Chapter 1

Introduction

1.0 Introduction

Although, most of the polymers that are used in daily life are insulators, this work is devoted to an important class of recently developed polymers that conduct. Many polymeric materials can be formed into thin, mechanically strong films. It is also desirable from the above fact that we can confer the additional property of electrical conductivity on these polymers. Consequently, a lot of research has been made towards developing plastic materials, which conduct ions and/or electrons [1].

1.1 Polymer

The word 'polymer' is of Greek origin, which describes many natural and synthetic materials. A polymer can be broadly defined as a high molecular weight molecule created by repetitive reaction of many thousands of small and simple chemical units or low molecular weight molecules called "monomers". In some cases, the repetition is linear, like a chain, which is built up from its links. In other cases, the chains are branched or interconnected to form three-dimensional networks [2-3]. These are illustrated in the figure [1.1].

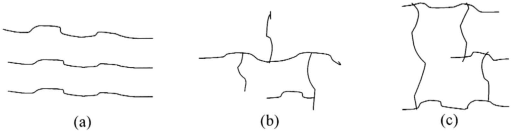
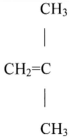
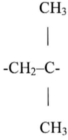
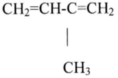
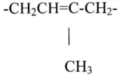
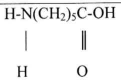
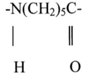

(a) (b) (c)

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

Covalent bonding links these units to each other. These bonds are formed when one or more pairs of valance electrons are shared between two atoms, again resulting in a stable electronic shell. The repeat unit of a polymer is usually equivalent or nearly equivalent to the monomer, or starting material from which the polymer is formed. For example, the repeat unit of poly(vinyl chloride) is $-CH_2CHCl-$; its monomer is vinyl chloride, $CH_2{=}CHCl$. Table [1.1] shows a variety of polymers with their monomers and repeat units.

Table [1.1]: Examples of polymers, their monomer and repeat units.

Polymer	***Monomer***	***Repeat Unit***
Polyethylene	$CH_2{=}CH_2$	$-CH_2CH_2-$
Poly (vinyl chloride)	$CH_2{=}CHCl$	$-CH_2CHCl-$
Polyisobutylene	 $CH_2{=}\overset{CH_3}{\underset{CH_3}{C}}$	 $-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-$
Polyisoprene (natural rubber)	 $CH_2{=}CH-\underset{CH_3}{C}{=}CH_2$	 $-CH_2CH{=}\underset{CH_3}{C}-CH_2-$
Polycaprolactam (6-nylon)	 $H-\underset{H}{N}(CH_2)_5\underset{O}{\underset{\Vert}{C}}-OH$	 $-\underset{H}{N}(CH_2)_5\underset{O}{\underset{\Vert}{C}}-$

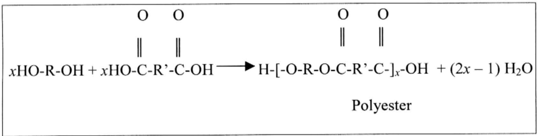
Naturally occurring polymers, biopolymers, include carbohydrates, proteins, nucleic acids, cellulose, lignin, etc. Cellulose, a polymer of glucose, is the major structural material of plants. It is a polysaccharide made up of β-D (+)-glucose residues joined in linear chains. Proteins, polymers of amino acids, are major constituents of living matter. Some serve as structural role; others are catalysts for virtually all-metabolic reactions. Nucleic acids, which are polymers of nucleotides, are carriers of genetic information. Synthetic polymers are made in laboratory and are familiar to us because we are literally surrounded with these substances. Examples include some of the clothes we wear, containers for food, computers, automotive parts, etc.

1.2 Polymerisation

The process in which monomers join to produce polymers is called polymerisation. The number of repeat units in the chain specifies the length of the polymer chain. This is called degree of polymerisation. In 1929, W.H.Carothers suggested a classification of polymers into 2 groups, condensation and addition polymers. These names indicate the type of reaction used to join monomers [4].

1.2.1 Condensation (Step Reaction) Polymerisation

Condensation polymers are those in which condensation takes place between two polyfunctional molecules to produce larger polyfunctional molecule with the possible elimination of small molecule such as water. The reaction continues until almost all of one of the reagents is used up and equilibrium is established that can be shifted at high temperatures by controlling the amounts of the reactants and products. Polyesters and polyamides are polymerised by condensation method One of the most common condensation reactions is the polycondensation of *x* moles of diol with x moles of a diacid that will give a polyester molecule. This is shown in the figure [1.2].



$$x\text{HO-R-OH} + x\text{HO-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-R'-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-OH} \longrightarrow \text{H-[-O-R-O-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-R'-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-]}_x\text{-OH} + (2x-1)\,\text{H}_2\text{O}$$

Polyester

Fig [1.2]: The formation of polyester by condensation reaction.

1.2.2 Addition (Chain Reaction) Polymerisation

Addition or chain reaction polymerisation involves chain reactions in which the chain carrier may be ion or a reactive substance with one unpaired electron called free radical. A free radical is usually formed by the decomposition of relatively unstable material called initiator. The free radical is capable of reacting to open the double bond of a vinyl monomer and add to it, with an electron remaining unpaired. Thus, within few seconds, many monomers add to the successive chain. Eventually, the process is terminated by some reaction that destroys the reactive site. Alkenes can be polymerised by addition reaction.

An example of addition polymerisation is the synthesis of polyethelyene via a radical addition mechanism. The radical generated from benzoyl peroxide (R•) attacks an ethelyene molecule to generate a radical which further reacts with another ethelyene molecule. A long chain of CH_2 group is formed rapidly. Eventually, this process is terminated by the combination of two long chain radicals to form a polymer called polyethylene [5]. This is being illustrated in figure [1.3].

1) $R\bullet + CH_2{=}CH_2 \longrightarrow R\text{- }CH_2\text{- }CH_2\bullet$

2) $R\text{- }CH_2\text{- }CH_2\bullet + CH_2{=}CH_2 \longrightarrow R\text{- }CH_2\text{- }CH_2\text{- }CH_2\text{- }CH_2\bullet$

3) $R\text{-}[CH_2\text{- }CH_2\text{-}]_x\text{-}CH_2\text{- }CH_2\bullet + R\text{-}[CH_2\text{- }CH_2\text{-}]_x\text{-}CH_2\text{- }CH_2\bullet \longrightarrow$
$\text{-}[\text{-}CH_2\text{- }CH_2\text{-}]_x\text{-}CH_2CH_2\text{-}CH_2CH_2\text{-}[\text{-}CH_2\text{- }CH_2\text{-}]_x\text{-}R$

Fig [1.3]: The formation of of polyethylene by addition reaction

1.3 Conducting polymers

Traditionally, polymers were thought of as insulators i.e., unable to conduct electricity because the electrons that form covalent bonds are tightly bound, thus preventing motion of electrons. However, some electron and ion conducting polymers have been synthesized, introducing another group of polymers known as conducting polymers [6]. Figure [1.4] exhibits the classification of polymers in terms of the conductivity.

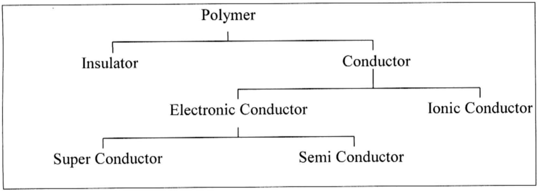


Fig [1.4]: classification of polymers from the conductivity point of view [7]

1.4 Electron conducting polymers

Electron conducting polymers are polymers that conduct electrons along their backbone chain [8]. This phenomenon can only occur in polymers with extended systems of conjugated double bonds along their backbone chain. One of the examples is the organic polymer polyacetylene [9-10], having chemical structure as shown in figure [1.5].

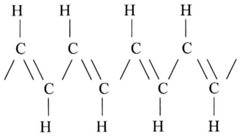
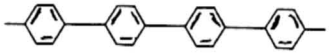
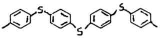
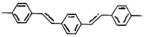
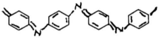
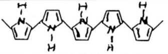
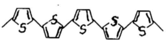


Fig [1.5]: Chemical structure of polyacetylene.

For electron conducting polymers, it is essential to have free electrons, which are fixed, in their positions. By removing one hydrogen atom from each carbon chain of polyethylene, the carbon atoms will have an extra electron available for conduction. The extra electron will form a double bond at one side of the carbon atom and the other side will form a single bond with their neighbouring carbon atom of the chain. The result is a sequence of alternating single and double bonds along the polymer backbone as shown in the figure [1.5]. The extra electron can then be induced to move along the polymer chain forming an electric current [11]. 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 [12]. Some examples of electron conducting polymers and their structures are shown in table [1.2].

Table [1.2]: Electron conducting polymers and their structures [13].

Polymer	**Chemical Structure**	**Conductivity (S/cm)**
PA		$10^3 - 10^5$
PPP		$10^2 - 10^3$
PPS		100 – 500
PPV		$3 - 5 \times 10^{-3}$
PAni		30 – 200
Ppy		$102 - 7.5 \times 10^3$
PT		$10 - 10^3$

1.5 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, σ 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 [14]. Ionic conduction in polymers depends on a number of factors. These include:

1. The solubility of the salt in the polymer.
2. The mobility of the ions; and
3. The availability of a connecting polar domain as the conducting pathway.

By optimising these factors, high ionic conductivity may be realised. Some examples of these polymers are PEO (Polyethylene oxide), PPO (Poly pyrrol oxide), PVdF (Poly vinyledene Fluoride), PVC (Poly vinyl chloride), PAN (Poly Acrylonitrile), PEG (Poly ethylene glycol), etc.

There are various types of polymeric conducting media having features, which distinguish them from each other. They can be classified under the following headings:

1. Polymer Electrolytes
2. Polyelectrolytes
3. Gel electrolytes

1.6 Polymer Electrolytes

A polymer electrolyte is a solid state material, which conducts ions but not electrons (or holes). Polymer electrolytes are usually exemplified by the polyethers such as Poly (ethylene oxide) PEO, Poly (propylene oxide) PPO. The number of known solvating polymers is rising; they include, in addition to PEO and PPO, poly (vinyl chloride), poly (ethylene succinate), poly (ethylene imine), poly (methylene sulphide), poly (ethylene adipate) and polyphosphozanes. These polymers coordinate with a wide range of inorganic salts, the most commonly used being lithium perchlorate ($LiClO_4$) Lithium triflouoromethanesulphonate (triflate) ($LiCF_3SO_3$) and Sodium thiocyanate (NaSCN).

Conductivity in polymer electrolytes is generally studied well above their glass transition temperature (T_g). It is nearly always interpreted in terms of the empirical Vogel-Tamman-Fulcher (VTF) equation or, more extensively, in terms of dynamic bond percolation theory. The VTF equation for conductivity, σ, of a polymer salt complex is written as

$$\sigma=A_oT^{\frac{1}{2}}\exp[-E_a/R(T-T_o)] \quad (1)$$

where A_o is a weakly temperature dependent prefactor, T_o corresponds to T_g and E_a is activation energy. The functional dependence can be described by a model in which the motion of the polymer chain is crucial for ion transport. Large-amplitude polymer backbone motion with simultaneous making and breaking of cation-oxygen interaction results in a mode of transport which is quite unlike the hopping mechanism observed in inorganic electrolytes.

1.7 Polyelectrolytes

A completely different type of conducting matrix is formed by the dissolution of an ionic polymer in an aqueous medium to give a 'polyelectrolyte'. Ionic polymers are hybrids of ionic salts and covalent polymers and can have structural features common to both. They are formed by the interaction of anionic and cationic moieties where, most commonly, one is polymeric while the other is a counter ion. Organic ionic polymers contain in-chain or, more characteristically, pendent charged groups, the density of which can vary, considerably affecting the physical and chemical properties.

1.8 Gel electrolytes

In polymer-salt-solvent systems the role of the polymer is secondary in the conducting matrix; it acts as a stiffener for the low molecular weight, high dielectric constant solvents which solvate the salt and act as the conducting medium. Polymers with a dipole moment, e.g. poly (vinylidene fluoride) and its analogues, form gels with some organic salt solutions. The conductivity follows Arrhenius type temperature dependence, both above and below the T_g, although a change in activation energy is usually observed at this temperature. The activation energy is, however, largely independent of polymer concentration, suggesting ion migration primarily through the solvent domain which surrounds the polymer matrix. In the absence of solvent there is some residual conductivity, probably as a result of ion hopping between localised sites, although the salt is largely dispersed as ion-pairs through the polymer [14].

1.9 Poly (Vinyl Chloride)

Polymers and copolymers of vinyl chloride are widely used as plastics and, to a much smaller extent fibers. In trade, these polymers are known as the "vinyls". Suspension polymer is used for the production of well over 80% of PVC. Poly (vinyl chloride) is a partially syndiotactic material, with sufficient irregularity of structure that crystallinity is quite low. The possibility of chain branching and the tendency of the polymer to associate in solution complicate its structural characterization. PVC is relatively unstable to heat and light. Thermal initiation involves loss of chlorine atom adjacent to some structural abnormality, which reduces the stability of the C-Cl bond, such as terminal unsaturation. The chlorine radical so formed abstracts hydrogen to form HCl; the resulting chain radical then reacts to form chain unsaturation with regeneration of chlorine radical. Stabilizers are almost invariably added to improve the heat and light stability of the polymer. Free radical acceptors appear to be a prominent mechanism of stabilization [4].

1.10 Low molecular weight organic solvents

Typical ambient temperature conductivities fall in the range of 10^{-7}to10^{-8} S/cm. To prepare electrolytes of higher performance, a number of workers have made homogeneous hybrid films of polymer, salt and a plasticiser which is a low molecular weight polar solvent. Due to their high dielectric constant, such plasticizers also tend to dissociate ion pairs into free cations and anions while assuming a conventional model of ion motion through the mixed systems, the low solvent viscosities should effectively lower the potential barrier to ion transport with increased conductivity ensuing. However, viscosity and ion mobility do not follow the simple relationship of common electrolytes, distinction has to be made between macroscopic and microscopic viscosity. Such systems offer an alternative approach to polyether-salt-based complexes as ionically conducting solid electrolytes [14].

Plasticizers are added to plastics to improve flow and, therefore, processability, and to reduce the brittleness of the product. This is achieved by reducing the glass transition temperature below room temperature, thus achieving change in properties from those of hard, brittle, glasslike solid to those of a soft, flexible, tough material. A plasticizer must posses basic properties such as compatibility and permanence. The plasticizer must be miscible with the polymer. This implies a similarity in the intermolecular forces active in the two components. Permanence requirements demand low vapor pressure and a low diffusion rate of the plasticizer within the polymer [4].

1.11 Polymers behave like solids and also like liquids

Polymers can hardly be regarded as single phase because they are composite materials, consisting of many phases. They are crystalline, glassy, elastomeric and even liquid phase. The elastomeric phase is unique to polymer. This is a high temperature state, above T_g, in which along range mobility is prohibited either by chain entanglement or cross-linking. Macroscopically samples in this state are essentially soft, elastic solids, which retain their shape without containment. However, microscopically they are mobile and contain much interstitial space.

At a relatively low temperature where organic polymers can be studied and used, ionic conduction is nearly always greater in liquid than in their solid state, naturally. If the samples contain liquid or the closely related elastomeric phases, then that phase will bypass any conduction paths through solid or glass. Samples which donot contain these phases will be relatively poor conductors and also will be mechanically brittle, showing very little advantage of plasticity. This tells us that polymers with 'liquid like' transport mechanism property have to be selected to study electrical behaviour [7,15-21].

Among the four phases investigated, it was observed that elastomeric phase is solid but behaves really like a liquid. With 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.

1. negligible low vapor pressure
2. well defined shape under constant stress
3. negligible long range self-diffusion.

This behaviour gives us evidence to stress that the elastomeric phase is a state, which is neither a liquid nor a solid. It is this approach that we are trying to understand in order to grasp the polymer electrolyte's conduction properties.

Many studies on polymeric electrolytes have been directed towards understanding fundamental questions regarding the structure, mass and charge transport, ion-polymer interaction, ion-ion interaction, solvation mechanism and ion-conduction mechanism. 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. It is hoped that this continued work on PVC-MX salt systems studied for this project would throw little light on some of the matters mentioned above.

1.12 Description of polymer structure and mobility

This shows a two dimensional, molecular scale representation of a polymer. Relatively at low temperature, a network of coulombic hydrogen bond or Van-der-Waals attractions between the monomer units, ensures that it is in solid state in the conventional sense. In addition to these forces, we have the characteristic strings of directional and essentially unbreakable covalent bonds, but these are not closely packed. As long chain polymers are not closely packed, they can show amorphous arrangement in their arrangement. This brings about glass formation. A single long chain molecule can wind (refer to figure [1.7]) its way through crystalline and amorphous regions. The coulombic, hydrogen and Van-der-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 do break, then the material decomposes.

Phase changes

On heating, the amorphous region of the polymer becomes elastomeric or liquid at the glass transition temperature, T_g and at one or more melting points, maybe subsequently observed as the various possible ordered structures transform into elastomers and 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 elastomers as shown in figure [1.6].

Low molecular mass liquid like components may also be present. The elastomeric phase is the main concern, in which, the ion motion is coupled to that of the elastomeric host. The mobility of the elastomer and its guest ions will be considered to obey the free volume theory, which explains the nature of coupling between polymer segment and ion motion.

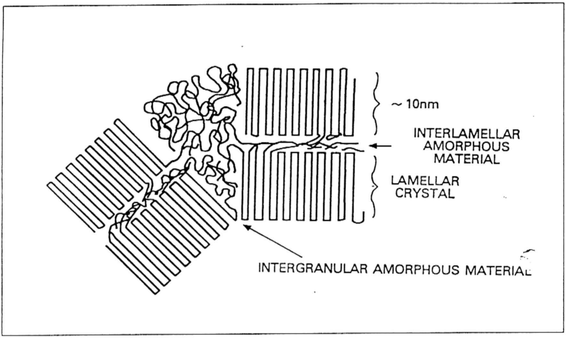


Fig [1.6]: Example of a polymer microstructure showing amorphous, crystalline and elastomer phases [15].

1.13 Mass transport in elastomer phase

Covalent bond chains prevent the polymer from being closely packed, structurally. So, the resulting vacancies are randomly arranged and static below the glass transition temperature. Even though they are quite abundant, forming about 2.5% of the total volume, they are unlikely to form a continuous tunnel to allow diffusion of foreign molecules [17,23]. However, at temperature higher than T_g the labile bonds can be broken by thermal energy, allowing chain segments capable of independent motion. These segments can move to a neighbouring vacancy, which is large enough. This movement brings a change in the conformation of the polymer chain, which shows the elastic deformation on the macroscopic scale.

This gives mechanism of random redistribution of the vacant space and allows long range diffusion of small molecules through the structure. This vacancy distribution is a primary route for ion transport and is a major factor in determining the ion mobility. Therefore, T_g marks the onset of the three transport processes:

a) Short range translations of chain segments

b) Small molecule diffusion.

c) Ionic conductivity.

1.14 Factors which determine the conductivity

Tortuosity factor:

Polymer solvates are similar to liquid solutions in high solubility limits. For example, regular PEO which has the symmetry to form crystals exhibits the phase behaviour illustrated in figure [1.7]. It can be seen from the figure that the non-conducting crystalline fraction is a major component above the O/Li ratio of 6:1 over a wide temperature range. The conductivity in this region is due to the residual elastomeric phase, which percolates an extensive insulating crystal network [15]. The ratio between the conductivity of the conducting elastomer and the actual mixed phase is called the tortuosity factor. This looks to be the primary factor controlling the conductivity below about 80^{0}C.

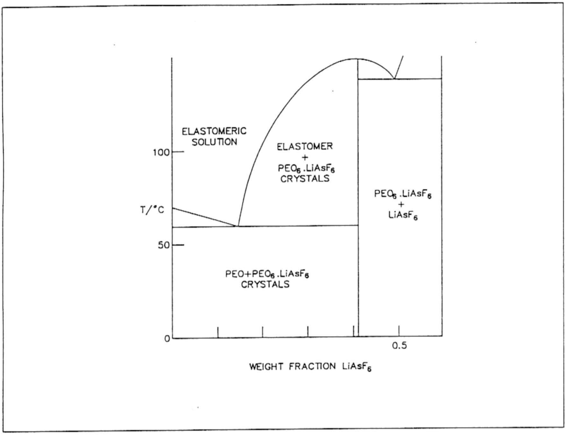


Fig [1.7]: Phase diagram for PEO/LiAsF$_6$ system [15].

The dynamic percolation requirement for ion mobility:

Ion mobility can be estimated approximately from the free volume and configurational entropy treatments by appropriate substitution of the action volume term. The mobile ion species simply just cannot jump into inner space structure. Logically, the ions have to transfer from one ligand site onto another ligand. Unlike the solid state ionic crystalline materials such as Ag$^+$ systems in which all the hopping sites are connected in a regular network, the ligand sites in polymeric materials are randomly connected. They are also randomly redistributed throughout the inner space. It has been pointed out that this redistribution is crucial in carrying the ion forward because in this manner random continuous paths can explain the motion. The redistribution frequency or time scale is dictated by the polymer's segmental motion.

Effective mobile ion concentration:

Although cations and anions are well separated in very dilute solutions, ion association effects come into 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 immobilize.

Applying these results for the polymer electrolytes is difficult. There are a couple of reasons for this. First, the concentration range of interest is so high that even triple ion mobiles break down in favour of the fused salt model, in which ion pairs are so close to neighbouring ions. Second, because of the long-range immobility of the solvent, the strong cation solvent interaction is expected to play a greater role in elastomer than in a liquid. Systematic analysis of the variation of conductivity with concentration is complicated by the simultaneous increase in glass transition temperature, T_g.

Transport numbers:

Because of the difficulties of measurement of transport numbers, conductivity values are usually quoted as the sum of contributions from anions and cations. This is unfortunate, because many of the expected differences in transport mechanism between the species are masked in the available data [17-

22].

For most applications, the transport number is important only as a scaling factor to obtain conductivity of the electrode reversible ion from the total conductivity. For the lithium ion conductors as an example, the average transport numbers reported is about 0.4 with small anions. It is emphasized here that the transport numbers of the cations or ion species involved is not calculated. The total conductivity is taken as an appropriate value to discuss the results, which will be presented.

1.15 The mechanism of ionic conductivity

Ionic conductivity in a material is expressed as the product of number of free ions n, their charge q, and the self diffusion coefficient D [7,20]

$$\sigma = fnq^2(D/kT) \qquad (2)$$

f is a geometrical correction factor close to 1. According to the above expression, conductivity is proportional to n, the number of free ions. This is not so, when actually only a small proportion of the ions are sufficiently mobile to conduct. On the macroscopic view, concept of diffusion represents motion of particles in terms of continuous movement of matter. The diffusion coefficient can be expressed as product of square of the average ion jump distances $<x>^2$ and frequency of jumps in a particular direction, v.

$$D = <x>^2 v \qquad (3)$$

The jump distance can be taken as the distance of ether oxygens of PEO. The jump rate depends on the basic mechanism of transport. Possibilities of transport mechanism of solid like and liquid like are contrastingly shown in figure [1.8].

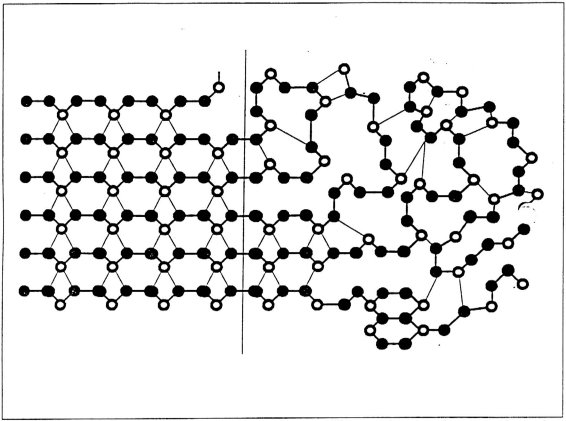


Fig [1.8]: Schematic representation of crystalline and amorphous regions in PEO[20].

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

$V = v_0 \exp[-E_A/kT]$ (4)

In 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

$V=v_0\exp[-v_A/v_f]$ (5)

Where v_f is 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 by the expansion coefficient α, we get

$V = v_0 \exp[-v_a/\alpha(T-T_0)]$ (6)

Where the expression of v_f is assumed to start from zero at the theoritical glass transition temperature, T_0.

With all these, we get VTF equation for temperature dependence of conductivity, which replaces the Arhennius equation used for solids. VTF (Vogel-Tamman-Fulcher) equation is given below with a slightly temperature dependent coefficient A.

$$\text{VTF: } \alpha = A \exp [-B/T - T_0] \tag{7}$$

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

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:

$$\sigma(T)=\sigma_{T_r}\exp\left\{\frac{C_1(T-T_r)}{C_2+(T-T_r)}\right\} \tag{8}$$

Where C_1 and C_2 are constants. 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 $T_g + 150^0$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 fit. The values of C_1 and C_2 depend on the choice of reference temperature, although they are commonly normalized to the reference temperature T_g [15].

1.16 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 of hard spheres (ions in the case of polymer electrolytes) which are free to move in a volume fraction (voids), called free volume, and derived the probability distribution of void volumes in the total volume of the system. Following the Cohen and Turnbull treatment, the free volume expression for diffusion 'D' has been derived to be:

$$D = g\ a\ u\ \exp[-\gamma v/\alpha v'_M(T-T_0)] \qquad (9)$$

Where g is geometrical factor, a is molecular dimension, γ is Lagrange parameter, v is critical free volume. Following the Nernst – Einstein relation, the free volume theory results in the equation (1), which is the VTF equation that explains σ 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 σ-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. Confusion arises when the free volume model is used for the treatment of flexible molecules. When the free-volume theory is corrected, it becomes similar to configurational entropy model given by Gibbs and coworkers. The model was originally developed as lattice model in which the single parameter 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 behaviour, which describes the behaviour of most of the polymer electrolytes, has been derived using configurational entropy model by Adam and Gibbs.

1.17 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 behaviour of hosts, not the ionic motion in polymer-salt complexes. Further, the free-volume theory is not able to explain the microscopic behaviour such as mechanistic aspects, transport properties as a function of the 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 framework. The well-known experimentally observed property that crystalline phase has no conductivity 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 [24], have given a generalised '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 ι_r ($\lambda=1/\iota_r$). This 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 translational 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 or the polymers, molecular weight, applied pressure, effect of host polymer change, frequency dependence of conductivity, etc.

1.18 Methods of introducing ions

a) Addition of salt to a solvating polymer:

The two components are usually dissolved in a common liquid solvent like methanol, tetrahydrofuran, acetonitrile to homogenize the mixture and then the solvent is evaporated off.

The polymer must contain solvating group in the structure. The most common solvating group is the ether oxygen as found in polyethers. The ether group solvates most of the metal cations by coordination of oxygen to a sufficient extent to provide solubility, provided the salt has a small lattice energy. A strong attraction between the polymer and the cation often increases the glass transition temperature. This is undesirable because this will subsequently reduce conductivity according to the VTF equation. Another important consideration is the extent of dissociation. Most of the salt remains as ion pairs, so that the real carrier concentration may be much smaller than that of the added salt. [25-30].

b) synthesis of salts of polymeric ions:

Free ions can be accommodated within the polymer molecules as counterions to charged groups bound to the polymer. A polymeric acid is reacted with a base to form a polymeric salt with potential mobile cations. Adding a solvent can substantially increase the structural and ionic mobility.

c) addition of salt dissolved in a plasticizer or co-solvent:

Polymer with little ion solvating properties can be made to conduct ions by adding a compatible electrolyte solution. Plasticizers are used to lower the glass transition temperature of polymers. The liquid is absorbed in the polymer structure and the sample appears as a single-phase material. The conductivity enhancement is also attributed to the decrease in the degree of crystallinity.

1.19 Results from earlier work on polymer electrolytes

Prior to 1970, there was very little work on conducting polymers. Polymers were not known to be able to conduct electricity. A number of useful discoveries during the 1970s have contributed to the growing interests in polymers with electrically conducting properties. Firstly, polymeric materials have been successfully used in electrographic copying machines. Carbon and metal filled polymers have been used as moldable semiconductors in the electronic industry. In recent years, studies of charge transport in polymers and the discovery that dopants can be added to make polymers semiconducting and ultimately metallic in character, have motivated a lot of research. The aim of these studies is to combine the desirable properties of polymers, such as low cost, light weight, moldable and flexible, with electrical behaviour characteristics of semiconductors or metals. In this section, a brief account of the development of polymer electrolytes and batteries will be given.

Polymer electrolytes can be defined as thin solid films consisting of ionic salts dissolved in an appropriate polymer. The polymer acts as an immobile solvent for the ionic salts. They are ionic conductors and electronic insulators [31]. An unusual feature of most polymer electrolytes is that both cations and anions are mobile, unlike in glassy inorganic electrolytes [32,33,34] where usually only the cations are mobile.

The initial conducting polymers systems such as PEO(Poly ethylene oxide) complexes with sodium and potassium thiocynates and sodium iodide, were insoluble, intractable and non-melting, with relatively poor mechanical properties. However the discovery of solvents such as water or common organic solvent enables the polymers to be processed into films or fibres and also enables it to be complexed with other metallic salts which are also soluble in the same solvent. The electrical conductivity of the initial systems also improved when complexes are formed. Not only did the electrical properties improved, but the mechanical properties were also enhanced at the same time. However, polymer electrolytes generally have low conductivity at and below room temperature. This is because they have low viscosity and some of them cyrstallise at room temperature, for example (PEO)$LiCF_3SO_3$. Since higher conductivities are associated with amorphous regions of the polymers, attempts have been made to preserve the amorphous nature of PEO at room temperature by radiation crosslinking of the polymer [35,36,37]. Similar methods have been applied to increase the viscosity of polymers such as the polyphosphazenes.

Another attempt to improve the electrolyte property is to include another polymer that is, to make a polymer blend such as using a combination of PEO and poly[bis(methoxyethoxy)phosphazene](MEEP) and other polymers such as polypropylene oxide (PPO), polymethyl methacrylate(PMMA) and polystyrenes. In this case, although the amorphous nature was retained at room temperatures, the conductivity however did not improve substantially [38,39,40].

Another type of polymer electrolytes, are those that contain a ceramic component such as PEO complex and β-alumina (PEO_8LiClO_4+α-$LiAlO_2$)[41,42]. In this case the polymers are generally dispersed on ther ceramic with a high surface area. Plasticised polymer electrolytes as they are more commonly known, is yet another type of conducting polymer. This type consists of a polymer and a liquid phase added to it [43,44]. Typical plasticizer examples are sulfolane, ethylene carbonate (EC) and propylene carbonate (PC).Table[1.3] lists some of the polymer electrolytes currently being studied together with their conductivity values. The list of polymer electrolytes are obtained from references[45].

Table[1.3]: List of polymer electrolytes and their conductivity values.

Sl.No.	Electrolyte Composition	Conductivity (S/cm)
	Polymer Electrolytes	
1	$(PEO)_{10}LiClO_4$	6.0×10^{-3}
2	PDMS/HMDI	1.0×10^{-3}
3	$PEEVE/LiBF_4O/Li$	4.0×10^{-3}
4	Polytetrahydrofurane	1.9×10^{-3}
	Polymer Blends	
5	$MEEP/PEO\text{-}LiBF_4$	2.4×10^{-3}
6	$PMMA/PVC\text{-} LiCF_3SO_3/EC/PC$	1.4×10^{-3}
	Polymers and ceramics	
7	$(PEO)_{10}LiCF_3SO_3 + Li_3N$	3.0×10^{-4}
8	$(PEO)_8LiClO_4+\alpha\text{-}LiAlO_2$	5.0×10^{-2}
	Plasticised polymer electrolytes	
9	$PAN/ LiClO_4/EC/PC$	1.7×10^{-3}
10	$PVC/LiN(SO_2CF_3)_2/PC$	1.1×10^{-3}
11	$Li Nafion/LiClO_4/PEO$	1.5×10^{-3}

Abbreviations:

PDMS - Poly (dimethylsiloxane-grafted ethylene oxide)
HMDI - Hexamethylene diisocyanate
PEEVE - Ethoxy-ethoxy-ethoxy-vinyl ether polymers
PMMA - Poly (methyl methacrylate)

Together with the efforts towards materials improvement, a number of potentially important areas of application have been identified. There are four specific areas namely, conducting polymers as electrochemically active materials, as electrochromic materials, as nonlinear optical materials and conducting polymer blends as composite materials. In this section only the use of conducting polymer as an electrolyte in solid-state polymer batteries will be presented.

Polymer batteries consist of an anode and a cathode separated by a polymer electrolyte. They produce power by a redox reaction between the anode and cathode species, oxidation taking place at the anode and reduction at the cathode. The ions involved in the cell reaction travel through the electrolyte while the electrons travel through the external circuit. In a polymer battery the cathode may also contain flexible, plastic or elastic polymeric material usually called a composite cathode, while the anode is usually a metal foil. Sometimes an intercalation cathode material is used in polymer batteries. The advantage of using the intercalation compound is that it allows the cathode material to swell when ions go in them.

The use of conducting polymer as an electrolyte in solid-state batteries was first identified in 1978 by Armand [46] and the first report of battery performances came soon after in 1983[47]. The initial batteries consisted of lithium as the anode, a polymer electrolyte and an intercalation material as the cathode. The electrolyte used was $(PEO)_9LiCF_3SO_3$ while the intercalation material was TiS_2. The performance of this battery was found to be reasonably good, however the battery data were obtained at high temperatures. Other battery systems studied were those that consists of a polymer, a solid and a liquid, that is a ternary system. In this system, the cathode was based on V_6O_{13} and a liquid propylene carbonate based electrolyte was added to cathode. This design requires the use of an electrolyte separator such as $LiI\text{-}Li_2S\text{-}B_2S_3$ whose role is to insulate against direct short circuits between the plates of opposite polarity while allowing ionic transport.

A relatively new development involves the use of $LiI\text{-}Al_2O_3$-PEO-PMMA based polymer electrolyte and a metallic lithium foil as the anode. This battery was found to have a reasonable current density. Polymer batteries using polymer blend and plasticised polymer as the electrolyte have also been investigated, however the battery data presented is limited.

Much of the work involving polymer batteries have evolved around the usage of lithium as the negative electrode [19]. Recently, lithium batteries using polymer electrolytes have been introduced. Table [1.4] shows the sequence of development of the components and systems for lithium batteries[48].

Table[1.4] : Overview of the development of lithium batteries

Year	**Development of components**			**Systems**
	Anode	**Cathode**	**Electrolyte**	
70's	Lithium metal Lithium alloy	Transition metal sulphides (TiS_2, MoS_2) Transition metal oxides (V_2O_5, V_6O_{13}) Liquid cathodes (SO_2)	Liquid organic electrolytes Solid inorganic electrolytes (Li_3N)	$Li/LE/TiS_2$ $Li/S0_2$
80's	Li-intercalation ($LiWO_2$)	Selenides ($NbSe_3$) Discharged cathode ($LiCoO_2$, $LiNiO_2$)	Polymer electrolytes	$Li/LE/MoS_2$ $Li/LE/NbS_2$ $Li/LE/LiCoO_2$
90's	Li-carbon (LiC_{12}) (coke) Li-carbon (LiC_6) (graphite)	Manganese oxide (Li_xMnO_2) Manganese spinels ($LiMn_2O_4$)	Plasticised polymer electrolyte	$Li/PE/V_2O_5$ V_6O_{13} $Li/LE/MnO_2$ $C/LE/LiCoO_2$ $C/LE/LiMn_2O_4$

(LE – Liquid organic electrolyte, PE- Polymer electrolyte)

In a recent development of lithium battery [45], a highly propylene carbonate plasticised film of PEO and $LiCF_3SO_3$ was used as electrolyte. The cathode is based on MnO_2 while metallic lithium was used as anode. Although the electrolyte can be consideredto be a plasticised polymer material, it is significantly different from other similar systems in that it is a single phase material. Many of the other plasticised systems tend to be multi-phased and therefore contain additional interfaces which increases the resistance of the electrolytes. The performance of this battery system has been reported to be far more superior when compared with other well known solid electrolyte systems. The superior performance can be attributed to the single-phase nature of the polymer electrolyte. The performance of the battery is further enchanced by reducing the interfacial resistance between the various solid components. This has been achieved by a coating-radiation curing process in which both the cathode and the electrolyte are coated onto to the current collector while in the liquid state. At present this battery system is commercially available.

The phenomenon responsible for the changes in electrical and optical properties of conducting polymers have generated new concepts and the potential for new and improved applications. Based on the excellent progress, these materials will continue to evolve to the point where they can be in a wide variety of applications.

1.20 Aim of the present work

It is the aim of the present work to study the characteristics of another polymer, poly (vinyl chloride), PVC when doped with certain impurities like inorganic salts. PVC is a readily available, inexpensive polymer and therefore will be of interest for the development of inexpensive consumer batteries and electrochromic devices. Earlier attempts by Watanabe et al to prepare solid electrolytes with PVC were unsuccessful. However, the difficulty was overcome by the use of a solvent in which all the electrolyte components are soluble[49].

Polymer electrolytes containing liquid plasticizers have gained wide acceptance. These plasticizers are high in dielectric constant, low vapor pressure, and extensively dissociate Li salts. Although plasticized electrolytes lack the beauty of the virgin solid polymer electrolytes, their exceptionally high ambient temperature conductivities, usually around 10^{-3} S/cm, and processability as thin films, have made them attractive as novel electrolytes possessing ionic conductivity approaching that of organic liquid electrolytes and mechanical stability reminiscent of solid polymer electrolytes[50] So, once a film of high conductivity is obtained, plasticizers will be used to improve upon the conductivity. Finally, the plasticized polymer electrolyte with the best conductivity will be used to make a battery. It was reported that the $LiMn_2O_4$ was used as a cathode material. We shall use another cathode material like $LiCoO_2$ and examine the battery. Apart from these, the materials prepared will be characterised using XRD (X-ray Diffraction Analysis), SEM (Scanning Electron Microscope) and EDAX (Energy Dispersive Analysis of X-rays).