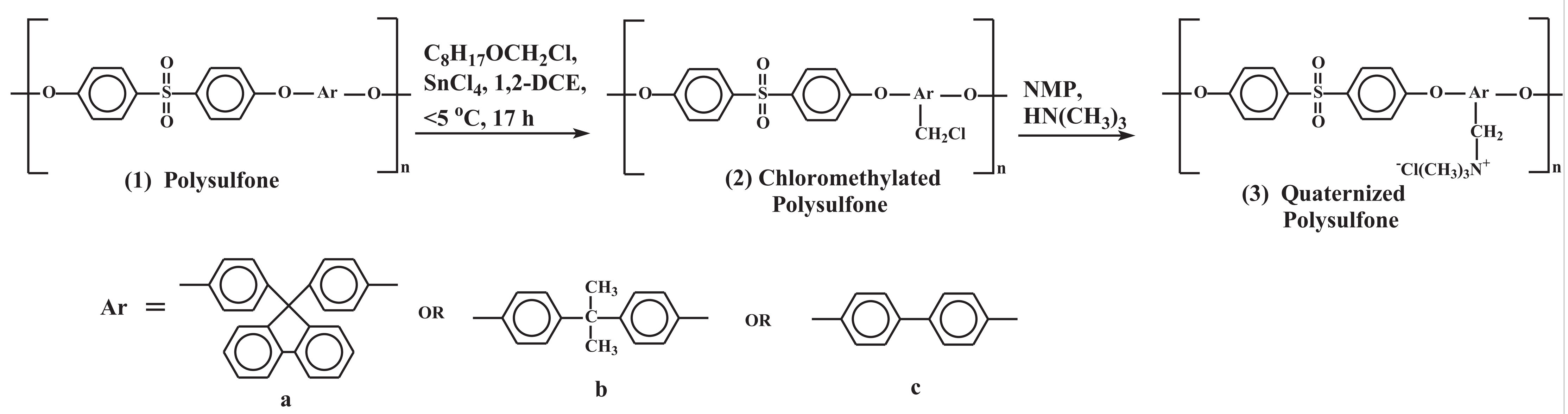
INTRODUCTION

Proton conductive polymers such as Nafion and Flemion (perfluorinated ionomers) have been extensively studied especially in fuel cell applications [1,2]. Despite their advantages of high conductivity, good chemical and mechanical properties, certain drawbacks restricted their use in fuel cells, such as, high costs of membrane electrode assembly (MEA), high methanol permeability in direct alcohol fuel cells, and relative low activity at temperatures above 80 °C [3,4]. A possible solution to these obstacles has been found in the development of alternative ionomers, these include, anionic polymers [5,6,7], which can exhibit high conductivity and reduced alcohol permeation.

Several reviews on the chemical modification of polysulfone by different mechanisms for the introduction of functional groups into the backbone have been reported [8]. As a class of high performance engineering thermoplastic materials, polysulfones, have a high glass transition temperature, high thermal stability, good mechanical properties and good resistance to hydrolysis and oxidation. These mentioned advantages of polysulfones prompted us to utilize them in developing anionic polymers that can be applied in alkaline fuel cells. The work presented here involves the preparation and characterization of quaternized polysulfones following the procedure reported by Komkova et al [9,10].

EXPERIMENTAL WORK

PREPARATION OF QUATERNIZED POLYSULFONES



Scheme 1: Multi-step synthesis of quaternized polysulfones [9].

RESULTS AND DISCUSSION

1. FT-IR SPECTRA

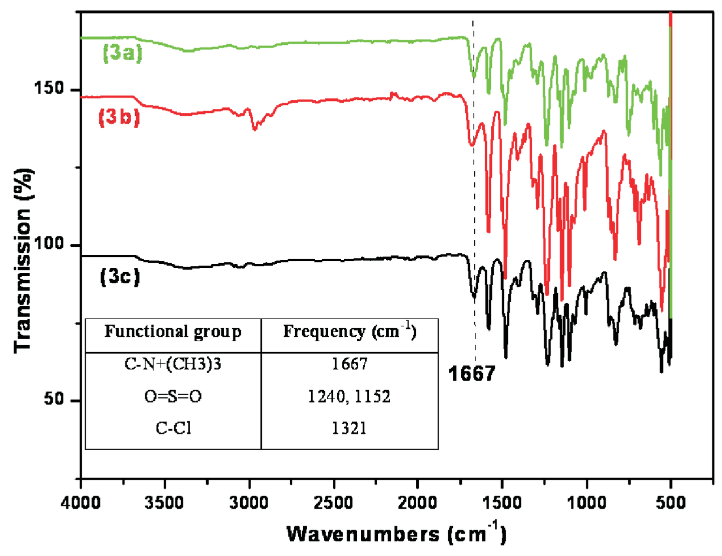


Figure 1: FT-IR spectra of (3a), (3b) and (3c) respectively.

2. THERMAL ANALYSIS

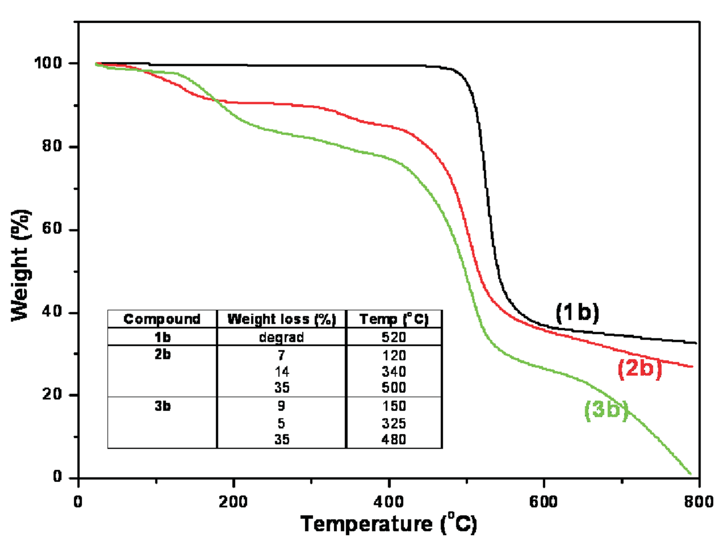


Figure 2: TG curves of compounds (1b), (2b) and (3b). All samples were heated at 10 °C/min under N_2.

3. WATER SORPTION MEASUREMENTS

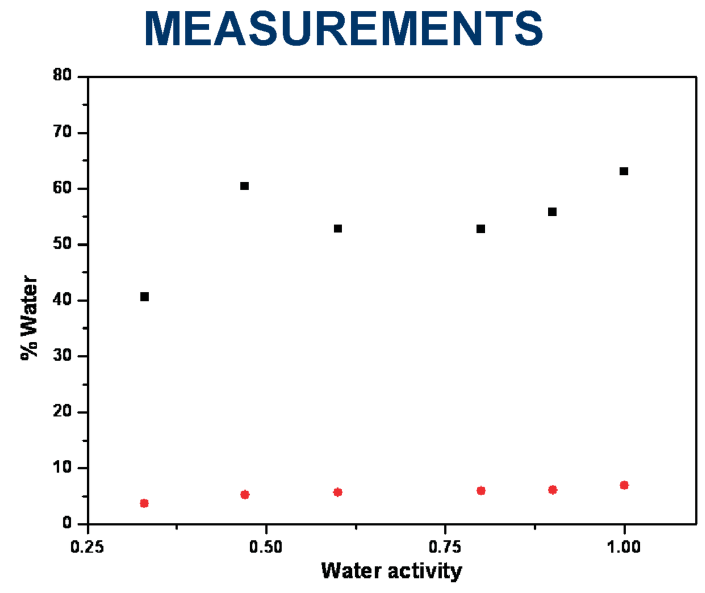


Figure 3: Water sorptions of the thin films of 3b and Nafion at 40 °C using quartz micro-balance [11].

- All chloromethylated polymer structures as well as their purity were confirmed by [1]H-NMR in $CDCl_3$. No NMR spectra for quaternized polymers (not soluble in $CDCl_3$).
- FT-IR spectra displayed absorbance at 1667 cm^{-1} for all quaternized polymers, indicating that the reaction proceeded as expected.
- TGA results were focused only on compounds (b), which showed three stages of decomposition as indicated in Fig 2. Percentage weight loss between 25 and 120 is due to water removal. Weight loss (%) between 200 and 240 °C is due to the removal of quaternary ammonium groups and the second loss at higher temperatures up to 500 °C is due to polymer backbone degradation. For compound (1b), only one weight loss stage was observed.
- Water sorption isotherms showed that compound (3b) absorbs more moisture than Nafion film (ca. 1mg respectively). Measurements were conducted by purging compressed air through the saturated solutions of $MgCl_2$ (RH = 33%), $Li(NO_3)$ (RH = 47%), NH_4NO_3 (RH = 61%), KBr (RH = 80%), $BaCl_2$ (RH = 90%) and pure water (RH = 100%).

CONCLUSIONS AND FUTURE WORK

- All quaternized polymers were successfully synthesized with minor impurities.
- FT-IR confirmed the formation of quaternized polysulfones.
- Thermal studies of compounds **(1b – 3b)** demonstrated good thermal properties and higher degradation temperatures comparable to that of Nafion [12].
- The difference in water sorption behaviour is related to the relative degree of hydration of the ions, which is responsible for water uptake at low and high vapour pressure.
- Future studies will be conducted to compare ionic conductivity of all quaternized polysulfones at temperature range of 25 – 70 °C.
- Compare water and methanol (different concentrations) sorption of all quaternized polysulfones.
- Methanol permeability of the all quaternized polysulfones 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

[1] K. A. Mauritz, R. B. Moore, *Chem. Rev.*, **104** (2004) 4535.
[2] O. Savadogo, *J. New Mater. Electrochem. Syst.,* **1** (1998) 47.
[3] M. A. Hickner, H. Ghassemi, Y. S. Kim, B. R. Einsla, J. E. Mcgrath, *Chem. Rev.*, **104** (2004) 4587.
[4] O. Savadogo, *J. Power Source*, **127** (2004) 135.
[5] J. R. Varcoe, R. C. T. Slade, *Fuel Cells*, **5** (2005) 187.
[6] J. J. Kang, W. Y. Li, Y. Lin, X. P. Lin, X. R. Xiao, S. B. Fang, *Polym. Adv. Technol.*, **15** (2004) 61.
[7] L. Li, Y. X. Wang, *J. Membr. Sci.*, **262** (2005) 1.
[8] F. Wang, M. Hickner, Y. S. Kim, T. A. Zawodzinski, J. E. Mcgrath, *J. Membr. Sci.*, **197** (2001) 231.
[9] E. N. Komkova, D. F. Stamatialis, H. Strathmann, M. Wessling, *J. Membr. Sci.*,**244** (2004) 25.
[10] K. Mitayake, Y. Chikashige, M. Watanabe, *Macromolecules,* **36** (2003) 9691.
[11] P. Krtíl, A. Trojáněk, Zdenek Samec, *J. Phys. Chem.*, **105** (2001) 7979.
[12] J. Surowiec, R. Bogoczek, *J. Thermal Anal.*, **33** (1988) 1097.