CHAPTER ONE

1.1 Background

The great potentialities of polymer electrolytes have been demonstrated by experiment[1]. The ability to form polymer electrolytes arises from a subtle balance of energy factors. This is best summarized by a brief consideration of the most straightforward preparation process that can be used to produce polymer electrolytes. A large number of polymer salt complexes has been studied, and poly(ethylene oxide) or PEO has been the widely investigated system because of its exceptional ability to solvate ionic salts [2–3]. Typically, the salts are dissolved in a suitable ‘casting solvent’ (acetonitrile, methanol or even water) and then mixed with a dilute solution of the polymer, leading to variety of polymer electrolytes [4]. The electrochemical behavior of polymeric electrolytes is that the cationic transport number is substantially less than unity in many cases showing that the anions also participate in the charge carrying process. This is in contrast with the majority of glasses, in which ionic charge is solely carried either by anions as in $O^-$ ion conductors or by cations, as in Ag$^+$, Li$^+$, Cu$^+$ ion conductors.

As in the case of all electrolytes conductivity is a very important property. It is not possible to measure the conductivity of an isolated electrolyte. Instead, a test cell has to be used, in which the electrolyte is sandwiched between a pair of conducting electrodes. Two types of a.c techniques are normally employed. Most of the older studies used a constant frequency technique to overcome the effect of concentration polarization. In this there is no real means of separating the contributions of the electrolyte from those of the other components in the test cell.
In consequence now it is common to carry out measurements at variable frequencies.

The current passing through the cell and the voltage across it are both measured as a function of frequency. Since the test cell contain capacitative (and perhaps also inductive) components as well as resistance, it is better to obtain the impedance ‘Z’, rather than the resistance ‘R’.

1.2 Polymer

Polymers may behave as liquids or solids, or as composites of both of these phases, depending on their nature. The structure of polymers is necessarily more complicated than that of solids or liquids composed of small molecules[4]. ‘Polymer’ is a Greek word which describes many natural and synthetic materials. A broad definition will include any material which consists of large molecules that are formed from the repetition of small and simple chemical units. These units are linked to each other by covalent bonding.

![Schematic Representation of (a) Linear, (b) Branched and (c) Network Polymers.](image)

Fig 1.1. Schematic representation of (a) linear, (b) branched and (c) network polymers.

In some cases the repetition is linear, much as a chain is built up from its links. In other cases the chains are branched or interconnected to form three dimensional
networks [5]. The repeat units of the polymer are usually equivalent or nearly equivalent to the monomer, starting materials from which the polymer is formed. For example, the repeat unit of poly(vinyl chloride) is \(-\text{CH}_2 \text{CH} \text{Cl}\) and its monomer is vinyl chloride, \(\text{CH}_2=\text{CHCl}\) Table 1.1 shows a variety of polymers with their monomers and repeat units[6].

Natural polymers include proteins, nucleic acids, cellulose (polysaccharide) and natural rubber (polyisoprene). Most synthetic polymers are organic compounds such as nylon, poly(hexamethyleneadipamide), poly(ethyleneterephthalate), plexiglass and poly (methyl methacrylate) [5].

Particle irradiation is a dimension of materials science which, like temperature, potentially affects all processes and properties. Ion molecules, radical–pairs, single radicals, and charged species are generated in polymers by the use of electron beams and gamma-ray sources. In pure alkyl- polymers a large proportion of the deposited energy results in radical–pair formation. The alkyl–polymers are evacuated of air gases, particularly oxygen, then impregnated with bridging agents, which facilitate the propagation of chain-reactions and annealed. Networks of crosslinking are rapidly formed. Such networks are useful in reducing creeps, raising the high temperature moduli, extending the melting range and inducing partial memory into the polymers. Polymers of this type, with increased melt-integrity, are advantageous in high temperature applications and also in conditions where reduced ageing or creep is required. Dr. R.A Jones and co-workers [62] have extended the principles of chain reaction crosslinking to other polymers which do not have such a high yield of radical- pairs following irradiation. Such
studies are relevant to the understanding of the effects of displacement and ionization in producing particle fluxes on materials[62].

1.3 Polymerization

Polymerization is the process where small molecules or repeating units are joined together to create large molecule synthetic polymers. Pioneering works in polymer science revealed that polymers can be produced by two familiar types of organic reactions, i.e condensation and addition reactions [6].

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Monomer</th>
<th>Repeat unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>CH₂=CH₂</td>
<td>-CH₂CH₂⁻</td>
</tr>
<tr>
<td>Poly (vinyl chloride)</td>
<td>CH₂=CHCl</td>
<td>-CH₂CHCl⁻</td>
</tr>
<tr>
<td>Polyisobutylene</td>
<td>CH₃</td>
<td>CH₃</td>
</tr>
<tr>
<td></td>
<td>CH₂=CH</td>
<td>-CH₂-C-</td>
</tr>
<tr>
<td></td>
<td>CH₃</td>
<td>CH₃</td>
</tr>
<tr>
<td>Polysoprene (natural rubber)</td>
<td>CH₂=CH-C=CH₂</td>
<td>-CH₂CH=C-CH₂⁻</td>
</tr>
<tr>
<td></td>
<td>CH₃</td>
<td>CH₃</td>
</tr>
<tr>
<td>Polycaprolactam (6-nylon)</td>
<td>H-N(CH₂)₃C-OH</td>
<td>-N(CH₂)₃C-</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>O</td>
</tr>
</tbody>
</table>

Table 1.1 Examples of polymers, their monomers and repeat units.
1.3.1 Condensation (step-reaction) Polymerization

Condensation polymers can be formed from the reaction between two species each containing a functional group, which results in the elimination of a small molecule such as water. The reaction continues until almost all the reagents are used up and an equilibrium is established that can be shifted at high temperatures by controlling the amounts of the reactants and products. One of the most familiar condensation reactions is that of the polycondensation of ‘x’ moles of diol with ‘x’ moles of a diacid that will give a polyester molecule. This is shown in figure 1.2 [7-8].

\[
\text{Diol} + \frac{\text{diacid}}{\text{o} \quad \text{o}} \quad \frac{\text{polyester}}{\text{o} \quad \text{o}} = \frac{x \ \text{HO-R-OH} + x \ \text{HO-C-R’-C-OH}}{\text{H[-O-O-C- R’ -C-]x.OH+ (2x-1)H_2O}}
\]

**Fig 1.2**: The formation of polyester by condensation reaction

In the polyester molecule above, the structure in brackets is the repeating unit which distinguishes one polymer from another. The quantity ‘x’ is the degree of polymerization i.e., the number of repeating units strung together in the polymer chain. The ester linkage characterizes all polyesters.

1.3.2 Addition (chain-reaction) Polymerization

The second type of polymer formation reaction is known as addition polymerization and its products are known as addition polymers. Addition polymerization involves chain reaction in which the chain carrier may be an ion or reactive substance with one unpaired electron called a free radical. A free radical migration is necessary to start the reaction. In a very short time (usually a
few seconds or less) many more monomers add successively to the growing chain. Finally two free radicals react to anilde each other’s growth activity and form one or more polymer molecules. Since no molecule is eliminated in the process, the repeating unit has the same chemical formulae as the monomer. An example of addition polymerization is the synthesis of polyethylene via a radical addition mechanism as shown in Fig 1.3. The radical generated from benzoyl peroxide (R•) attacks an ethylene molecule to generate a new radical, which further reacts with another ethylene molecule. A long chain of CH₂ group is formed rapidly. Eventually, this process is terminated by the combination of the two long-chain radicals to form a polymer called polyethylene [9.]

1) R• + CH₂=CH₂ → R-CH₂-CH₂ •

2) R- CH₂-CH₂ • +CH₂=CH₂ → R-CH₂-CH₂-CH₂-CH₂ •

3) R-[CH₂-CH₂]ₓ-CH₂-CH₂•+R-[CH₂-CH₂]ₓ-CH₂-CH₂• → -[CH₂-CH₂]ₓ-CH₂CH₂-

CH₂CH₂-[CH₂- CH₂]ₓ- R

Fig 1.3. The formation of polyethylene by addition reaction.

Most of these polymers are conventionally regarded as insulators, not being able to conduct electricity because the electrons that form covalent bonds are tightly bound, thus not allowing motion of electrons. However, recent advances have made them otherwise, being able to conduct electronically and ionically. This has introduced another class of polymers known as conducting polymers[10].
1.4 Conducting Polymers

Conducting polymers include both electron and ion conductors[11]. Fig 1.4 exhibits the classification of polymers in terms of the conductivity.

![Classification of polymers from the conductivity point of view][1]

*Fig 1.4. Classification of polymers from the conductivity point of view.*[12].

1.4.1 Electron Conducting Polymer

Electron conducting polymers are polymers that conduct electrons along their backbone chain. It is important to note that only some polymers conduct electrons along their backbone chain[13]. This can only occur in polymers with extended systems of conjugated double bonds along their backbone chain. One example is the organic polymer polyacetylene[14-15], having chemical structure as shown in Fig 1.5
By removing one hydrogen atom from each carbon chain of polyethylene \([-\text{CH-CH}]_x-\), the carbon atoms will have an extra electron available for conduction. The extra electron will form a single bond at one side of the carbon atom and the other side will form a single bond with the neighbouring carbon atom of the chain. The result is a sequence of alternating single and double bonds along the polymer backbone as in Fig 1.5. The extra electron can then be induced to move along the polymer chain forming an electric current [17]. This conductivity can be further enhanced by doping the polymer with small quantities of electron-accepting or electron-donating species which is termed ‘p-doping’ and ‘n-doping’, respectively [18].

1.4.2 Ion Conducting Polymers

Ion conducting polymers are solid polymers containing mobile anionic or cationic ions which act as the conducting species in the medium. The ionic conductivity, \(\sigma\), is proportional to the product of ion concentration and mobility. Ionic conductivities can be achieved in polymer systems by incorporating additives in the form of inorganic salts and or solvents into the polymer
matrix [19]. Table 1.2 shows some of the different ways in which ions can be incorporated in to polymers.

The gel polymer electrolyte is simply a polymer swollen with a solution of a salt in a liquid solvent. The salt is dissolved in the liquid, which is in solution in the polymer. The polymeric salt contains anionic or cationic groups which are bound to the polymer chain. These anionic or cationic groups act as counter-ions to small, unbound and potentially mobile ions. However, the mobility of the latter is severely restricted by strong cumbolic attraction if there is no solvent present. Upon addition of liquid solvent, the unbound ions become mobile as in the case of ionomers (cross linked and therefore insoluble, solvent-swollen polymers used as ion exchange resins) and polyelectrolytes (soluble polymers used as surfactants).

<table>
<thead>
<tr>
<th>Type</th>
<th>Composition</th>
<th>Mobile species</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gel polymer electrolyte</td>
<td>Polymer, salt and solvent</td>
<td>Cations, anions and solvent</td>
<td>1'VF₂, PC + LiClO₄</td>
</tr>
<tr>
<td>Ionomer or polyelectrolyte</td>
<td>Polymeric salt</td>
<td>None, unless wet</td>
<td>Nafion</td>
</tr>
<tr>
<td>Solvating polymer</td>
<td>Polymeric solvent / salt</td>
<td>Cations and anions</td>
<td>PEO + LiClO₄</td>
</tr>
</tbody>
</table>

Table 1.2 shows some of the different ways in which ions can be incorporated into polymers.

Abbreviations:

\[
\begin{align*}
PVF₂ & \quad \text{Poly(vinylidene fluoride)} \\
PC & \quad \text{propylene carbonate} \\
PEO & \quad \text{Poly(ethylene oxide)}
\end{align*}
\]
LiClO₄ - lithium perchlorate

The most important class is the solvating polymer in which the polymer itself has the ability to dissolve certain salts and support ionic mobility. This ability is an essential prerequisite for fast ion conduction in a dry polymer. Since the solvating polymers do not require the addition of a liquid supporting solvent, they can be classed as genuine solid polymer electrolytes [20]. Some examples of these solid polymer electrolytes are PEO, poly(propylene oxide)PPO, poly[(alkoxy) phosphazene], poly(ethylene imine) and POMOE (polyoxymethylene oligo oxyethylene).

1.5 Solvating Polymers

Solvating polymers or solid electrolytes are defined as thin films of solid ionic conductors formed by the dissolution of salts in an appropriate polymer containing solvating ether atoms [21]. Solvating polymers have received considerable interest because of the interesting scientific problems which they pose and due to their potential applications as solid-state electrolytes in electrochemical devices including all solid state batteries, sensors, electrochromic displays, electrochromic windows, solid-state photoelectrochemical cells and electrochemical transistors [22-23]. The most common examples of solvating polymers are complexes formed by the dissolution of alkali metal salts in poly(ethyleneoxide)[PEO]. Table 1.3 shows a variety of polymers which have been reported to solvate ions or form complexes[24].
<table>
<thead>
<tr>
<th>Solvating group</th>
<th>Polymer</th>
<th>Cation Solvated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ether(R-O-R')</td>
<td>PEO</td>
<td>Various</td>
</tr>
<tr>
<td>Ester(R-C-OR')</td>
<td>PE succinate</td>
<td>Li⁺</td>
</tr>
<tr>
<td>Amine (R-NH₂)</td>
<td>PE imine</td>
<td>Li⁺</td>
</tr>
</tbody>
</table>

Table 1.3. Solvating groups in polymers (note R,R' is an alkyl group)

Generally, polymer electrolytes have a multiphase nature, consisting of salt-rich crystalline phase, pure polymer crystalline phase and amorphous phase containing the dissolved salts. As mentioned earlier, solid state polymer electrolytes are able to conduct ions, in the form of anions and cations. The conduction occurs primarily through the amorphous elastomeric phase of the polymer, with both ionic aggregation effects and local segmental motion of the polymer backbone playing a major role[25-26]. Ionic conductivity is high only above the glass-rubber transition temperature, because the long range ionic transport is strongly correlated with the cooperative movements of the polymeric chains which occur in the amorphous phase of the complex above the glass transition temperature Tg. However, the conductivity drops to very small values in crystalline phases [27-28]. Electrical properties of polymer electrolytes depends on the structure of polymer matrix. Dynamic property of amorphous phase and crystallinity of electrolyte would affect the conductivity of polymer electrolytes.
1.6 Poly(ethylene Oxide) [PEO]

Since this dissertation is about polyethylene oxide, it is thus necessary to write some review about the material itself. Poly(ethylene oxide), a typical polyether is a linear polymer consisting of the monomer ethylene oxide (EO) [29]. It is a thermoplastic, water soluble and highly crystalline material with melting point at about 65°C and glass transition temperature of the amorphous elastomeric phase at about -55°C. The general formulae of poly(ethylene oxide) is shown in Fig 1.6(a). Unlike most polymer systems, PEO is available in a wide range of molecular weights. The lower molecular weight members of the series, with the ‘n’ value up to about 150, are generally known as polyethylene glycol, while the higher molecular weight members are known as poly(ethylene) oxide. The higher molecular weight members of the PEO series, can be classified as true thermoplastic while the low molecular weight members as wax like solids.

![Diagram of Poly(ethylene oxide)](image)

**Fig.1.6a. General formulae of Poly(ethylene oxide)**

The light molecular weight fraction is extremely soluble in water while the higher molecular weight fraction of about 1000 and above, is insoluble in water [30].
PEO has attracted considerable attention because of the following characteristics

1. Good ion solvating property.

2. Lone pair electrons on the oxygen has sufficient donor power to form coordinate bonds with cations.

3. Low barriers to bond rotation so that segmental motion of the polymer chain can take place readily.

Several monovalent, divalent and trivalent salts have been found to dissolve in PEO leading to a variety of polymer electrolytes. Following this Wright and coworkers have reported on the enhanced conductivity of PEO containing NaI, NaSCN, or KSCN [31-32]. These additives were found as crystalline complexes with a 1:4 (salt/EO) stoichiometry and melting points well above that of pure PEO. Infact, the salts easily form complexes when the common solvent used has a low electron pair donor power (e.g. acetonitrile) and does not compete with the ether oxygens. In many cases, the complex precipitates upon mixing the components in low dielectric constant liquids (e.g. LiBr and PEO in THF). Three parameters are important for the control of salt/neutral molecule interactions. They are

1. Donor number (DN)

2. Acceptor number (AN)

3. Entropy term

Donor number (DN) measures the ability of the solvent to donate electrons to solvate the cation considered as Lewis acid. On the other hand, the acceptor number qualifies the possibility for anion solvation. The entropy term depends on the optimal spatial disposition of the solvating units. The PEO helix has a much
more open structure as shown in Fig.1.6(b). The other cell parameters are reported to be \( a = 0.805 \text{ nm} \) and \( b = 1.304 \text{ nm} \) and \( \beta = 125.4^\circ \) with the most probable space group \( P_{21/a} - C_{2h} \) and molecular structure (compared with that in Fig 1.6 b) is equal to 7.2 helix.

Ionic soilds dissolve in polymers such as PEO, because the lone pair electrons on the polymer oxygens coordinate with the cations in a manner similar to crown ethers. This implies that the spacing and conformational flexibility proved by the PEO unit, \(-\text{CH}_2-\text{CH}_2-\text{O}\) is optimal for coordination.

![Schematic model of poly (ethylene oxide)](image)

**Figure 1.6 b**: Schematic model of poly (ethylene oxide) [33].

The chemical stability of the ether functional group strengthens the superiority of PEO as a host for a solid polymer electrolyte(SPE), but the conductivities at room temperature are still poor.
Chapter One

1.7 PEO Content, Electrical Conductivity and Glass Transition Temperature ($T_g$)

The material(s) added to PEO in the effort to maintain the high electrical conductivity at room temperature is (are) commonly called impurity(ies). The ionic mobility correlates closely with the relaxation modes of the host polymer. This is demonstrated by the observed increase in glass transition temperature ($T_g$) of polymeric systems as the concentration of the added salt is increased.

![Graph showing variation in conductivity with salt concentration](image)

Figure 1.7: Variation in conductivity with salt concentration for an amorphous poly (ethylene oxide) polymer containing Li ClO$_4$ (33)

The reduction in segmental motion is usually interpreted as being the result of the effects of an increase in intramolecular and intermolecular coordination between coordinating sites on the same or different polymer chains caused by the ions.
acting as transient cross links. The availability of vacant coordinating sites is greatly reduced at high salt concentrations by the stiffening of the matrix which reduces the conductivity. Also, as the salt concentration varies the degree of crystallinity of the polymer correspondingly varies but not proportionately. It was observed that as the crystallinity of the polymer decreases, the conductivity increases (33). Thus it is necessary to control the degree of crystallinity. In general, if a graph is plotted with conductivity along Y-axis and concentration of the salt along X-axis, a trend as shown in Fig 1.7 is observed, whereby the electrical conductivity increases with the salt concentration, reaches a maximum at a particular salt concentration and then decreases with additional salt content.

1.8 How Is PEO Produced?

PEO is produced from the ring-opening or addition polymerization of ethylene oxide, \( \text{H}_2\text{C}-\text{O}-\text{CH}_2 \). Ethylene oxide is important as a highly reactive chemical intermediate due to the large strain energy of its three membered ring, the presence of an oxygen-ethylene ‘pi’ bond and the existence of resonance hybrid forms i.e. \( +\text{CH}_2\text{CH}_2\text{O} \) and \( -\text{OCH}_2\text{CH}_2^+ \).

In general, the polymerization of ethylene oxide can be classified into three types, namely 1) anionic polymerization, induced by alkali. 2) Cationic polymerization is induced by Lewis acid and 3) Coordination polymerization where by a catalyst is added to the monomer to activate it for attack by an anion. The anionic and the cationic polymerization produce relatively low molecular weight polymers (MW~ 20000gmol\(^{-1}\)) that for the most part are liquids or waxy
solids. The coordinate anionic polymerization produces extremely high molecular weight (up to $5 \times 10^6$ g mol$^{-1}$) [34] and tough, thermoplastic polymers.

### 1.8.1 Low Molecular Weight Polymer Synthesis

To obtain low molecular weight polymers, ethylene oxide is polymerized in the presence of an initiator such as alcohol, ethylene glycol or water. Other compounds that contain a reactive functional group may also be used. An example of anionic polymerization induced by an alkali (NaOH) is as follows [34].

**Initiation:**

$$\text{H}_2\text{C-CH}_2 + \text{ROH} \rightarrow \text{ROCH}_2\text{CH}_2\text{O}^-\text{Na}^+$$

**Propagation:**

$$\text{ROCH}_2\text{CH}_2\text{O}^-\text{Na}^+ + \text{H}_2\text{C-CH}_2 \rightarrow \text{ROCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}^-\text{Na}^+$$

This step is then repeated until a total of ‘n’ ethylene oxide units have been added to the polymer chain.

**Termination:**

When the reaction has been completed, the system may be terminated by neutralization.

$$\text{O}((\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_2\text{CH}_2\text{O}^- + \text{Na}^+ + \text{HCl} \rightarrow \text{RO}-(\text{CH}_2\text{CH}_2\text{O})_{n+1}\text{H} + \text{NaCl}$$
1.8.2 High Molecular Weight Polymer Synthesis

High molecular weight polymers can be formed in the presence of alkaline earth carbonates. The initiation of polymerization is inhibited by the presence of an adsorbed anion such as chlorate, nitrate and thiosulphate. Therefore, the polymerization of ethylene oxide with these catalysts was considered to be anionic in nature and it appears to involve a heterogeneous reaction system with propagation of the polymer appearing to take place on the catalyst surface. It has been reported [34] that the catalytic polymerization of ethylene oxide takes place as follows.

1. The monomer is physically adsorbed on the catalyst and this is followed by ring- opening through the carbon-oxygen bond.
2. Chemisorbed polymer gradually forms followed by the growth of the polymer chains.

1.9 PEO-Salt Complexes

Polymer complexes consisting of PEO and alkali metal salts are one of the best studied polymer electrolytes due to the wide range of possible applications in various electrochemical devices.[35] PEO has been the favoured solvating medium for alkali metal salts on account of its ability to coordinate effectively with the salt cations and form homogenous solutions [36].

In PEO-salt complexes, complexation between the salt cations and PEO takes place at the lone pair electrons on the oxygen ie, the heteroatom (polar group) of PEO. Also, the complexed salts in PEO derives from large delocalised anions, a
criterion encountered with aprotic solvents[37]. The simplest formula of the salt co-ordination complexes in PEO is as below

\[
-(\text{CH}_2-\text{CH}_2-\text{O})_n + \text{MX} \rightarrow -(\text{CH}_2-\text{CH}_2-\text{O})\text{MX-}
\]

polymer salt complex

Here, oxygen acts as a donor for the cation $M^+$ while the anion $X^-$ generally of large dimension, remains in close proximity to preserve local charge neutrality. Therefore, the ionic transport in most of PEO based polymer electrolyte is cooperative with the segmental motion of the main chain, because cations in the polymeric phase are strongly solvated by the PEO segments.

The complexing capabilities of PEO towards divalent cations mainly alkaline earth, have also been reported and reveal an extraordinarily rich coordination for this polymer. Several monovalent and divalent cations which have been reported to form complexes with PEO are listed in table 1.4[38].

<table>
<thead>
<tr>
<th></th>
<th>Li$^+$</th>
<th>Na$^+$</th>
<th>K$^+$, Rb$^+$, Cs$^+$, NH$_4^+$</th>
<th>Mg$^{2+}$</th>
<th>Ca$^{2+}$</th>
<th>Zn$^{2+}$</th>
<th>Cu$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>F$^-$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
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<td>+</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>I$^-$</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
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<td>+</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>+</td>
<td>-</td>
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<td>+</td>
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<td></td>
</tr>
<tr>
<td>SCN$^-$</td>
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<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
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<tr>
<td>ClO$_4^-$</td>
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<td>+</td>
</tr>
<tr>
<td>CF$_3$SO$_4^-$</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>BPh$_4^-$</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
<td>+</td>
</tr>
</tbody>
</table>

Table 1.8 salt forming (+) and not salt forming (-) adducts with PEO
1.10 Preparation Techniques of PEO-Salt Complexes

PEO-salt complexes can be prepared by two main techniques, i.e., solution casting method and melt method.

1.10.1 Solution Casting Method

Most thin film PEO-salt complexes have been prepared by casting a solution of components onto Teflon discs and slowly evaporating the solvent. This method is simple and components are homogeneously mixed. However, the residual solvent is extremely difficult to eliminate and may adversely affect the conductivity[39-40].

1.10.2 Melt Method

Gray et alies [41] successfully prepared thin films by melt or hot pressing method. To optimize distribution of salt throughout the polymer, the PEO and salt were ground together in a specially constructed ball mill and then annealed before pressing. This method avoids all problems associated with residual solvent and is preferable when dealing with co-mixed polymer systems.

1.11 Characteristics Of PEO-salt Complexes

PEO-salt complexes are characterized by their multiphase behavior, morphology and ionic transport mechanism [36].

20
1.11.1 Multiphase Behavior

PEO-salt complexes generally have a multiphase nature consisting of PEO-Salt crystalline phase and a PEO-salt amorphous phase,[42]. In the crystalline phase, the PEO chains are rigid and thus the ion mobility is almost negligible and the overall conductivity is very low. Even as temperature increases, both crystalline PEO and the salt rich crystalline complex in the bulk sample inhibit conductivity. Effective conduction occurs only in the amorphous elastomeric phase. The overall conductivity behavior is determined by several phenomena, and is not merely due to activated ion motion[43].

At a relatively low temperature where organic polymers can be studied and used, ionic conduction is nearly always greater in the liquid than in the solid state. Naturally, if the samples contain liquid or closely related elastomeric phases, then the phase will bypass any conduction paths through solid crystalline phase. Samples which do not contain these phases will be relatively poor conductors and also will be mechanically brittle, showing very little plasticity. This tells us that polymers with liquid-like transport mechanism property have to be selected to study electrical behavior (44-50).

Among the four phases investigated, it was observed that the elastomeric phase is solid but behaves really, like a liquid. Based on this observation, we can argue that the host phase for conduction in a polymer electrolyte is not really a liquid but an elastomeric phase. This is a phase in which local motion is liquid like but long range displacement is forbidden. An elastomer will fulfill the following solid like properties.

a) negligible low vapor pressure
b) well defined shape under constant stress

c) negligible long range self diffusion

This behavior gives evidence that the elastomeric phase is a state which is neither liquid nor solid. It is through this approach that an understanding of the polymer electrolyte’s conduction properties has to be grasped.

Many studies on polymer electrolytes have been directed towards understanding the fundamental questions regarding the structure, mass and charge transport, ion interaction, ion-ion interaction, solvation mechanism and ion conduction mechanism.

![Diagram of polymer microstructure](image)

**Figure 1.8: Example of a polymer microstructure, showing amorphous regions of PEO (44)**

No unified theory has emerged to explain all the properties of polymer electrolytes except for the conclusion that ionic conduction occurs principally in the amorphous phase.
1.11.2 Description of Polymer Structure and Mobility

Figure 1.8 shows a two dimensional, molecular scale representation of a polymer. At relatively low temperatures, a network of columbic, hydrogen bond or van der Waals attraction between the monomer units ensures that it is in solid state in the conventional sense. As long chain polymer are not closely packed, they can show amorphous nature in their arrangement. This brings about glass formation. A single long chain molecule can wind (refer to Figure 1.8) its way through crystalline and amorphous regions. The columbic, hydrogen and vander Waals bonds are generally weak and these bonds can be disrupted by raising the temperature or adding a solvent in exactly the same way as in our assembly of small molecules. However, the covalent bonds are very strong and they are not easily broken. If these bonds break, then the material decomposes.

1.11.3 Morphology

For PEO-Salt complexes, the form of the crystalline region is often dendritic or spherulitic [51]. The latter consists of interconnected crystalline regions radiating out from common center, like florets on an onion flower. The spherulites contain amorphous material trapped between the crystalline region. More importantly, the spherulites themselves are embedded in an amorphous matrix, which is the 'solution' of metal salt in polymer. It is in this amorphous 'solution' that ionic conduction takes place, typically both anions and cations are mobile to some extent. It also appears that some local freedom of motion of the cation is necessary to permit the anions to be mobile, even in the case of systems for which the cation transport number is effectively zero. Otherwise, highly
crystalline PEO-salt complexes in which the cations are immobile would display significant anionic conduction [52].

1.11.4 Ionic Transport Mechanism

It has been established that conductivity occurs by the migration of ions in the form of cations and anions which takes place preferentially in the amorphous phase of PEO-salt complexes. This ionic transport is cooperative with the segmental motion of the main chains, because cations in the polymeric phase are strongly solvated by the PEO segments [52]. From several spectroscopic and conductivity studies, it is generally accepted that significant ion pairing occurs in the polymer electrolytes [53]. The segmental motion normally involves more than 10 repeat units, which is a main reason for the WLF-type large temperature dependence of ionic conductivity of the polymer electrolytes in spite of the small size of the carrier ions [54]. Many theoretical models have been proposed to explain the ionic transport mechanism in the polymer electrolytes and their conductivity variation as a function of temperature and composition [37].

1.11.4.1 Some Empirical Relationships

In the solid phase, motion is thermally activated; the jump rate equals an attempt frequency, $v_0$ multiplied by a probability of surrounding energy barrier, $E_A$

$$v = v_0 \exp \left[ -\frac{E_A}{kT} \right]$$

In the elastomer phase, an additional mode of transport becomes available using the free volume. Here the diffusing unit effectively takes a ride in the free volume as it moves around the fluid. This jump is volume activated and the jump rate is given by
\[ v = v_0 \exp\left[ -v_a / v_f \right] \]

where \( v_f \) is the average free volume in the vicinity of the unit and \( v_a \) is the volume of diffusing unit.

The effect of temperature on mobility in a liquid or elastomer is given by the expansion coefficient \( \alpha \) in the expression

\[ v = v_0 \exp\left[ -v_a / \alpha (T-T_0) \right] \]

where '\( v \)' is assumed to start from zero at the theoretical glass transition temperature, \( T_o \). With all these, we get the VTF (Vogel-Tamman-Fulcher) equation for temperature dependence of conductivity, which replaces the Arrhenius equation used for solids. The VTF equation is given below with a slightly temperature dependent coefficient \( A[24] \).

\[ \alpha = A \exp[ -B / (T - T_0) ] \quad (1.1) \]

The important aspect of the equation is that it stresses the need for a low transition temperature to achieve high good conductivity value and also the requirement for a high free ion concentration.

The \( \sigma \) vs \( 1/T \) plots generally show a sudden conductivity jump, in most cases, approximately at the melting temperature \( T_m \), when semicrystalline to amorphous phase transition takes place. The \( \sigma \) vs \( 1/T \) plots are generally linear typical of Arrhenius behavior:

\[ \sigma(T) = \sigma_o \exp(-E_a / kT) \quad (1.2) \]

but for most cases, \( \sigma \) vs \( 1/T \) plot has curved nature with VTF (Vogel-Tamman-Fulcher) type behavior expressed as[24].

\[ \sigma(T) = A T^{1/2} \exp[-E_a / k(T-T_0)] \quad (1.3) \]
where $A$ is the pre-exponential factor, $E_a$ is pseudo activation energy and $T_o$ is the equilibrium glass transition temperature. The VTF behavior is more general (than exception) when the measurements are extended over a wide range of temperature. In general $T_o$ is 50 K lower than actual glass transition temperature $T_g$. The above equation is the derived form of an empirical VTF equation originally developed to explain the viscosity behavior of glassy liquids.

Another empirical relationship is based on William, Landel and Ferry (WLF) equation of viscosity modified due to different relaxational processes in the amorphous materials. The WLF equation is [24]

$$
\sigma (T) = \sigma T_r \exp \frac{C_1 (T - T_r)}{C_2 + (T - T_r)}
$$

(1.4)

where $C_1$ and $C_2$ are constants. The values $C_1$ and $C_2$ depend on the choice of reference temperature, although they are commonly normalized to the reference temperature $T_g$ [25]. $C_2$ relates the WLF reference temperature $T_r$ with VTF temperature $T_o$ as $C_2 = T_r - T_o$. The reference temperature, $T_r$ may be chosen anywhere between $T_g$ and $T_g +150^\circ C$, according to experimental convenience. Thus a property can be specified over a wide temperature range by tuning $C_1$ and $C_2$ to give the best data.

1.11.4.2 Free Volume Theory And Configurational Entropy Models

The WLF and VTF fittings are empirical relations which can be explained on the basis of free-volume theory. However, the free-volume picture is entirely an independent phenomenon given by Cohen and Turnbull. They considered the liquids as hard spheres (ions in the case of polymer electrolytes) which are free to
move in volume fractions (voids), called free volume, and derived the probability distribution of void volume in the total volume of the system. Following the Cohen and Turnbull treatment, the free volume expression for diffusion coefficient 'D' has been derived to be

\[ D = g u a \exp \left[ -\gamma v / \alpha V' m (T - T_0) \right] \]  

(1.5)

Here \( g \) is a geometrical factor, \( u \) is molecular dimension, \( \gamma \) is Lagrange parameter, \( v \) is critical free volume. Following the Nernst-Einstein relation, the free volume theory results as the equation (1.3) which is the VTF equation that explains \( \sigma \) vs \( 1/T \) behaviour of many polymer electrolytes. The main attraction of the free volume theory is its simplicity. This theory, although explains some properties of polymer electrolytes via VTF equation, only involves the consideration of motion of polymer hosts (not the ionic hopping in the polymer-salt complexes). The \( \sigma -T \) relationship of different polymer electrolytes does not merely follow the VTF behaviour derived from free-volume theory. Secondly, free volume theory is realistic only for rigid molecules. A confusion arises when the free-volume model is used for the treatment of flexible molecules. When the free-volume theory is correct, it becomes similar to 'configurational entropy model' given by Gibbs and co workers. This model was originally developed as lattice model in which the single parameters of the free volume theory has been replaced with two parameters; one counts the number of lattice points and the other the number of distorted bonds. The WLF behavior which describes the behavior of most of the polymer electrolytes, has been derived using configurational entropy model by Adam and Gibbs [55].
1.11.4.3 Dynamic Bond Percolation Model: A Microscopic Theory

The WLF and VTF equations, free-volume theory and configurational entropy models are the quasi thermodynamic macroscopic pictures which are able to describe some broad physical properties of polymer electrolytes such as temperature dependence of conductivity, diffusivity and viscosity etc. Secondly, these models only describe the behavior of hosts, not the ionic motion in polymer-salt complexes. Further, the free-volume theory is not able to explain the microscopic behavior such as mechanistic aspects, transport properties as a function of molecular weight, dielectric relaxation etc.

Many microscopic models based on 'percolation' have been given for ionic motion in the polymer electrolyte. The static bond percolation model deals with the ionic motion in the electrolyte of rigid frame work. The well known experimentally observed property and amorphous phase is responsible for ionic conduction in polymer electrolytes, can be explained on the basis of static bond percolation model. But in the polymer electrolytes above the glass transition temperature (T>T_g) the ionic motion is due to the combination of ionic translational motion / hopping and dynamic segmental motion of the polymer hosts which assists the ionic motion. Druger et al [56] have given a generalized 'dynamic bond percolation model' in which the segmental mobility has also been included along with the ionic motion. In this generalized model, the bonds which are closed or open changes with characteristic rate λ or characteristic renewal time τ, (λ=1/τ). The change or renewal event is related with the segmental motion which either permits the ions to hop from one site to another site or give a pathway for ions to move, or in other words the segmental
movement of the polymer facilitates the transitional ionic motion. The dynamic bond percolation model is able to describe the various physical properties of polymer electrolytes such as dependence of conductivity on chain length of the polymers, molecular weight, applied pressure, effect of host polymer change, frequency dependence of conductivity etc.

1.12 Phase Changes

On heating, the amorphous region of the polymer becomes elastomeric or liquid at the glass transition temperature, $T_g$, and one or more melting points may be subsequently observed as the various possible ordered structures transform into elastomers or liquids. Generally at intermediate temperatures, polymers often contain crystalline regions, separated by thick elastomeric grain boundaries. If the chains are long enough to pass through the crystals, the crystals can act as cross links which mechanically stabilize the elastomer as shown in Fig 1.8. Low molecular mass liquid like components may also be present. The elastomeric phase is the main concern, in which the ion is coupled to that of the elastomeric host. The mobility of the elastomer and its guest ions will be considered with reference to free volume theory, which explains the nature of the coupling between polymer segment and ionic motion.

1.13 Mass Transport in Elastomer Phase

The covalent bond chains prevent the polymer from forming close packed structure. The resulting vacancies are randomly arranged and static below the
glass transition temperature ($T_g$). Although the vacancies are quite abundant, forming about 2.5 percent of the total volume, they are unlikely to percolate into continuous tunnels allowing diffusion of foreign molecules [47,57] However, at temperatures above $T_g$, the labile bonds can be broken by thermal energy, so that a chain segment which is now capable of independent motion, can move into a neighboring vacancy provided it is sufficiently large. The monovalent represents a change in the conformation on the macroscopic scale. This also gives a mechanism for a continuous, random redistribution of the vacant space and allows long-range diffusion of small molecules through the structure. The same vacancy distribution is the primary route for ion transport, and therefore a major factor in determining the ion mobility. Therefore $T_g$ marks the onset of three transport processes,

a) short range translation of chain segments
b) small molecules diffusion
c) ionic conductivity

1.14 Factors which Determine the Conductivity

1.14.1 Tortuosity Factor

Polymer solvates are similar to liquid solutions in having solubility limits. For example, regular PEO which has symmetry to form crystals, exhibits the phase behavior illustrated in Fig 1.9. It can be seen from the figure that the non-conducting crystalline fraction is a major component above O/Li ratio of 6:1 over a wide range of temperatures. The conductivity in this range is due to a residual elastomeric phase which percolates an extensive insulating crystal
network (44). The ratio between the conductivity of the conducting elastomer (sec 1.11.1) and the actual mixed phase is called the tortuosity factor. This appears to be the primary factor controlling the conductivity below or at about 80 °C.

![Phase diagram for PEO-Li As F₆ System](image)

**Figure 1.9: Phase diagram for PEO-Li As F₆ System (44)**

1.14.2 Effective Mobile Ion Concentration

Although cations and anions are well separated in very dilute solute solutions, ion association effects come in to play well before the optimum concentrations for high conductivity are reached. This is the weak electrolyte model, which assumes that only a small portion of the ion concentration contributes to the conductivity while the majority of the ions are paired, neutralized and therefore immobilized. At high concentrations, an increase in mobility is often encountered, and this has
been rationalised in terms of triple ion formation. Applying these results to polymer electrolytes, is however, fraught with difficulties. There are a couple of reasons for this. Firstly, the concentration range of interest is so high that even triple ion models break down in favour of the fused salt model, in which ion pairs are so close to neighbouring ions that they cannot be considered as separate entities. Secondly, because of the long-range immobility of the solvent, the strong cation-solvent interaction is expected to play a greater role in an elastomer than in a liquid. Systematic analysis of the variation of conductivity with concentration is complicated due to the simultaneous increase in glass transition temperature, \( T_g \).

1.15 Applications of PEO-Salt complexes

The PEO salt complexes are used as electrolytes in different electrochemical devices such as electrochemical sensors, electrochromic devices and solid state electrochemical cells.

1.15.1 Electrochemical Sensors

Sensing devices measure chemical or physical quantities, and to be practical they must be handy, speedy and easy to use. Thus the output signals are ordinarily in electrical quantities. The essential part of sensing devices is the sensor itself, which transduces a quantity to be measured into an electrical signal [58]. A number of sensor designs based on electrochemical cells can benefit from miniaturization and mass production by using polymer electrolytes. These types of sensing devices are called solid state electrochemical sensors and used for determining concentrations of atoms, molecules or ions. One of the examples is
the potentiometric all solid-state gas sensors which represents the simplest
galvanic cells in solid state electrochemistry[59].

1.15.2 Electrochromic Device

Electrochromism is the phenomenon related to changes in colour induced in
certain materials by reversible electrochemical process which involves either
electron or ion inception. The common ion used for insertion are H⁺, Li⁺, Ag⁺
and Na⁺. The materials which change colour on charge insertion could be
inorganics (eg. WO₃, NiO, MoO₃, etc) or organics (eg. Polyanilene,
polythiopane). A common electrochromic device structure is shown in the
following Figure 1.10. On application of low d.c voltage, the cations (A⁺) from
the ion conducting electrolyte get inserted in the electrochromic materials
(ECHs). To ensure neutrality, the insertion of one cation must be accompanied by
the ejection of one electron comes from the other electrode [60]. The overall
reaction that takes place is as follows.

\[
\text{ECM} + x\text{A}^+ + xe^- \rightarrow Ax \cdot \text{ECM}
\]
**Fig 1.10. Common structure of electrochromic device.**

### 1.15.3 Solid State Battery

Batteries are devices which provide electrical energy from spontaneous electrochemical reactions of the chemical material stored within the devices whenever required. Conceptually, the simplest solid state polymer battery system consists of two solid electrodes, an anode and a cathode, separated by a solid polymer electrolyte as shown in Fig 1.11(a).
Fig 1.11 (a) Solid state polymer battery  (b) Discharge characteristic

They produce power by a redox reaction between anode and cathode species, reduction taking place at the cathode and oxidation at the anode. The ions involved in the cell reaction travel through the electrolyte whereas the electrons take a different pathway, through an external circuit. By doing so, the electrons can do external work, providing power. That is, the chemical work associated with the cell reaction is converted into electrical work. The change in Gibb’s free energy, $\Delta G$, involved during oxidation-reduction provides the zero-current voltage, $E$, given

$$E = \frac{\Delta G}{|Z| F}$$  \hspace{1cm} (1.6)

Here $Z$ is the valency of the conducting species and F is the Faraday’s constant.

For an ideal battery, the voltage should remain constant when current is being drawn from it. However, such a characteristic is generally not obtained. Fig 1.11(b) shows a typical battery characteristic [61].

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1.16 Objectives of the Present Work

PEO has been extensively studied because it can solvate many types of salts. The salt and polymer forms a complex and spectroscopic studies can show the PEO-salt interaction. The choice of salt is also important in producing a high conductivity complex. There has not been many studies that involves PEO with organometallic compounds. Organotin compounds are air-stable products with already a wide range of chemical application which tend themselves as good substrates for such studies. In this thesis, we have selected two compounds which are tin thiocyanate and tetramethyl ammonium dichlorotriphenyl stannate (IV). In most inorganic salts involving tin, the tin cation can be either in the $2^+$ or $4^+$ state. It is also known that polyvalent cation in polymers do not exhibit high ionic conductivity. In triphenyltin thiocyanate the cation containing tin is monovalent, while in tetramethylammonium dichlorotriphenyltin the anion contains tin and is also monovalent. The choice of these two organotin compounds would enable us to study the effect of tin being a part of the monovalent cation as in triphenyltin thiocyanate and tin being a part of the monovalent anion in tetramethylammonium dichlorotriphenyl tin. Hence using organotin compounds it is possible to have a monovalent ion containing tin compared to inorganic compounds containing tin where the ions are of multiple valency. As in other studies, X-ray diffraction will be carried out to justify if the compound can reduce the crystalline non-conductive phase of the PEO and IR spectroscopy to justify if complexation has occurred. Transference number measurement will provide evidence whether the materials prepared are ionic.
conductors or otherwise and if the conductivity is sufficient whether there is potential for the materials to be used in solid state batteries.