

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Introduction

The ionic conductor also known as the electrolyte is one of the important components in electrochemical devices. There has been growing interests among researchers to develop polymer electrolytes with properties such as good ionic conductivity, good mechanical strength *etc*, which make them suitable for use in various applications *i.e.* lithium ion batteries [Manuel Stephan et al., 2006], fuel cells [Ihonen et al., 2001], electrochromic windows [Vieira et al., 2007], supercapacitors [Gamby et al., 2001] and solar cells [Buraidah et al., 2011].

High thermal stability of electrochemical cells is important as evaporation and leakage of solvents from the electrolyte will affect the life-time of such devices. This property is crucial especially for outdoor applications as in solar cells and electrochromic windows for buildings and rear-view mirror of vehicles.

Polymer electrolytes are safer as compared to liquid electrolytes. Polymer also imparts its mechanical strength and flexibility to polymer electrolytes. The flexibility of polymers allows the electrolyte to withstand volume changes that occur during charging and discharging processes of the electrochemical cell without degrading the electrode-electrolyte interfacial contacts. Flexibility of polymer electrolytes also enables them to be moulded into any size or shape. Very thin polymer electrolyte films of large surface area are expected to produce very low internal resistance and thus increase the conductivity and consequently the power density [Armand, 1994].

Hence, a polymer electrolyte with good ionic conductivity, good mechanical stability and high thermal decomposition limit can be used as ionic conductor for Li batteries, ECDs and solar cells. A polymer electrolyte can also act as the separator, thus reducing the cost of production. Nevertheless, polymer electrolytes possess lower ionic conductivity than liquid electrolytes and researchers are looking into various methods to improve the electrical properties.

## 2.2 Polymer electrolytes

Polymer electrolytes (PEs) consist of inorganic salts dissolved in solid polymers. The polymer serves as a medium to hold the conducting ions. Several components may be present in a polymer electrolyte system, the simplest being the polymer host and an inorganic salt.

### 2.2.1 Polymer host

The polymer must contain at least a Lewis base (i.e. O, N or F atom) which contains at least a pair of electrons that can be donated to a Lewis acid. The electrostatic attraction between the negatively charged atom with the positively charged cation (or Lewis acid) such as  $\text{Li}^+$ ,  $\text{Na}^+$  or  $\text{H}^+$  result in coordination or complexation. Coordination of the cation to the polymer host will cause the cation to be separated from the anion thus promoting dissolution of the salt [Karan et al., 2008]. However, the cation–Lewis base bonding must be labile to allow ion mobility [Gray, 1991]. The cation will then dissociate from the coordination site in order to move across the polymer electrolyte matrix. Table 2.1 lists several types of polymers which are commonly used as polymer host in polymer electrolytes and some of their properties.

Table 2.1 Chemical structures and physical properties of common polymers used in polymer electrolytes

Polymer <sup>a</sup>	Dielectric constant, $\epsilon$	Glass transition temperature, $T_g$ (°C)	Melting point, $T_m$ (°C)
$\text{H}-\ddot{\text{O}}-\text{CH}_2-\text{CH}_2)_n-\ddot{\text{O}}\text{H}$ <p>Poly(ethylene oxide) (PEO)</p>	5	-64	66-75
$\begin{array}{c} \text{CH}_3 \\   \\ -(\text{CH}_2-\text{C})_n- \\   \\ \text{C}=\ddot{\text{O}} \\   \\ \text{:O:} \\   \\ \text{CH}_3 \end{array}$ <p>Poly(methyl methacrylate) (PMMA)</p>	2.6	105	160
$\begin{array}{c} \text{CH}_3 \\   \\ -(\text{CH}_2-\text{C})_n- \\   \\ \text{C}=\ddot{\text{O}} \\   \\ \text{:O:} \\   \\ \text{CH}_2-\text{CH}_3 \end{array}$ <p>Poly(ethyl methacrylate) (PEMA)</p>	-	65	135 - 140
$\begin{array}{c} -(\text{CH}_2-\text{CH})_n- \\   \\ \text{:OH} \end{array}$ <p>Poly(vinyl alcohol) (PVA)</p>	1.9-2.0	85	≈200
$\begin{array}{c} \text{:F:} \\   \\ -(\text{CH}_2-\text{C})_n- \\   \\ \text{:F:} \end{array}$ <p>Poly(vinylidene fluoride) (PVdF)</p>	7.72	-40	177

(Table 2.1, continued)

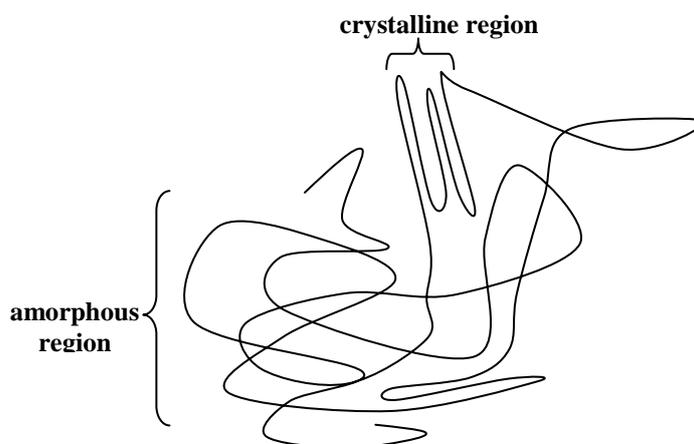
Polymer <sup>a</sup>	Dielectric constant, $\epsilon$	Glass transition temperature, $T_g$ ( $^{\circ}\text{C}$ )	Melting point, $T_m$ ( $^{\circ}\text{C}$ )
$\begin{array}{c} \text{---}(\text{CH}_2\text{---CH})_n\text{---} \\   \\ \text{:Cl:} \end{array}$ Poly(vinyl chloride) (PVC)	3.4	82	295
$\begin{array}{c} \text{---}(\text{CH}_2\text{---CH})_n\text{---} \\   \\ \text{C} \\     \\ \text{N} \\ \text{:} \end{array}$ Poly(acrylonitrile) (PAN)	6.5	120	326
$\begin{array}{c} \text{---}[(\text{CH}_2\text{---}\overset{\text{:F:}}{\underset{\text{:F:}}{\text{C}}})\text{---}(\overset{\text{:F:}}{\underset{\text{:F:}}{\text{C}}})\text{---}(\overset{\text{:F:}}{\underset{\text{:F:}}{\text{C}}})]_n\text{---} \\   \\ \text{C} \\ / \quad \backslash \\ \text{:F:} \quad \text{:F:} \\   \\ \text{:F:} \end{array}$ Poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP)	8.4	-35	143

<sup>a</sup> Black dots represent electrons

Among all polymers, poly(ethylene oxide) (PEO) is the most studied polymer host for polymer electrolytes due to the optimal distance and orientation of the ether oxygen atoms in the polymer [Gray, 1991]. However, PEO-based polymer electrolytes suffer from low ionic conductivity ( $\sigma \approx 10^{-8} \text{ S cm}^{-1}$  at room temperature) due to its high crystallinity (about 70–95 % of pure PEO), and loss of mechanical stability beyond its melting temperature at about 65  $^{\circ}\text{C}$  [Money and Swenson, 2013].

It is generally accepted that the crystalline phase contributes much lower ionic conductivity than the amorphous phase [Berthier et al., 1983]. Crystalline regions of a polymer are made up of polymer chains which are closely packed or regularly arranged

whereas amorphous regions are highly disordered with randomly arranged or tangled chains. As the polymer chains are not packed tightly in amorphous regions and are more flexible to move, there is larger space between polymer chains which can enhance both segmental motion and the migration of ions. Hence, researchers prefer to use amorphous polymers as polymer hosts to achieve higher ionic conductivities. Figure 2.1 illustrates the schematic diagram of the crystalline and amorphous phase of a semi-crystalline polymer.



**Figure 2.1 Schematic diagram of amorphous and crystalline regions of a polymer**

Polymethacrylates are one of the most commonly used as polymer hosts in PEs. Their properties include excellent chemical resistance, high surface resistance and offers high optical transparency which have found their way to applications such as biomedical such as dentures, implants in bone cement, cosmetic surgeries and glass substitutes for aquariums, windows and exterior lights lenses of automobiles. In fact, due to the excellent optical properties coupled with biological inertness, homopolymers and copolymers of the non-toxic PMMA have found its way in the production of permanent implant for the intraocular lens for post cataract surgeries, contact lenses and eye glasses [Carvalho et al., 2009]. However PMMA lacks mechanical strength and tend to be brittle [Brown, 1991].

The use of poly(ethyl methacrylate) (PEMA) as a polymer host was first reported by Han et al. (2002) and Ahmed et al. (2000). PEMA is reported to exhibit higher mechanical strength than PMMA. PVC/PEMA–LiPF<sub>6</sub>–EC–PC displayed higher elastic modulus and elongation as compared to PVC/PMMA–LiPF<sub>6</sub>–EC–PC polymer electrolyte [Han et al., 2002]. In addition, EMA monomers were also reported by Reiter and co-workers (2006) to exhibit higher boiling point (114.5 °C) and therefore lower volatility than MMA monomers (100 °C). PEMA also exhibits lower glass transition temperature,  $T_g$  at 65 °C as compared to 105 °C of PMMA.

High transparency, sufficient mechanical strength, elasticity and good adhesion onto substrates make PEMA suitable for use as a polymer host for ionic conduction in optical devices such as solar cells and electrochromic devices [Reiter et al., 2009b; Reiter et al., 2011] in addition to other applications which include lithium ion batteries, proton batteries [Balian et al., 2011], supercapacitors, etc. Methacrylates are transparent as their bandgaps have energies that are lower in wavelength than the visible range of the electromagnetic spectrum from 380 to 750 nm, hence allowing visible light to pass through.

Fluoropolymers, polymers which contain fluorine (F) atoms, are well-known for their good properties in terms of chemical, thermal, and high resistance to ageing and oxidation [Anderson and Punserson, 1979; Abu-Isa and Trexler, 1985; Frapin, 1987]. Fluorinated polymers are made up of strong C–F bonds, which contribute to its good mechanical strength. Fluorine-containing polymers are used in many applications such as in paints and coatings, petrochemical and automotive industries, aerospace and aeronautics, chemical engineering, optics, textile treatment, microelectronics, cable insulation, etc [Johns and Stead, 2000, Imae, 2003; Ameduri and Boutevin, 2004].

Poly(vinylidene fluoride-co-hexafluoropropylene) is a copolymer which consists of crystalline VdF and amorphous HFP units which allow ionic conductivity to occur with ease [Gozdz et al., 1994]. PVdF-HFP also has high dielectric constant  $\epsilon=8.4$  which aids in greater ionization of inorganic salts hence providing high concentration of charge carriers in polymer electrolytes. In fact, the first practical rechargeable Li-ion plastic battery was developed using PVdF-HFP-based electrolyte [Tarascon et al., 1996]. PVdF-HFP-based polymer electrolytes are expected to exhibit good electrochemical stability in terms of high anodic stability and non-combustibility due to the presence of strong C-F bonds (about  $110 \text{ kcal mol}^{-1}$ ) and C-C bonds ( $97 \text{ kcal mol}^{-1}$ ) [Renard et al., 2003]. Since its development by Bellcore Corporation in 1993 [Gozdz et al., 1993], PVdF-HFP has gained great interest from researchers and is recognized as a promising material as polymer host.

Both PEMA and PVdF-HFP contain electron pairs that can coordinate with cations from inorganic salts, *i.e.*  $\text{Li}^+$ ,  $\text{H}^+$ , to form polymer-salt complexes and hence can produce ionic conduction. Electron pairs are found on oxygen atoms of C=O and C-O-C groups of PEMA and fluorine atoms in PVdF-HFP.

### 2.2.2 Lithium ion salt

Polymer electrolytes are usually incorporated with inorganic salt(s) to provide charge carriers or ions for electrical transport. An inorganic salt is comprised of a metal-based cation and usually large-sized anion. Examples of metal-based cations reported in PEs are lithium ( $\text{Li}^+$ ) [Ulaganathan et al., 2013], sodium ( $\text{Na}^+$ ) [Osman et al., 2005], potassium ( $\text{K}^+$ ) [Bhattacharya et al., 2009], silver ( $\text{Ag}^+$ ) [Kang et al., 2006], magnesium ( $\text{Mg}^{2+}$ ) [Pandey and Hashmi, 2009], zinc ( $\text{Zn}^{2+}$ ) [Sellan and Hashmi, 2012] and barium ( $\text{Ba}^{2+}$ ) [Gasa et al., 2007]. Non-metal cations such as ammonium ( $\text{NH}_4^+$ ) are

also used to provide protons ( $H^+$ ) in proton batteries and fuel cell applications [Kumar et al., 2005]. Anions in the form of iodide ( $I^-$ ) [Buraidah et al., 2011], perchlorate ( $ClO_4^-$ ) [Kumar et al., 2006], hexafluorophosphate ( $PF_6^-$ ) [Sharma et al., 2012], tetrafluoroborate ( $BF_4^-$ ) [Low et al., 2011], triflate ( $CF_3SO_3^-$ ) [Cione et al., 2009], imide ( $N(CF_3SO_2)_2^-$ ) [Idris et al., 2005] and bis(oxalate)borate ( $B(C_2O_4)_2^-$ ) [Reiter et al., 2009] have also been used by researchers in PEs.

Among the different types of cations,  $Li^+$  ion-based salts are most preferred as the ion source for electrochemical devices although other types of cations are also being considered as alternatives to the former. This is due to the attractiveness of Li having the lowest atomic number and is the most electronegative ( $-3.10$  V vs. standard hydrogen electrode) and the lightest metal ( $0.54$  g  $cm^{-3}$ ) in the periodic table. Hence, rechargeable batteries based on  $Li^+$  ions possess the largest theoretical specific capacity, can give the highest cell voltage and can contribute to the highest gravimetric as well as specific energy densities. Being small-sized also facilitates the mobility of the ions across the medium in polymer electrolytes. For example,  $Li^+$  ions can diffuse easily in tungsten trioxide ( $WO_3$ ) which is the most commonly used inorganic electrode to produce coloration in electrochromic devices [Masetti et al., 1995].

Inorganic salts are composed of positively charged cations and negatively charged anions attracted to each other via coulombic forces. In order to dissociate the salt into free ions, the lattice energy of the salt has to be overcome. So, salts containing large sized-anions are favored as they exhibit lower lattice energy and are expected to promote greater dissociation of salt, thereby providing higher concentration of ions to contribute in ionic conduction [Macro et al., 1996; Armand, 1994; Chakrabarti et al., 2007]. This is in accordance to Coulomb's Law (equation 2.1) which describes the

relationship of the electrostatic attraction,  $F$  with the ionic radii,  $r$  and the magnitude of charge,  $Z$  of the two electrically charged particles or ions.

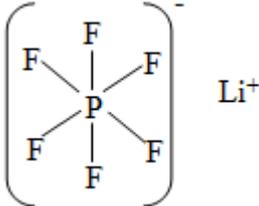
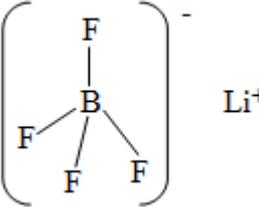
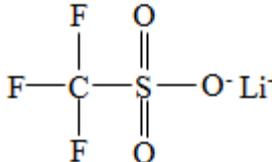
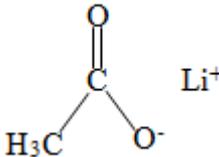
$$F \propto \frac{Z^+ Z^-}{r^+ r^-} \quad (2.1)$$

where the superscript + and – signs represent that of the cation and anion respectively. Thus, in order to minimize the migration of anions in PEs, salts containing large anions are preferred. However, anions of larger size could cause the mobility of ions to be reduced in the electrolyte. Table 2.2 illustrates several examples of lithium salts and their ionic radii, lattice energy and decomposition temperature.

Salts with highly delocalized electrons in the anion (i.e.  $\text{Tf}^-$  or  $\text{CF}_3\text{SO}_3^-$ , bis(trifluoromethylsulfonimide)  $[\text{N}(\text{CF}_3\text{SO}_2)_2^-]$ ) are also desired. The delocalization of charge reduces the electrostatic attraction between the cation and the anion in the electrolyte which results in high electrical conductivity. There is less interionic interaction between cation and anion which causes the lattice energy of the salt to be low. Figure 2.2 shows the chemical structure of  $\text{LiTf}$  and its delocalization structures. The  $\text{Tf}^-$  ion achieves its stability due to resonance stabilization which causes the negative charge to be spread over the three oxygen atoms and the sulfur atom.

Anions of a salt can exist in several forms – free, paired and aggregates. Free ions correspond to cation and anion which are separated and mobile; ion pairs and ion aggregates are less mobile and are usually formed at higher salt concentration. The amount of each ionic species, namely free ions, ion pairs and ion aggregates, can be determined using FTIR by deconvolution.

Table 2.2 Physical properties of some lithium-based inorganic salts

Salt	Ionic radii of anion, $r^-$ (pm)	Lattice energy, $U$ ( $\text{kJ mol}^{-1}$ ) <sup>a</sup>	Decomposition temperature, $T_d$ ( $^{\circ}\text{C}$ )
 Lithium hexafluorophosphate ( $\text{LiPF}_6$ )	256	677.7	250
 Lithium tetrafluoroborate ( $\text{LiBF}_4$ )	228	737.4	320
 Lithium trifluoromethanesulfonate ( $\text{LiTf}$ )	~230	730.3	450
 Lithium acetate ( $\text{LiAc}$ )	160	921.4	above 300
$\text{Li}^+ \text{ I}^-$ Lithium iodide ( $\text{LiI}$ )	213	769.3	–

<sup>a</sup> calculated using Kapustinskii equation,

$$U = \frac{1.202 \times 10^5 V Z^+ Z^-}{r^+ + r^-} \left( 1 - \frac{34.5}{r^+ + r^-} \right)$$

where  $Z^+$  = number of charge on  $\text{Li}^+$  = 1,  $Z^-$  = number of charge on anion,  $V$  = number of ions per formula unit,  $r^+$  = ionic radii of  $\text{Li}^+$  = 60 pm and  $r^-$  = ionic radii of anion.

For example, the symmetrical  $\text{SO}_3$  stretching band [ $\nu_s(\text{SO}_3)$ ] belonging to  $\text{Tf}^-$  anion can be used to provide information regarding the ionic interactions involving the  $\text{Tf}^-$  anion. This is because ion association between  $\text{Li}^+$  and  $\text{Tf}^-$  occurs at the  $\text{SO}_3$  end of the anion which causes the  $\nu_s(\text{SO}_3)$  band to be highly sensitive to the change in the coordination state of the anion. The  $\nu_s(\text{SO}_3)$  band is nondegenerate; its symmetry can be lowered by coordination to a cation. The presence of free ions, ion pairs and ion aggregates in a PE system containing a single salt can be determined from the several peaks that can be obtained from the IR band upon deconvolution.

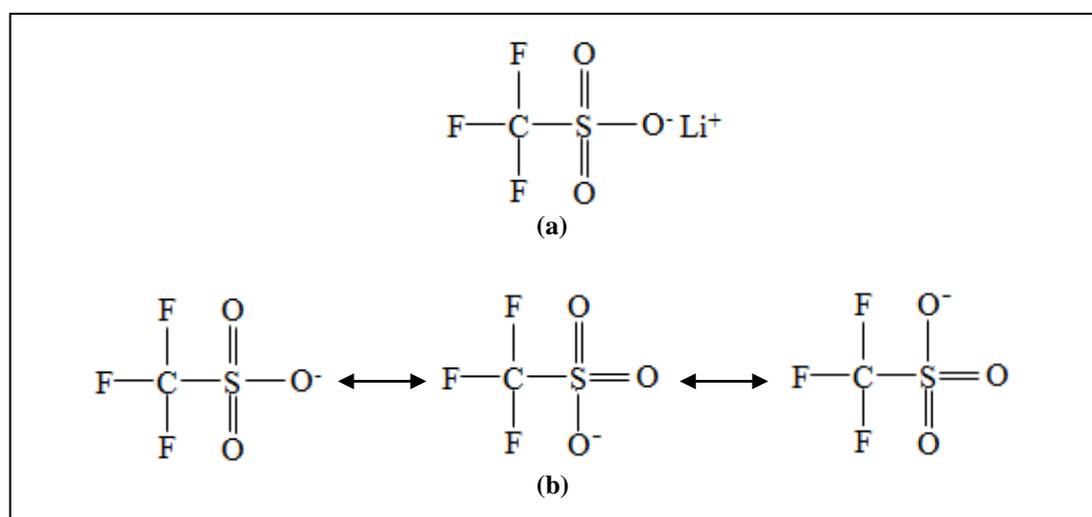


Figure 2.2 Chemical structure of (a)  $\text{LiTf}$  and (b) delocalization of negative charge in triflate anion

### 2.3 Polymer blending

Limitations of a single polymer have prompted researchers to turn to polymer blending as a method to improve the properties of PEs. Polymer blending is a useful and simple preparation method which involves the mixing of at least two polymers together to form a blend system with improved properties (*i.e.* conductivity, mechanical, optical *etc*) as that exhibited by each individual polymer. The properties can easily be controlled by optimizing the composition of each polymer in the blend to suit an application [Tang and Liao, 2000; Pieliowski and Hamerton, 2000].

Examples of polymer blend systems that have been reported by other researchers are PAN/PMMA [Flora et al., 2012], chitosan/PVA [Buraidah and Arof, 2011; Lewandowska, 2009], PVdF/PEO [Xi et al., 2006], PVdF/PEMA [Sivakumar et al., 2007], PVC/PMMA [Ramesh et al., 2002], PVC/PEMA [Han et al., 2002], PVC/PEO [Ramesh et al., 2002] PEO/PAN [Choi et al., 2000], PVDF–HFP/PVAc [Choi et al., 2001] and PVdF–HFP/PHEMO [Wu et al., 2009].

One of the advantages of polymer blending is the ability to develop a new system which possesses the desired physical properties such as improved ionic conductivity, increased transparency, enhanced mechanical strength and increased thermal stability which cannot be achieved by a single polymer alone. For example, PVdF experienced improved ionic conductivity from  $\sim 10^{-5} \text{ S cm}^{-1}$  up to  $10^{-4}$ – $10^{-3} \text{ S cm}^{-1}$  when added with various contents of PEO and soaked in  $1 \text{ mol L}^{-1} \text{ LiClO}_4/\text{PC}$  solution [Xi et al., 2006]. Barbosa and co-workers (2010) produced polymer blends with improved mechanical strength and transparency upon incorporation of poly(trimethylene carbonate) (pTMC) into PEO matrix. The decomposition temperature of polymer blend system based on poly(3–{2–[2–(2–hydroxyethoxy)ethoxy]ethoxy)methyl–3′–methyloxetane (PHEMO) was increased from  $365 \text{ }^\circ\text{C}$  to about  $408 \text{ }^\circ\text{C}$  upon blending with PVdF–HFP [Wu et al., 2009].

It is crucial that the polymer components are compatible or miscible with each other so that no phase separation occurs upon blending. Polymers interact with each other through intermolecular interactions. Various ways can be used to investigate the miscibility between the polymers in a polymer blend. For example, Lewandoska (2009) attributed the shift of decomposition temperature due to chitosan by thermogravimetric analysis (TGA) from  $200 \text{ }^\circ\text{C}$  to  $\sim 340 \text{ }^\circ\text{C}$  in chitosan acetate/PVA due to the interactions

between the two polymers in the blend. Kuo and Chang (2001) observed a chemical shift of 1.2 ppm of the C=O carbon atom in the  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectrum which suggested the existence of specific interaction between the carbonyl group of poly(vinylphenol) (PVPh) and the OH group in poly(vinylpyrrolidone) (PVP) in the PVPh/PVP blend. Yang et al. (2008) obtained single glass transition ( $T_g$ ) from differential scanning calorimetry (DSC) for PEO/PVdF blend samples which showed miscibility of the system. Hence, miscibility between two polymers can be studied using characterizations such as TGA, NMR and DSC.

PEMA offers good optical properties and has been employed in electrochromic devices due to its high transparency [Suttiruengwong and Sricharussin, 2010]. Reiter et al. (2009) have successfully fabricated an electrochromic device employing PEMA-based PEs which exhibit good ionic conductivity up to  $10^{-4} \text{ S cm}^{-1}$ . As with other methacrylates, PEMA is amorphous. However, PEMA is brittle as most amorphous polymers lack uniformity of polymer chains in the polymer matrix.

On the other hand, PVdF-HFP exhibits good ionic conductivity and high mechanical strength contributed by the amorphous HFP and crystalline PVdF phases respectively. PVdF-HFP-based electrolytes are either translucent or opaque [Huang and Wunder, 2001; Wu et al., 2006] due to the light scattering of crystalline regions. For example, PVdF-HFP-based polymer gel electrolyte films incorporated with HEMImBF<sub>4</sub> and HEMImPF<sub>6</sub> appeared to be opaque at PVdF-HFP contents above 66.7 wt.% and as white rubbery gels at lower polymer contents [Yeon et al., 2005]. The lack of transparency of PVdF-HFP-based electrolytes hinders its use in optical devices. Polymers with high transparency have the potential in not only lithium ion batteries, fuel cells, supercapacitors but also solar cells and electrochromic devices.

A number of polymethacrylate/PVdF–HFP–based blend electrolytes have been reported in literature [Ding et al., 2009; Elmer and Jannasch, 2007; Saikia and Kumar, 2005]. This shows the compatibility between the two polymers. Ding et al. (2009) briefly reported the FTIR changes due to the PVdF–HFP bands such as  $\text{CF}_2$  asymmetric stretching vibration and  $\text{CF}_3$  rocking vibration when blended with PMMA. They did not mention the changes exhibited by PMMA bands. Elmer and Jannasch (2007) studied PVdF–HFP blended with polymethacrylates having poly(ethylene carbonate–co–ethylene oxide) side chains but did not study the interaction between the components. The interactions of the functional groups in the polymethacrylates would provide useful information which could explain the ionic conduction of the samples. Saikia and Kumar (2005) studied the interaction in PVdF–HFP/PMMA–LiTf–EC/DEC– $\text{SiO}_2$  films through vibrational changes of component bands. However, they did not determine the amount different ionic species namely, free ions, ion pairs and ion aggregates which could explain the electrical properties of the system. The literature mentioned above shows that the information conveyed by the authors about polymethacrylates is still insufficient. Hence, additional analyses should be carried out to obtain more detailed information such as carrying out deconvolution on certain IR bands to determine the amount of different ionic species which can be used to correlate to the ionic conductivity.

#### **2.4 Plasticized polymer electrolytes**

SPEs often suffer from low ionic conductivities ( $10^{-8}$ – $10^{-7}$  S  $\text{cm}^{-1}$ ) at room temperature. Thus, researchers have incorporated additives to enhance the ionic conductivities of PEs; plasticizers being one of them. A gel polymer electrolyte (GPE) is formed when a low molecular weight plasticizer is incorporated into a polymer matrix. The plasticized PEs are more stable as compared to liquid electrolytes in the

case that no leakage of the electrolyte occurs as they are entrapped in the polymer system, and therefore are dimensionally stable at room temperature.

GPE exhibits high ionic conductivity close to that of commercial liquid electrolytes [Kelly et al., 1985] but at the expense of the mechanical stability especially when loaded with high plasticizer content [Croce et al., 1993; Lewandowski and Swiderska, 2004]. GPEs with low mechanical strength are often incorporated with ceramic fillers to improve the film strength. Nevertheless, GPEs provide better electrode–electrolyte contact which makes them more suitable for use in solid–state electrochemical devices.

The roles of plasticizer(s) in PEs have been reported below [Wilson, 1995; Dillip et al., 2008]:

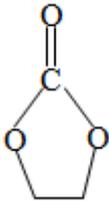
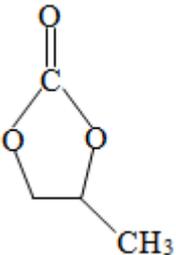
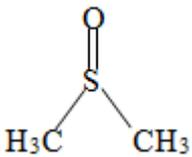
- 1) helps to dissolve and dissociate the salt,
- 2) provides a medium for conduction,
- 3) increases flexibility of polymer chain,
- 4) decreases the melting temperature of mixture
- 5) decrease the intermolecular forces of polymeric network
- 6) increases the amorphousness of polymers
- 7) dissociates ion aggregates
- 8) decreases the glass transition temperature ( $T_g$ )

Overall, the role of the plasticizer is governed by factors such as the viscosity and dielectric constant as well as polymer–polymer, polymer–plasticizer and ion–plasticizer interactions [Bandara et al., 1998]. All of the above can help to improve the ionic conductivity of PEs either by increasing the concentration of charge carriers

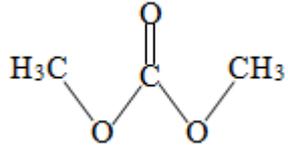
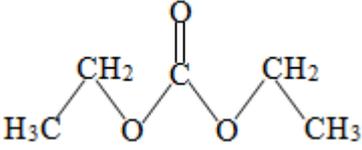
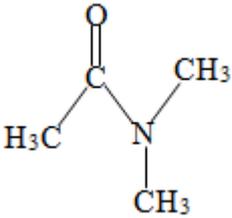
or/and increasing the mobility of charge carriers, which enhances the conductivity. Plasticizers with high dielectric constant and low viscosity values are usually introduced into PEs in order to improve the ionic conductivity. The dielectric constant,  $\epsilon$  of the plasticizer(s) used plays an important role whereby a higher value is desired to ensure high number of free charge carriers are dissociated from the salt by reducing electrostatic forces between oppositely-charged ions. On the other hand, plasticizers with lower viscosities can facilitate the mobility of charge carriers.

Plasticizers must be able to dissolve inorganic salts by containing polar groups such as carbonyl (C=O), nitrile (C≡N), sulfonyl (S=O) and ether-linkages (–O–) [Xu, 2004]. Table 2.3 lists some plasticizers commonly used in PEs and their properties.

**Table 2.3 Physical properties of common plasticizers used in polymer electrolytes**

Plasticizer	Dielectric Constant ( $\epsilon$ ) at 25 °C	Viscosity at 25 °C (cP)
 Ethylene carbonate (EC)	89.60 <sup>a</sup>	1.92 <sup>a</sup>
 Propylene carbonate (PC)	64.40	2.53
 Dimethyl sulfoxide (DMSO)	46.70	2.00

(Figure 2.3, continued)

Plasticizer	Dielectric Constant ( $\epsilon$ ) at 25 °C	Viscosity at 25 °C (cP)
 Dimethyl carbonate (DMC)	3.12	0.59
 Diethyl carbonate (DEC)	2.82	0.75
 Dimethylacetamide (DMA)	37.80	1.94

<sup>a</sup> at 40 °C

Cyclic solvents have the advantages over acyclic ones due to higher dielectric constants,  $\epsilon=40$  to  $90$ , as compared to  $\epsilon=3$  to  $6$  of the latter [Xu, 2004]. This explains the significantly higher dielectric constant value of EC and PC as compared to others listed in Table 2.3. Due to their ability to produce high conductivity, carbonate based solvents are used in commercial liquid electrolytes. For example, Ali and co-workers (2007) demonstrated that the conductivity of PMMA-based gel electrolytes by using lithium bis(trifluoromethanesulfonimide) (LiIm) or LiTf as the salt could be improved from  $10^{-8}$  to the range of  $10^{-6}$  to  $10^{-4}$  S  $\text{cm}^{-1}$  by using propylene carbonate (PC) and ethylene carbonate (EC) plasticizers.

Investigations on the interactions between plasticizer(s) and the other components of PEs such as the polymer host and/or inorganic salt have provided two

different findings; in some PE systems, interactions of the plasticizer(s) could not be observed through molecular studies such as Raman and FTIR spectroscopies. Several researchers reported that no interaction occurs between the polymer and plasticizer for example in equal weights of PMMA-grafted natural rubber (MG30) and PC [Ali et al., 2008], MG30-EC [Kumutha and Alias, 2006] and hexanoyl chitosan-EC-DEC [Winie and Arof, 2006]. According to them, little or no difference in the FTIR spectra of the plasticized samples could be observed upon the addition of plasticizer. The conclusion that no interaction has occurred is logical as any interaction between the plasticizer and the polymer system would have contributed to molecular changes especially at the main functional groups (i.e. carbonyl (C=O) in PMMA and MG30), and at the N(COR)<sub>2</sub> and OCOR bands of hexanoyl chitosan). As there is no plasticizer-polymer interactions, the polymer systems can be treated as mixed phase electrolyte systems [Huang et al., 1996].

However, there are also reports which state that interactions between polymer and plasticizer are possible in PE systems. The FTIR study of PAN in PC solution by Starkey and Frech (1997) suggests that significant degree of interaction between PAN and PC occurs based on the broadening of the PC vibrational modes upon addition of PAN. According to them, the interaction occurs between the C≡N group of PAN and PC. Wang et al. (1999) experimentally found from Raman and FTIR studies that significant interactions do occur between PAN and plasticizers such as EC, PC, DMF and DMSO. The polymer-plasticizer interactions were believed to occur between the polar group of PAN, which is the cyano (C≡N) group with the carbonyl (C=O) group in EC, PC and DMF, and the sulfoxide (S=O) group in DMSO.

Choi and co-workers (2005) also confirmed that Li<sup>+</sup> ions interact with both the C=O group of the carbonate solvents and the C≡N group of PAN in PAN-EC/DMC-

LiPF<sub>6</sub> system. This is due to the presence of negatively charged O atoms in EC which can be electrostatically attracted to the Li<sup>+</sup> ions from LiTf salt. From their findings, they suggested that the Li<sup>+</sup> ions predominantly associate with the ethylene carbonate molecules after which the Li<sup>+</sup>-solvated EC become a major path of lithium ion transport.

Marcilla et al. (1995) studied the plasticization of PVC with various types of plasticizers, namely dibutyl phthalate (DBP), dioctyl phthalate (DOP) and diisodecyl phthalate (DIDP). They observed that the compatibility between the plasticizer and PVC influences the interaction between the two components. Compatibility measures the ability of a plasticizer to form a homogeneous system with the polymer. The IR spectra of most compatible PVC–DBP sample showed most distinct intensity reduction of the crystalline bands of PVC located at 1427 and 637 cm<sup>-1</sup> which are attributable to stronger interactions, (DBP > DOP > DIDP). Their findings may imply that PEs and plasticizer which are more compatible will results in interaction between the components that can be examined through molecular vibration studies.

## **2.5 Room temperature ionic liquid (RTIL)–based polymer electrolytes**

Room temperature ionic liquids (RTILs) are molten salts at room temperature which consist of a large asymmetrical cation and a weakly coordinating inorganic or organic anion. ILs have found their way into applications such as catalysis, extraction, absorption, distillation, and chromatography [Ludwig and Kragl, 2007; Wang et al., 2007]. ILs are receiving great attention as ion source or additives in PEs due to their interesting characteristics such as high ionic conductivity, non-volatility, non-flammability, wide electrochemical window, etc. [Chiappe and Pieraccini, 2005]. High thermal stability of ionic liquids is a good advantage as it increases safety in solid-state

applications. The applications of protic ILs based on allylammonium and propylammonium cations in PEs include being a replacement of water as proton transporting media at high temperatures in fuel cells [Zhou et al., 2005; Schechter and Savinell, 2002] and a substitute for liquid iodide electrolyte solution in dye-sensitized photoelectrochemical cells in the case of 1-butyl-3-ethylimidazolium iodide (BMII) [Bonhote et al., 1996].

ILs are comprised entirely of ions within a wide temperature range [Seddon, 2003] due to the bulky asymmetrical nature of the cation (and also the large sized anion) which hinders the regular packing in a crystal lattice caused by the lower attractive force between the two oppositely charged ions. Hence, low energy is needed to break the electrostatic attraction in the ionic liquids which possess low lattice energy due to the presence of large cation.

These are the reasons that promote the use of ILs as electrolyte and/or solvent to replace conventional inorganic salts and/or organic solvents respectively [Shin et al., 2005]. This is due to their low vapour pressure which could circumvent the problem of loss of solvent in PEs into the environment and atmospheric pollution. Another advantage of ILs is their recyclability.

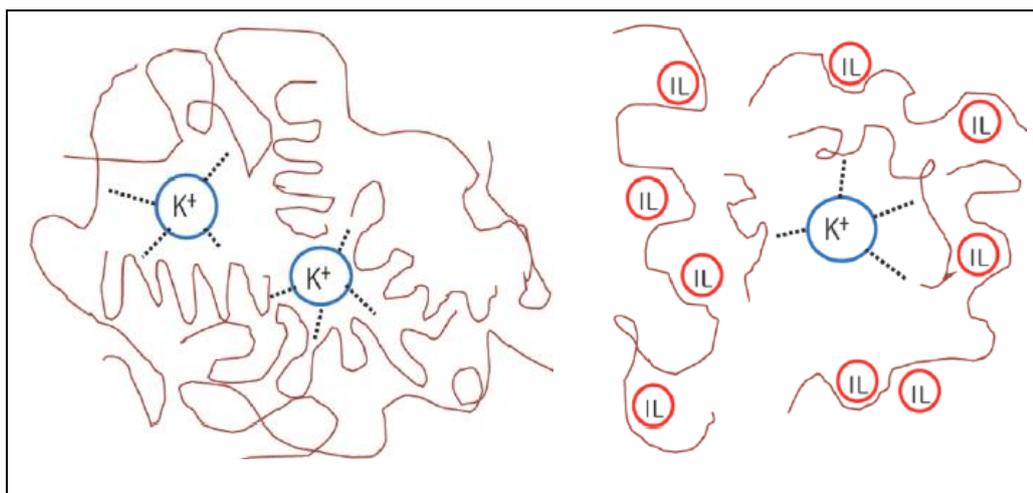
Most ionic liquids, for example imidazolium-based have decomposition temperatures ranging from 200 to 450 °C depending on the nature of anions rather than the cations [Kosmulski et al., 2004]. Although ILs are known to have high thermal stability, they can still evaporate under harsh temperature and vacuum conditions [Xu et al., 2005]. However, due to their low vapour pressure, the evaporation occurs at much lower rates as compared to normal organic solvents.

The high conductivity exhibited by ILs have pushed researchers to use them as the main source of charge carriers in the absence of target ions (i.e.  $\text{Li}^+$ ,  $\text{Na}^+$ ) in PE systems such as succinonitrile incorporated with 1-butyl-1-methylpyrrolidinium bis(trifluoromethyl-sulfonyl)imide (BMPTFSI) or 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMITf) [Suleman et al., 2013]. Although these PEs are not suitable to be used in lithium rechargeable batteries, they are applicable in energy charge storage devices namely supercapacitors.

The benefits of utilizing ILs in polymer electrolytes have been reported below:

- 1) can increase the number of charge carriers [Lewandoski and Swiderska, 2004].
- 2) can reduce the crystallinity and increase the amorphousness [Ueki and Watanabe, 2008; Singh et al., 2008; Ramesh and Lu, 2012].
- 3) act as plasticizer [Singh et al., 2008].

Figure 2.3 illustrates the effect of ionic liquid in PE system as reported in Singh et al. (2008).



**Figure 2.3 Schematic diagram showing effect of IL doping into polymer electrolyte matrix where  $\text{K}^+$  is potassium cation and IL is ionic liquid [Taken from Singh et al. (2008)]**

Since the discovery of 1-ethyl-3-methylimidazolium chloroaluminate by Wilkes and Zaworotko (1992), imidazolium based ionic liquids have been widely

developed. Imidazolium-based ionic liquids are of great interest due to its aromatic structure which enables the construction of low melting point salts due to the low charge density. Other types of bulky cations composed in ILs include ammonium, phosphonium, pyridinium and pyrrolidinium. The chemical structures of BMITf and BMII are shown in Figure 2.4.

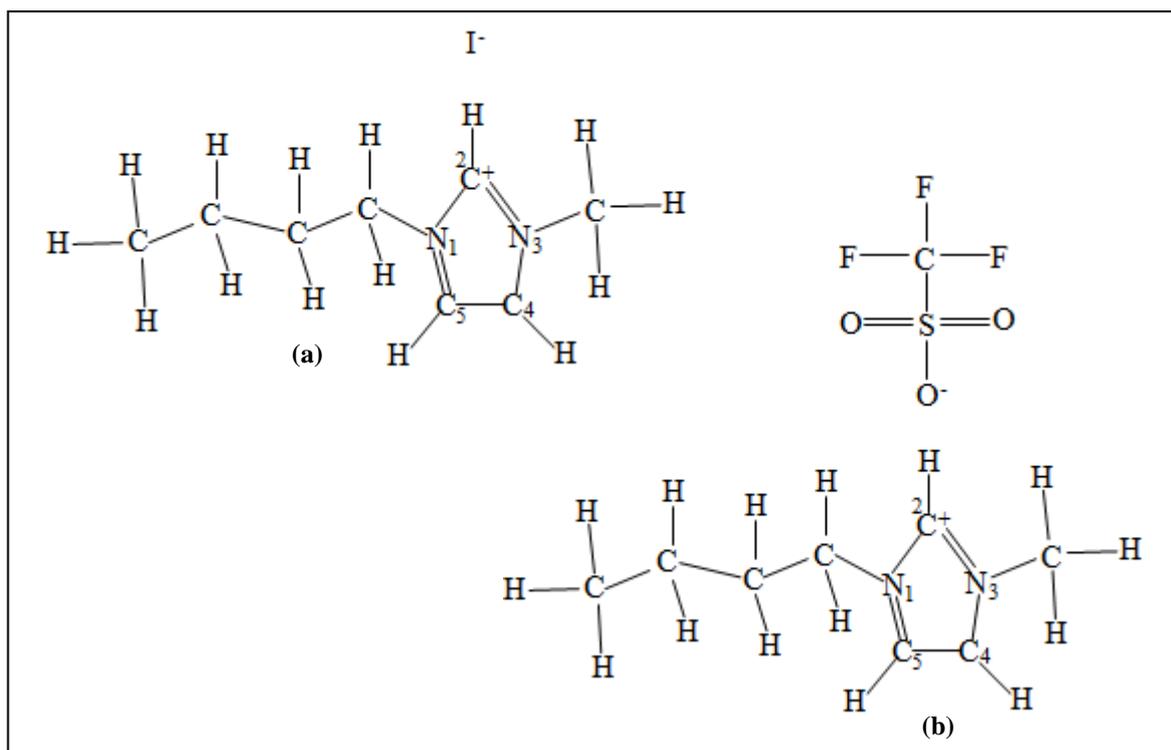


Figure 2.4 Chemical structures of (a) BMII and (b) BMITf

Kang and co-workers (2006) investigated the use of ionic liquids BMImNO<sub>3</sub> and BMImBF<sub>4</sub> in poly(2-ethyl-2-oxazoline) (POZ)/silver nitrate (AgNO<sub>3</sub>) based system to control the interactions between Ag<sup>+</sup> and NO<sub>3</sub><sup>-</sup> that caused the silver (Ag<sup>+</sup>) ions to become more strongly coordinated to the oxygen atoms in POZ. According to them, this phenomenon is attributed to the interaction between BMI<sup>+</sup> and NO<sub>3</sub><sup>-</sup> of salt which weakened the ionic bonding between Ag<sup>+</sup> and NO<sub>3</sub><sup>-</sup> to produce free ions. Tang and co-workers (2008) revealed that the incorporation of BMImBF<sub>4</sub> can weaken the interaction among polymer chains and also restrict the crystallization of PEO side

chains in a copolymer of acrylonitrile (AN), methyl methacrylate (MMA) and poly(ethylene glycol) methyl ether methacrylate (PEGMEMA).

Similar to inorganic salts containing small sized cation (i.e. LiTf), ionic liquids which contain a bulky cation i.e., BMITf and BMII can complex with negatively charged polar atoms such as O, F and N on polymers, etc. This is due to the attractive forces that exist between the positively charged cation (i.e. Li<sup>+</sup>, BMI<sup>+</sup>, etc) and the negatively charged atoms with lone pair electrons available for complexation to occur. The occurrence of complexation between small sized cation (i.e. Li<sup>+</sup>, Mg<sup>2+</sup>, Ag<sup>+</sup> etc) and polymers or plasticizers have been widely reported by researchers [Pandey et al., 2009; Hirankumar et al., 2006] through FTIR spectroscopy. On the other hand, studies on the complexation between ionic liquid and polymers as investigated by FTIR are limited. Therefore, it is crucial to investigate the interactions that occur between ionic liquids and polymers to ascertain whether BMI<sup>+</sup> can complex to the polar atoms of the polymer. This can shed some light on the enhancement of ionic conductivity of PEs which is usually obtained upon the addition of ionic liquids.

Several researchers have reported that the bulky cation of ionic liquids can complex to the polymer. Costa and co-workers (2007) studied on poly(ethylene glycol) dimethyl ether (PEGdME) incorporated with 1-butyl-3-methylimidazolium hexafluorophosphate (BMIPF<sub>6</sub>) and have proven from molecular dynamics simulation that imidazolium cations are coordinated not only by the anions but also with the O atoms of the polymer chain. FTIR study on sulfonated poly(ether ether ketone) (SPEEK)/1-butyl-3-methylimidazolium tetrafluoroborate (BMIBF<sub>4</sub>) system by Yi et al. (2011) indicates that the sulfonic acid (SO<sub>3</sub><sup>-</sup>) groups of SPEEK have interacted with the positively charged imidazolium cations through electrostatic attraction. Interaction

of imidazolium cation can occur by forming hydrogen bonds between H atom of N–H with electronegatively charged atoms. According to Jiang et al. (2006), the IR spectra of PMMA–BMImPF<sub>6</sub> showed changes in the  $\nu(\text{C}=\text{O})$  and  $\nu_{\text{a}}(\text{C}-\text{O}-\text{C})$  vibrations belonging to PMMA and the  $\nu(\text{N}-\text{H})$  band of BMIPF<sub>6</sub> which suggests that the O atoms of the polymer have interacted with the H atoms in N–H. Duarte and co-workers (2012) reported that interactions between the acetate containing ionic liquid, BMImAc and corn starch/poly( $\epsilon$ -caprolactone) (PCL) polymer blend occurred. They attributed the interaction occurs between BMI<sup>+</sup> cation and the O atom of the polymer blend.

## 2.6 Ionic conduction

The ion conduction in PEs is influenced by several factors such as degree of salt dissociation and its concentration, dielectric constant of polymer host and other components, degree of ion aggregation, mobility of polymer chains and ions, and temperature [Dillip et al., 2008].

The ionic conductivity,  $\sigma$  of a polymer electrolyte is generally governed by the content of the charge carriers and their mobility, and can be described by the equation below:

$$\sigma = \sum nq\mu \quad (2.1)$$

where  $n$  is the number of charge carriers,  $q$  refers to the charge and  $\mu$  is the mobility. For a PE system employing a fixed salt, the ionic charge  $q$  is the same, hence the resultant ionic conductivity depends only on  $n$  and  $\mu$ .

Generally, a maximum ionic conductivity is obtained with increasing inorganic salt. The increase in the ionic conductivity at low salt concentrations is due to the increase in the number of charge carriers. Above the critical salt concentration, a drop in

ionic conductivity follows which occurs due to ionic association which increases viscosity and suppresses mobility of ions [Kumar and Scanlon, 1994].

Other than studying the ionic conductivity at ambient temperature, temperature-dependent ionic conductivity can also reveal the mechanism of ion transport. Among the models used to describe the ion transport mechanism in PEs are the Arrhenius and Vogel–Tammann–Fulcher. Generally, ionic conductivity increases with temperature. The increase in the ionic conductivity with temperature can be interpreted as a hopping mechanism between coordinating sites, hopping being assisted by local structural relaxations and segmental motions of the polymer salt complexes [Reddy et al., 1999; Baskaran et al., 2004].

### 2.6.1 Arrhenius

In a plot of logarithmic (log) ionic conductivity versus reciprocal temperature, the ionic conduction is said to follow the Arrhenius rule if a linear plot is obtained. The linear regression value,  $R_2$  of the linear line is almost 1. Linearity of the plot shows that the ionic conduction is thermally activated and that the migration of the ions is not associated with the thermal relaxation of the polymer chains; ionic conduction occurs through hopping of ions from one coordination site to another and the polymer only provides structural integrity. The Arrhenius equation is as follows:

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{k_b T}\right) \quad (2.2)$$

where  $\sigma_0$  is a pre-exponential factor,  $E_a$  is the activation energy,  $T$  is the temperature in Kelvin, and  $k_b$  is the Boltzmann constant ( $1.38 \times 10^{-23}$  J K<sup>-1</sup>). Figure 2.5 shows the temperature-dependent conductivity plots of nanocomposite polymer electrolytes (CPEs) based on PAN, LiClO<sub>4</sub> and silica aerogel powder (SAP).

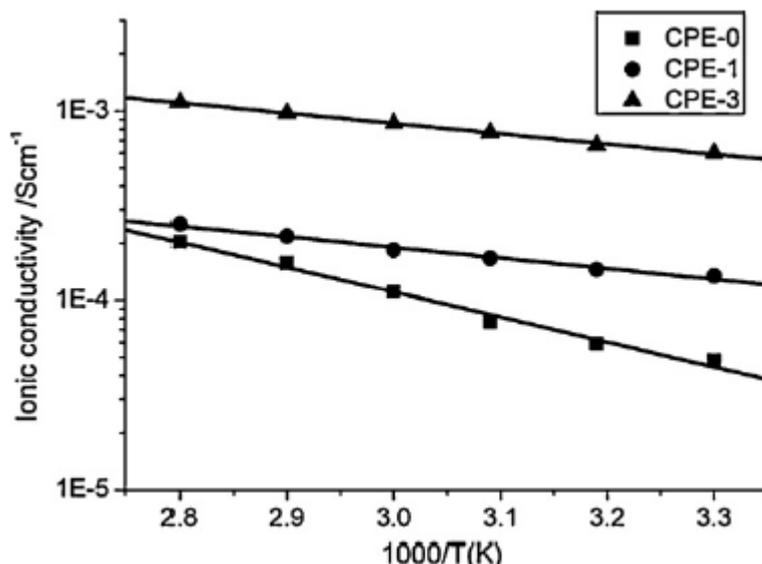
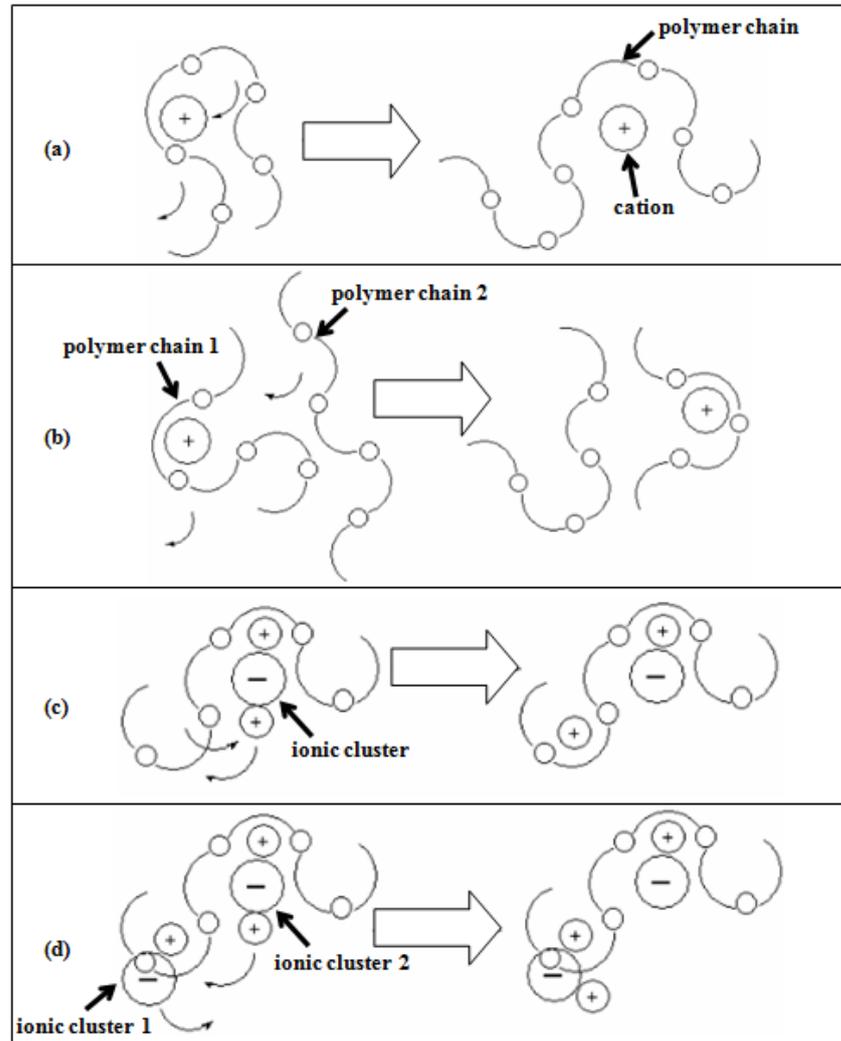


Figure 2.5 Temperature dependence plots of the conductivity of PAN-LiClO<sub>4</sub> containing 0 (CPE-0), 1 (CPE-1) and 3 (CPE-3) wt.% SAP [Taken from Chen et al. (2011)]

The conductivity trend of Chen et al. (2011)'s work is seen to increase linearly with temperature, and obeys the Arrhenius rule. Information which can be obtained from the Arrhenius plot is the activation energy,  $E_a$ .

### 2.6.2 Vogel–Tamman–Fulcher (VTF)

This model can be recognized from the non-linearity or curved plot obtained when conductivity is plotted against inverse of temperature. Ion conduction with respect to temperature follows a free-volume law and usually occurs in amorphous phase [Cohen and Turnbull, 1959; Cohen and Grest, 1980] of electrolytes whereby the ionic transport occurs through the polymer segmental motion [Ratner, 1987]. The segmental motions are thought to promote ion mobility by making and breaking the coordination bonds between cation and polymer which results in inter-chain and intra-chain ion hopping which leads to ionic conductivity enhancement. Figure 2.6 illustrates the cation motion via intra- and interpolymeric chains.



**Figure 2.6** Cation motion in a polymer electrolyte via (a) intrachain hopping, (b) interchain hopping, (c) intrachain hopping via ion cluster and (d) intercluster hopping [Taken from Gray, 1997]

The VTF equation is given as [Vogel, 1921; Tamman and Hesse, 1926; Fulcher, 1925]:

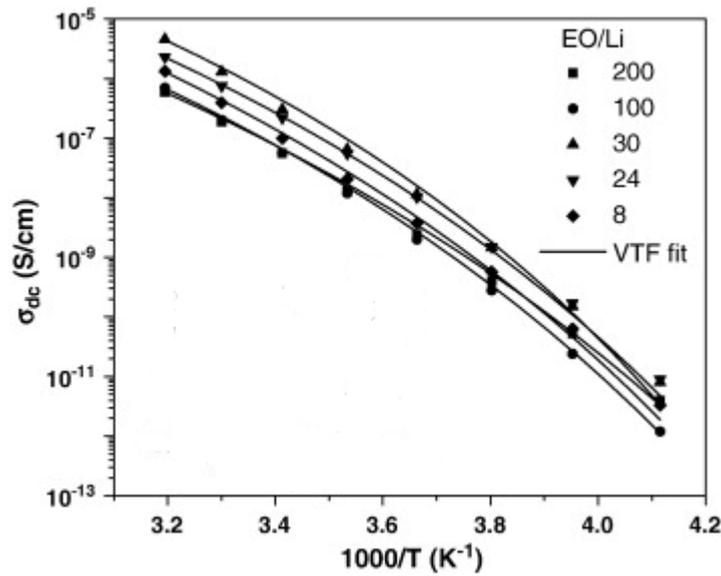
$$\sigma = \sigma_0 T^{-1/2} \exp\left(\frac{-B}{K(T_0 - T)}\right) \quad (2.3)$$

where,  $\sigma_0$  is the pre exponential factor,  $B$  is the pseudoactivation energy of the ion and  $T_0$  is the thermodynamic glass transition or ideal glass transition temperature,  $T_0 \approx T_g - 50$ . The  $T_0$  can either be determined experimentally from differential scanning calorimetry (DSC) or estimated from trial and error by substituting values of the  $T_0$  into the

logarithm form of equation (2.3) to obtain the highest regression value nearest to unit from the plot of  $\log \sigma T^{1/2}$  versus  $1000/(T-T_0)$ :

$$\log \sigma T^{1/2} = \log \sigma_0 + \log \exp\left(\frac{-B}{k_b(T-T_0)}\right) \quad (2.4)$$

Figure 2.7 illustrates the curvature of the temperature-dependent conductivity trend which obeys the VTF rule.



**Figure 2.7** Temperature dependence plots of the conductivity of PEO–LiTf comprised of various EO/Li ratios. [Taken from Karan et al. (2008)]

## 2.8 Summary

In this chapter, an inexhaustive overview of polymer electrolytes, lithium salts, polymer blends, plasticizers, ionic liquids and ionic conduction have been provided. The next chapter presents the materials, the preparation method of polymer electrolyte films and explains the roles of the various experimental techniques used to characterize the samples.