Bull. Mater. Sci., Vol. 18, No. 7, November 1995, pp. 917–920. © Printed in India.

$(PEG)_xNH_4ClO_4$: a new polymeric fast proton conductor[†]

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Abstract. A new polymer electrolyte $(PEG)_x NH_4ClO_4 (x = 5, 10, 15, 20)$ has been prepared that shows protonic conduction. The room temperature conductivities are of the order of 10^{-7} S/cm, and increase with decrease in salt concentration. NMR line width studies indicate fairly low glass transition temperatures of the polymer salt complexes.

Keywords. Polymer electrolyte; protonic conductor; $(PEG)_xNH_4ClO_4$; impedance analysis; NMR.

1. Introduction

Polymer electrolytes are polymers complexed with a salt that can bind to the polymer host. Usually they are shown as $(P)_x$ MX where P is the short name of polymer, M is the anion, X is the cation and x is the ratio of the number of monomers to that of cations.

Polymer electrolytes are easy to prepare flexible solids, which makes them ideal for use in solid state batteries, fuel cells and other electrochemical devices. In the past decade there has been a considerable amount of work in this area, which has lead to the synthesis of many new compounds, mostly lithium ion conductors based on polyethylene oxide (Bruce and Vincent 1993). Besides their high conductivity, much of the interest in lithium conductors is due to their potential application in solid state batteries. On the other hand not much attention has been given to protonic polymer electrolytes so far. Recently with the increasing interest in fuel cells (Prater 1994), these have gained importance as potential electrolytes for methanol fuel cells. Here we report a new polymer electrolyte, a polyethylene glycol (PEG) complexed with ammonium perchlorate, which exhibits protonic conduction.

2. Experimental

PEG of molecular weight 2000 and NH_4ClO_4 were supplied by Fluka, Switzerland. Appropriate proportions of PEG and NH_4ClO_4 were weighed and dissolved in methanol. The solution was stirred for 5 h, cast on teflon sheets and kept in nitrogen atmosphere for 30 h. The $(PEG)_xNH_4ClO_4$ $(x = 5, 10, 15, 20)$ films were vacuum dried and transferred into a glove box. The films are very hygroscopic, white in colour and of average thickness of 1 mm.

Conductivity measurements were carried out under vacuum, in the frequency range 50 Hz to 120 kHz, using a dual lock-in-amplifier (PAR 5210). The complex impedance plots were analysed by the package Equivalent Circuits. NMR measurements were done on Bruker MSL-300 spectrometer, with a B-VT 1000 temperature controller.

[†] Paper presented at the poster session of MRSI AGM VI, Kharagpur, 1995

3. Results and discussion

IR spectra confirmed the formation of the polymer-salt complex (figure 1). X-ray diffraction patterns (not shown) indicated that the films are semi-crystalline in nature. The complex impedance plots are shown in figure 2. The impedance of films as function of frequency traces just one semi-circle, which indicates absence of grain boundaries (Bauerle 1969). This behaviour can easily be modelled by a simple equivalent circuit as shown in figure 2. The bulk conductivities, at room temperature were found

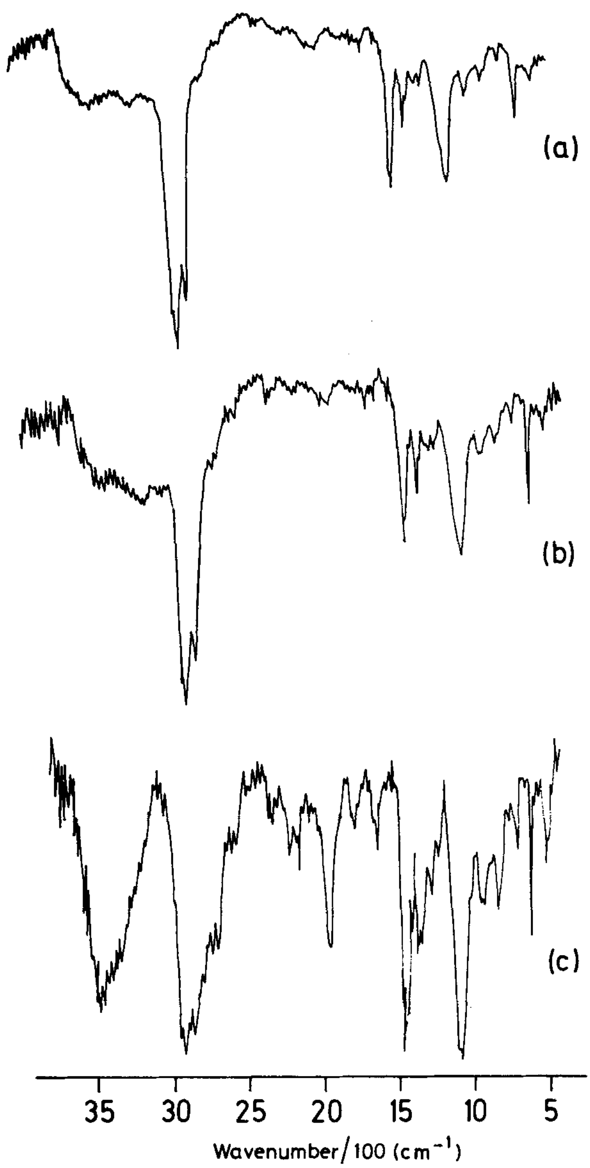

Figure 1. FTIR spectra of (a) $(PEG)_{20}NH_4ClO_4$, (b) $(PEG)_{10}NH_4ClO_4$ and (c) pure PEG.

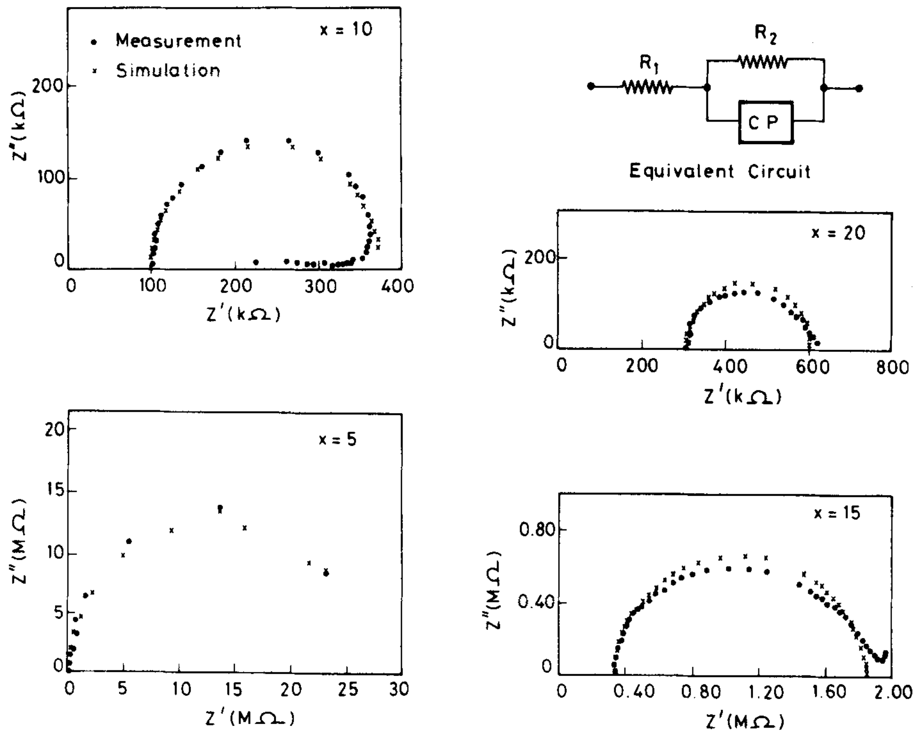

Figure 2. Complex impedance plots (imaginary Z'' vs real Z') of $(PEG)_xNH_4ClO_4$, for different salt concentrations. (●, experimental, ×, simulation). The equivalent circuit used for simulations is also shown.

to be:

$$\sigma = 1 \times 10^{-8} (\Omega\cdot cm)^{-1} \quad \text{for} \quad (PEG)_5NH_4ClO_4,$$

$$\sigma = 6 \times 10^{-8} (\Omega\cdot cm)^{-1} \quad \text{for} \quad (PEG)_{10}NH_4ClO_4,$$

$$\sigma = 7 \times 10^{-8} (\Omega\cdot cm)^{-1} \quad \text{for} \quad (PEG)_{15}NH_4ClO_4$$

and

$$\sigma = 2 \times 10^{-7} (\Omega\cdot cm)^{-1} \quad \text{for} \quad (PEG)_{20}NH_4ClO_4.$$

The ^1H line-width vs temperature plot of $(PEG)_{10}NH_4ClO_4$ is shown in figure 3. Motional narrowing of the signal starts at about 200 K, which we infer, is the glass transition temperature of the complexed polymer (Gupta *et al* 1993). An Arrhenius fit along with the BPP analysis of this data gives the following motional parameters:

$$\Delta E = 0{\cdot}26 \text{ eV},$$

and

$$\tau_0 = 9{\cdot}6 \times 10^{-11} \text{ s}.$$

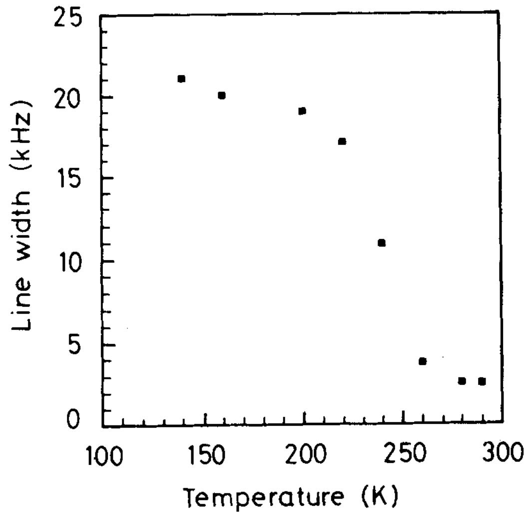

Figure 3. ^1H NMR line width vs temperature for $(PEG)_{10}NH_4ClO_4$.

4. Conclusion

The glass transition temperature of these polymer-salt complexes are low, i.e. ions are mobile even at low temperatures. The protonic conduction in these films shows an increase with decrease in salt concentration (for the salt concentrations studied here). Hence complexes with lower salt concentrations are being prepared to check for possible high room temperature conductivity.

Acknowledgement

The funding from the Council of Scientific and Industrial Research, New Delhi, for this work, is gratefully acknowledged.

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