

# **CHAPTER 1**

## ***INTRODUCTION***

## 1 INTRODUCTION

### 1.1 Background

The importance of ionic motion in solvent free polymeric matrices has only been recognized in the past decade. While polyelectrolytes, i.e. polymeric backbones with attached ionized groups are of considerable theoretical and practical importance; they are conductive only in the presence of polar solvents. The electrochemical properties of such polymers are limited by the solvent and the conductivity takes place in interconnected "pocket" of solvent + ions, whose structure is quite similar to that of free solutions. Polymer electrolytes (PE) correspond to a different concept: the polymer itself acts as solvent for a salt which becomes partially dissociated in the matrix, leading to ionic conductivity. No solvent is required for the conduction process though the preparation of the polymer-salt complex involves the use of a solvent for both constituents.

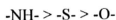
How is the polymer-salt complex formed? The existence of polar groups in polymers is a common feature. These polar groups can act as electron donors. These electron donors will form a dative bond with the cation of the salt. What kind of salt is suitable for use in the formation of such polymer-salt complexes? A salt contains the cationic part and the anionic part. Both parts play a key role in solvation. A cation can be "hard" or "soft". A hard cation is non-polarizable e.g. Lewis acid including alkaline and alkaline earth. Soft cations are those having partially filled "d" or to a lesser

extent "f" orbital. For non-polarizable cations the most suitable polymers are in the sequence, which follows the sequence of the best donors:

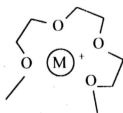


This means the polymers with oxygen electron donors are better than -NH- donors and which are much better than -S- donor to form a dative bond with the cation of the salt.

For salts with soft cations the more preferred polymer is one that contains secondary nitrogen (tertiary =N- usually shows steric restriction). The polymer sequence follows the sequence of the following electron donors:



Complexation is highly facilitated when the geometry of the ligand is pre-arranged to form cyclic structures where the ion is part of a 5-, more rarely a 6- membered ring [1].



From the above mention considerations, the most favorable sample polymer structure that will form complexes with a doping salt are:

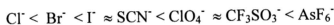
$(-\text{CH}_2\text{CH}_2\text{O})_n$ -poly(ethylene oxide)

$\begin{array}{c} \text{CH}_3 \\ | \\ (-\text{CH}_2\text{CHO})_n \end{array}$ -poly(propylene oxide)

$(-\text{CH}_2\text{CH}_2\text{NH})_n$ -poly(ethylene imine)

Most polymer electrolytes studied today include these units with the few exceptions of polyesters and nitriles.

What about anions? Large delocalized anions, either "soft" ( $\text{I}^-$ ) or "hard" bases ( $\text{ClO}_4^-$ ), require little solvation. In fact the order:



parallels that of the lattice energy of their salts. In water or methanol solutions, the hydrogen bonds exert a levelling effect on the stability of the negative charge carriers. In protic liquid or polymer solvents, dramatic differences can be observed that depends on the charge dispersion.

Poly(ethylene imine) or PEI with a NH secondary amine group represents another interesting class of complexing agents with "soft" nitrogen centers. PEI either linear or branched is a good complexing agent for  $\text{Ag}^+$ ,  $\text{Cu}^{++}$ ,  $\text{Co}^{++/+++}$ ,  $\text{Ni}^{++}$ , and  $\text{Zn}^{++}$  shows in addition a solvating power to work alkaline metal salts similar to that of PEO.

## 1.2 Aims of the Present Work

In view of the above, it is the aim of this study to use chitosan as the polymer host. This is due to the presence of the amine group in the polymer. In view of what has been said in the previous section, the salt  $\text{AgCF}_3\text{SO}_3$  (silver triflate) will be used to form the polymer-salt complex. To enhance the conductivity the polymer-salt complex will be plasticized with ethylene carbonate (EC).

The plasticized chitosan acetate-silver triflate complexes will be prepared by the solution cast technique. The film will be characterized by X-ray diffraction (XRD) to study the effect of the dissolution of the salt on the structure of the polymer. Fourier Transform Infrared (FTIR) spectroscopy will be carried out to double-check the occurrence of complexation between salt and polymer. X-ray photoelectron spectroscopy will also be carried out to confirm that the shift in XRD peaks and FTIR bands is due to Ag-N interaction. The transference number experiment will be carried out to determine whether the samples are ionic conductor or otherwise. Transient ionic current experiments will be carried out to calculate the mobility of the transporting ionic species. To see the morphology of the films, optical microscopy and SEM will be performed. The conductivity of the samples will be measured by impedance spectroscopy technique. The complex admittance plot will be used to verify the bulk resistance of the material. The film with the highest electrical conductivity will be used to fabricate a primary electrochemical cell. The cell will then be characterized by measuring their OCV and the internal resistance.