CHAPTER 8

DISCUSSION

The fast emerging economies and changes in life style has increased energy demand globally. Furthermore, world population is estimated to reach 7.5 billion people by 2020. These factors prompted the issue of the scarce fossil fuel and worries on oil price. As a result, it boosted research for the development of renewable energies such as solar energy, wind power, tidal or ocean energy, geothermal and biomass. Following this, good electrical energy storage systems (EES) must be created to store and manage energy properly. EES can meet the large demand of power output fluctuation in daily, monthly or even annual cycles. Batteries, supercapacitors and fuel cells are examples of EES technology that convert electrochemical energy into electrical energy.

EES such as battery is also highly demanded in portable devices and achieves annual worldwide sales of US$36 billion in 2008 [Kularatna, 2011]. Its production meets new challenges with the ever-increasing functionality of trendy tablet computer, eg. Iphone and Samsung Galaxy. EES devices can be based on electron conducting materials or ionic conducting materials that include polymer electrolytes. The general trends are light weight, small size and flexible, low production cost and heavy duty with high energy density. All these requirements could be realized by applying polymer electrolytes.

Production of good polymer electrolyte depends on the selection of the appropriate polymer with suitable salt and/or additive to enhance the conductivity. Choosing an eco-friendly material as polymer host to build a green polymer electrolyte can help to reduce the environmental loads. Such materials include natural biodegradable polymers such as cellulose, starch and chitosan or synthetic biodegradable polymers such as PVA and PCL. A number of attempts have been made to add metal salts into PCL matrix forming polymer electrolytes for smart window and battery applications. These metal salts includes lithium ($LiClO_4$, $LiCF_3SO_3$, $LiBF_4$), magnesium ($Mg(CF_3SO_3)_2$), europium ($Eu(CF_3SO_3)_3$) and potassium (KCF_3SO_3) salts.

In the present study, PCL-based solid polymer electrolyte was prepared using NH_4SCN as the incorporating salt to prepare a proton conducting electrolyte. To the author's knowledge, no such combination has been reported. In order to enhance the conductivity, EC was added as plasticizer to the most conducting PCL-NH_4SCN sample. All the samples were characterized using DSC, SEM, XRD, FTIR and EIS.

At first thought, one might think that there are two cation species in this polymer-salt system, i.e., either H^+ or NH_4^+. From the work of Binesh and Bhat (1996), ^1H NMR studies on PEG-NH_4ClO_4 system have shown that the conducting species is H^+. Srivastava *et al.* (1995) has done coulombmetric investigation on PEO-NH_4SCN system. They have also reported that the proton (H^+) is the cation contributing to the ionic transport. Similar results were also obtained from other researchers as well. Hashmi *et al.* (1990), Maurya *et al.* (1992) and Srivastava and Chandra (2000) reported protonic motion in different polymer-ammonium salt complexes such as PEO-NH_4ClO_4, PEO-NH_4I and PESc-NH_4ClO_4, respectively. To explain how H^+ is the conducting species, recall that the NH_4^+ cation has a tetrahedral structure [Hashmi *et al.*, 1990]. One of the four hydrogen atoms is most weakly bound to the nitrogen atom. It can be easily dissociated upon application of an electric field. These protons can jump from one coordinating site to an adjacent site. Thus, the conducting species is attributed to H^+. The vacancy is then filled by another H^+ or proton. In this work, we consider H^+ as the positive charge species.

For PCL-NH_4SCN system, DSC studies reveal that the crystalline melting point of PCL, T_{m1} (56.0 °C) reduces with increasing NH_4SCN concentration. According to literature [He *et al.*, 2004], NH_4SCN acts as impurities to lower the T_{m1} of PCL. As the salt content increases to 10 wt.%, the T_{m1} is observed (Fig.4.1) to broaden with a weak shoulder appearing on the higher temperature side. This shoulder becomes a prominent second crystalline melting peak, T_{m2} (57.1 °C) at 20 wt.% salt onwards, which can be attributed to a new crystalline phase of PCL-NH_4SCN complex [Dey *et al.*, 2008]. T_g is found to increase gradually (Fig. 4.2) with increasing NH_4SCN concentration. This demonstrates that the ammonium ions have formed virtual or transient cross-links with PCL chains. As a result, the film is found more brittle and shows a rough morphology as observed from SEM result. Similar behavior is observed by Idris *et al.* (2001) in the various types of natural rubber added with $LiCF_3SO_3$. The increase in T_g indicates that the rotation of the polymer segments and local chain are now restricted [Baril *et al.*, 1997, Hayamizu *et al.*, 1998]. Therefore, more thermal energy is required to create sufficient free volume to permit transition from rigid solid and brittle environment to leathery liquid and "plastic state". This also explains why a higher temperature T_{m2} is observed.

However, an opposite trend of T_g is observed when EC is added into PCL-NH_4SCN system. Massive drop of T_g is depicted in Fig. 4.5 upon addition of 30 wt.% EC onwards. The T_g reduces from -56.8 of 0 wt.% EC to -76.7 °C of 40 wt.% EC. Since T_g is a gauge to measure the polymer chain ability to rotate about the chain bonds, a decrease in T_g means the polymer segments are a lot more flexible [Bandara *et al.*, 1998; Kumar and Sekhon, 2002; Wang *et al.*, 2005c]. The effect of the decreasing T_g is observed in the surface morphology of the films as it becomes smoother with increasing EC content.

The complexations between PCL, NH_4SCN and EC have been verified by FTIR analysis in section 6.3 and 6.4. Fig. 6.6 shows the carbonyl stretching regions of PCL-NH_4SCN system. Although the carbonyl bands are still maintained at 1736 cm^{-1} and 1720 cm^{-1}, a new peak appears at 1623 cm^{-1} upon addition of 5 wt.% salt. This new peak increases in intensity with increasing salt content. According to many literature reports [Chiu *et al.*, 2004; Wu and Chang, 2007; Lin and Wu, 2011], this cation-oxygen interaction at the carbonyl band at 1623 cm^{-1} proves the interaction between PCL and NH_4SCN. The H atom of the NH_4^+ is believed to serve as coordination bond donor while O atom of the C=O serves as coordination bond acceptor. This interaction is in agreement with the increase of T_g in PCL-NH_4SCN complexes.

On the other hand, the lowering of T_g in PCL-NH_4SCN-EC system could be explained by IR spectra as presented in Fig. 6.19. The addition of EC into PCL-NH_4SCN complexes has created new EC-NH_4SCN interaction which is demonstrated as a new peak at wavenumber 1773 cm^{-1}. At the same time, the peak at 1623 cm^{-1} becomes very weak. It seems that the EC-NH_4SCN interaction has weakened the PCL-NH_4SCN

interaction. This indicates that EC is a stronger competitor than PCL for interaction with NH_4^+ of the ammonium salt. Thus, the formation of EC-NH_4^+ complex reduces the fraction of PCL-NH_4^+ complex. A more flexible PCL chains with less cross-linking is obtained, showing a reduced T_g value. Similar observation and conclusion were obtained by Qian *et al.* (2002). Fig. 6.19 also displays the complexation between PCL and EC as manifested by the appearance of second new peak at 1807 cm^{-1}. This new peak is an upshift of the C=O stretching mode of EC from 1784 cm^{-1}. This is in agreement with DSC studies where multiple T_m peaks are observed (Fig. 4.6) in PCL-NH_4SCN-EC system, demonstrating new PCL-EC complex phases. It also explains the new pore-like features from SEM studies which are phase separations corresponding to these new complex phases between PCL, EC and NH_4SCN.

The melting enthalpy, ΔH_m from DSC studies will provide information regarding the amorphous content of the polymer electrolytes. Both PCL-NH_4SCN and PCL-NH_4SCN-EC systems show a decrease of ΔH_m with addition of salt up to 26 wt.% (Fig. 4.3) and EC up to 50 wt.% (Fig. 4.7), respectively. These findings are in good agreement with the relative degree of crystallinity, χ_C obtained from XRD structural analysis in Chapter 5. The orthorhombic crystalline peaks at $2\theta = 21.4°$, $22.0°$ and $23.7°$ were deconvoluted from the amorphous spectrum centered around $2\theta = 21.0°$. For PCL-NH_4SCN system, the intensity of sharp crystalline peaks reduces with addition of salt (Fig. 5.7). For PCL-NH_4SCN-EC system, the amorphous spectrum becomes stronger and broader with increasing EC content (Fig. 5.10). From Fig. 5.8 and Fig. 5.11, the minimum value of χ_C is also obtained at 26 wt.% salt and 50 wt.% EC, respectively. The reduction in χ_C can be understood from FTIR analysis of ion-polymer, polymer-plasticizer and ion-plasticizer interactions. As more salt ions are interacted with polymer in PCL-NH_4SCN system, ion-polymer interactions inhibit and disrupt the order/folding pattern of polymer chain. Eventually, the ordered and rigid crystalline domains of the polymer are suppressed increasing the disordered amorphous domains. On the other hand, the polymer-plasticizer and ion-plasticizer interactions in PCL-NH_4SCN-EC system manage to interrupt polymer-polymer interaction either by occupying or increasing inter and intra-chain separations [Bandara *et al.*, 1998]. As a result, the crystalline domains are further disrupted [Kuila *et al.*, 2007]. The variation of χ_C obtained thermally and structurally in both systems are in reciprocity to the conductivity as shown in Fig. 7.3 and Fig. 7.31. This infers that decrease in crystallinity is accompanied by the increase in conductivity. Therefore, the highest conducting sample of the respective system exhibits the highest amorphous content. The amorphous state of the polymer matrix has been reported to play a dominant role compared to crystalline state in enhancing conductivity. This is due to the polymer segmental motion that increases with the increase in amorphousness [Berthier *et al.*, 1983; Scrosati, 1993]. In the amorphous region, the polymer chains are irregular and entangled, leading to a loose molecular packing with smaller density. On the other hand, the polymer chains in crystalline region are arranged regularly with high density molecular packing. Hence, it is easier to move the polymer chain in amorphous state than in crystalline state.

From FTIR studies, SCN^- stretching mode is used to study the effect of ion dissociation/reassociation in the present work. According to the literature [Cruickshank *et al.*, 1995; Xu *et al.*, 1996; Zhang *et al.*, 2003; Ramya *et al.*, 2007], this broad peak from 2030 to 2090 cm^{-1} is composed of three narrower peaks. These peaks are the free anions (SCN^-), contact ion pairs (NH_4^+ SCN^-) and ion aggregates located at ~2040 cm^{-1}, ~2058 cm^{-1} and ~2074 cm^{-1} respectively. Thus, the overlapping peaks under this broad envelope are separated (Fig. 6.8 and Fig. 6.21) in order to calculate the percentage of the different ionic species.

For PCL-NH_4SCN system, incorporation of ammonium ions up to a critical value (26 wt.%) pumps in corresponding free ions into PCL matrix. Beyond 26 wt.%, the solvated free ions are close enough to one another to cause formation of ion pairs or/and higher aggregates through coulombic force. Thus, when the number of free ion drops after 26 wt.% salt, both number of contact ion pairs and ion aggregates increase.

For PCL-NH_4SCN-EC system, the number density of free ions is observed to increase at the expense of contact ion pairs and ion aggregates. When 30 wt.% or more EC is added, the integral area fraction of ion aggregate drops to 0 % reflecting the absence of bigger size ion aggregates that do not contribute to conductivity in the sample. At the same time, percentage of contact ion pair decreases gradually while fraction of free ion enhance tremendously. For the first time, the percentage of free ions overtakes that of contact ion pairs. Refer back to the PCL-NH_4SCN system in Fig. 6.9, the percentage of contact ion pair is always higher than free ions, this could be explained by the low solvating power of PCL due to low dielectric constant value (a value of 2.3 as depicted from Fig. 7.4). However, the addition of EC into PCL-NH_4SCN-EC system has changed the entire scenario. Since EC possesses high dielectric constant value of 89.8, it has high dissociation ability to prevent ion-pair formation or high effectiveness on shielding the interionic coulombic attraction between cations and anions. According to Bjerrum [Bockris and Reddy, 1998], the critical distance, r for ion pair formation is reciprocal to the dielectric constant, ε' value as shown in the following equation:

$$r = \frac{|z_i z_j| e^2}{8\pi\varepsilon_0 \varepsilon' kT} \qquad (8.2)$$

Here, z is the valency of the cations and anions, e is the elementary electron charge, ε_0 is the dielectric constant in vacuum, k is the Boltzmann's constant (= 8.6173×10^{-5} eV K^{-1}) and T is temperature. Ion pair formation is likely to occur when the distance between cation and anion is smaller than r. According to equation 8.2, high ε' value means small r. Thus, in a system with high ε' value, it is more difficult for cations and anions to be close enough to fulfill the criteria (smaller than r) for ion pair formation to take place. In the present PCL-NH_4SCN-EC system, by taking ε' value at 1 MHz, r for 10, 30 and 50 wt.% EC are estimated to be about the distance formed by 30, 17 and 10 atoms arranged side by side.

Following the above discussion, in a polymer system incorporated with high ε' material like EC, ion association is unlikely to happen and most ions would stay free. Thus, EC is also acting as an additive to promote ion dissociation. Although EC is intended to be used as plasticizing solvent to enhance the conductivity by reducing T_g and degree of crystallinity, it is found that EC can also increase number density of free ions in the polymer electrolyte system. Chintapalli and Frech (1996) has shown higher dissociation rate of free ions using FTIR result by adding EC into their PEO-$LiCF_3SO_3$ system. On the other hand, Forsyth and co-workers (1995) used NMR result in their PEG-$NaCF_3SO_3$-PC system to draw the same conclusion. This result is also supported by the findings of other researchers. Two PE systems (PEO-NH_4F and PEO-DMA-NH_4F) were prepared by Kumar and Sekhon (2002). In the second system, a fix amount of DMA(19 wt.% of PEO) was added to PEO. The investigation was carried out by adding NH_4F into both systems. At low salt concentration, the conductivity of both systems increased with the addition of NH_4F (by almost the same magnitude) until a critical salt concentration. Beyond this critical salt content, PEO-NH_4F system began to show a decrease of conductivity attributing to the formation of ion aggregates. However, PEO-DMA-NH_4F system continues to show increment in conductivity at high salt content. They concluded that it was attributed to the dissociation of ion aggregates by DMA (with high dielectric constant value of 37.8). On the other hand, addition of DEC (with low dielectric constant value 2.38) into PEO-NH_4F system did not show conductivity enhancement at that high salt content region. In the present work, it is concluded that EC helps to dissociate ion pairs or/and higher aggregates leading to higher number of free ions. Thus, the drastic increase of number density of free ions in Fig. 6.21 is attributed to the high dielectric constant of EC. These percentage of different ionic species as a function of salt and EC concentration would give some insight in composition dependence conductivity studies.

In morphology studies, spherulites with definite boundaries are observed for PCL-NH_4SCN films. These round-shape spherulites come from the uniform radial lamella growth that forms the crystalline domains. Similar spherulitic morphology was reported in PEO-based polymer electrolyte films [Sreekanth *et al.*, 1999; Jaipal Reddy and Chu, 2002; Pereira *et al.*, 2009]. When more NH_4SCN is added, the number of spherulites increases with corresponding reduction in spherulite diameter (Fig. 5.2). This means an increase of the micro domain fraction. Micro domain is the intra-crystalline phase that is embedded between the spherulites, representing the amorphous domain. Therefore, addition of salt increases the amorphous domain of the sample. The surface morphology is a little rough but no clear phase separation is observed. Beyond 29 wt.% salt, an appearance of clusters is observed as deduced from SEM micrographs, attributing to the formation of ion aggregates. Thus, the films also become more brittle and rough. It is good to note that the lowering of spherulite size is accompanied by an increase in conductivity until 26 wt.% salt. It may therefore be inferred that the reduction of spherulite size indicates an increase in conductivity.

For the PCL-NH_4SCN-EC films, morphology studies by SEM reveal that incorporation of EC causes dramatic changes of surface morphology. When more EC is added to the highest conducting PCL-NH_4SCN film, the clear spherulite boundaries in Fig. 5.4 is no longer been observed as the surface becomes smoother and the film become softer. New pore-like phases also appear attributing to new complex phases between PCL, EC and NH_4SCN. This is supported by the existence of multiple T_m peaks from DSC analysis and appearance of two new peaks at 1773 cm^{-1} and 1807 cm^{-1} from IR studies as discussed previously. EC interrupts the crystalline phase to produce a soft film with smooth surface.

Impedance plot for PCL-NH_4SCN system reveals that the conductivity improves with increasing salt content (up to 26 wt.%) as proven by the reducing size of the depressed semicircle in Fig. 7.1. It has been observed that the conductivity of the samples increases from 1.86×10^{-10} S cm^{-1} of pure PCL film to a maximum value of 3.94×10^{-7} Scm^{-1} at 26 wt.% NH_4SCN and begin to decrease at higher salt content. The initial rise of conductivity along with the increase of salt content could be understood in terms of the number density of free ions. In principle,

$$\sigma = \sum_i n_i \cdot z_i e \cdot \mu_i \qquad (8.1)$$

where n is the number density of charge carrier, e is the electronic charge and μ is the mobility of charge carrier. The conductivity of a material could be enhanced by increasing n or/and μ . Fig. 7.3 can be divided into two regions, Region I and Region II. The steady conductivity increase in Region I could be correlated to the increase in the number density of free ions. This is supported by FTIR analysis as discussed in Section 6.3 (Fig. 6.9). After deconvolution, the peak representing free ions at 2040 cm^{-1}, has shown an increasing integral fraction area until a maximum and begin to fall after 26 wt.%. Pairs of salt cation-anion dissociate into free ions and complex with PCL. Addition of salt content means more free ions, contributing to the conductivity enhancement.

However, PCL has low dielectric constant, 2.3 and this limits the degree of ion dissociation. When the coulomb interactions between the free/mobile ions is not effectively screened, the excess free cations and anions can re-associate. Above 26 wt.% salt, the multiplied salt ions can no longer be solvated by PCL anymore, the excess of salt ions form ion pairs or/and multiple ion aggregates Therefore, the reduction of conductivity in Region II is attributed to the re-association of ions [Gray, 1997]. The increase of neutral ion pairs do not contribute to the conductivity. Instead, it causes a decline in the number density of free ions and also boosts up the medium viscosity. Higher medium viscosity means lower mobility of charge carriers.

On the other hand, formation of larger size ion aggregates means limited relative mobility due to the larger mass and also reduces the number density of free ions. Consequently, the conductivity is decreased. In PEO-LiTf system, Teeters *et al.* (1996) had observed the re-association of the surfactants (free ions) to form micelles (ion aggregates) after a critical salt concentration. They then concluded that the grouping of surfactants eventually lead to a reduction in dc conductivity after reaching a maximum conductivity of 7 x 10^{-4} S cm^{-1}. This is consistent with the result from IR studies (Fig. 6.9). Both number density of contact ion pair and ion aggregate increases greatly after 26 wt.% salt onwards. From structural aspect, the drop in conductivity could be due to the increase in the degree of crystallinity as illustrated by the XRD studies in Section 5.4 (Fig. 5.6).

For PCL-NH_4SCN-EC system, the conductivity versus EC content plot in Fig. 7.31 reveals a monotonous relationship between the two parameters. Conductivity is found to increase with increasing EC content from 3.94 × 10^{-7} S cm^{-1} at 0 wt.% EC until a maximum value of 3.8 × 10^{-5} S cm^{-1} at 50 wt.% EC. Refer to Equation 8.1, this increasing trend of conductivity is attributed to two factors, the increase in number density of ions and ion mobility. The increase of ion mobility will be explained in the temperature dependence conductivity studies. On the other hand, the increase of free ions has been discussed in the previous paragraph of IR studies and is also supported by dielectric analysis.

The tan δ as a function of frequency is plotted in Fig. 7.11 and 7.39 to analyze the relaxation behavior in the PCL-NH_4SCN and PCL-NH_4SCN-EC films, respectively. A well-defined peak is obtained and this loss tangent peak shifts to higher frequency with increasing salt content (up to 26 wt.%) and EC content (up to 50 wt.%), indicating shorter relaxation time. Fig. 7.12 and 7.40 clearly shows that the variation of relaxation time is the inverse of dc conductivity. With the enhancement of the amorphousness as concluded structurally and thermally, the polymer chain packing becomes loose and entangled, leading to a shorter relaxation time.

The understanding of ion transport mechanism could hold the key for a breakthrough to achieve high ionic conductivity at room temperature. However, the microscopic view of ionic transport above the glass transition temperature is not well understood yet. This is because the behavior of ion interaction is a complicated phenomenon due to complex ion-ion and ion-polymer interactions between many salt molecules and polymer polar group. Thus, conductivity in a PE system is a very complex process. The dielectric behavior analysis is carried out in an attempt to provide some insight on the ion transport properties of the present work.

For PCL-NH_4SCN system, Fig. 7.5 demonstrates that the variation of ε' is in accordance with the variation of conductivity as a function of salt concentration. Referring to Equation 7.4, the changes of ε' value reflects the changes of charge carriers number density. There are two types of charge carriers within the frequency window investigated. Salt ions (pairs of cation-anion) that dissociate into free ions and localised dipoles from carbonyl of PCL that exhibit an imbalance of charge. Since the number density of polymer dipoles do not change with increasing salt content, the variation of ε' is due to the salt ions. Therefore, the variation of conductivity in Fig. 7.3, the enhancement in Region I and reduction in Region II are attributed to the increasing and decreasing number density of free ions, respectively.

For PCL-NH_4SCN-EC system, incorporation of EC has amplified the value of ε' many folds (Fig. 7.33). At low frequencies, ε' has increased from a value in 10^3 order to 10^5 order for 0 wt.% and 50 wt.% EC, respectively, a 100 times amplification. The variation of ε' as a function of EC content is similar as the conductivity variation. ε' is found to increase with increasing EC content. Since ε' reflects the number density of free ions (equation 7.4), therefore the increasing trends of conductivity is a result of growing number density of free ions.

Back to the variation of $\log \varepsilon'$ versus $\log f$ plot, a dispersion with high value of ε' is observed in the low frequency region (Fig. 7.4 and 7.32), due to electrode polarization effect. Under an electric field influence, charge carriers will move and migrate along the field direction appropriately. However, they cannot cross the electrode-electrolyte interface because the blocking electrodes do not permit charge transfer into the external circuit. Then, these trapped charge carriers become space charges (reversible) that accumulate at the interface of opposite polarity electrodes. Eventually, it become localised and forms temperarily a heterocharge layer. If the thickness of the sample is much greater than the dimension of this heterocharge layer, the charge density will rise rapidly leading to electrode polarization [Howell *et al.*, 1974]. Besides salt ions, the carbonyl group of PCL chain also carries permanent dipoles (together with induced dipoles surrounding it) that will align favorably in the electric field direction through conformational changes. According to Urakawa *et al.* (1994), there are two components of PCL dipole, which are normal and parallel to the main polymer chain. Beginning from average equilibrium positions, the positive charged regions will rotate towards the field while the negative charged regions rotate away from the field. Finally, these dipoles contribute to the polarization effect [North, 1979].

At high frequency region, ε' is seen to decrease rapidly. The periodic reversal of the electric field occurs too fast that practically there is no sufficient time for the charge carriers and dipoles in the polymer chain to translate and orient, respectively. Eventually, there is almost no excess dipoles motion in the direction of the field

[MacDonald, 1987]. This in turn reduces the contribution to the polarization and ε' shows less frequency dependency with increasing frequencies.

A strong dependence of conductivity on ε' value is also revealed in both PCL-NH_4SCN and PCL-NH_4SCN-EC polymer electrolyte systems as displayed in Fig.7.6 and Fig. 7.34, respectively. The ε' value could be tuned by the salt content in the formal system and EC content in the latter system. These results are in agreement with Petrowsky and Frech (2008; 2009) who worked with organic liquid electrolyte systems. They have investigated various lithium-based liquid electrolyte systems by using different solvents like alcohol [Fleshman *et al.*, 2011], alkly bromide, nitrile and acetate [Bopege *et al.*, 2012] to tune the value of ε'. They concluded a new Arrhenius formalism, $\sigma_{dc}(T,\varepsilon') = \sigma_o(\varepsilon')\, e^{-E_a/K_BT}$. σ_{dc} depends on both parameters of T and ε' where ε' is contained in σ_o. Thus, in the present work, the dependence of the dc conductivity on the system ε' is expected to contain in the exponential prefactor term, σ_o.

At a fixed salt and EC content, the dispersion of ε'' at low frequencies and the drastic drop at high frequencies is observed (Fig. 7.7 and 7.35) which could be understood as follows. Both ions and dipoles have finite masses which mean they carry the effect of inertia. At low frequencies, the polarity of the electric field reverses slowly. The ion’s translational motion and dipole’s rotational motion would go through a process of deceleration (slowing down), stop and acceleration (speeding up) in reverse direction. Consequently, heat is generated through internal friction and causes energy to dissipate. The amount of energy loss and degree of out of phase with the initial electric field are reflected in ε'' which is why it is also termed as dielectric loss. As the frequency increases, no more ions or dipoles are able to follow the high speed periodic reversal leading to a drastic drop of ε'' at high frequencies. When more salt or EC is added, higher number density of charge carriers participate in the ion transport causing the corresponding larger energy loss.

However, the expected ε'' peak is not observed in both PE systems, contradicting to literature. A dielectric loss peak is reported at around 60 kHz for a dilute solution of PCL in dioxane [Baysal and Stockmayer, 1994] and semidilute solution of PCL in benzene at 298 K [Urakawa *et al.*, 1994]. The researchers reported a small peak magnitude around 0.2 and 1.0, respectively and termed it as dipolar relaxation. It is good to note that both systems were polymer systems without any salt or additive. For the present work, the small dipolar relaxation peak could possibly be masked by the large electrode polarization effect. In order to study the relaxation dynamics, electric modulus, M analysis is employed because it can suppress the electrode polarization effect at low frequencies and enhance small features at high frequencies. A single and broad peak (FWHM > 1.144 decades) is depicted from M'' versus log f plot in Fig. 7.9 and 7.37. The peak shifts to the right towards higher frequency with increasing salt and EC content, indicating a reduction in relaxation time. This single peak predicts the conductivity relaxation [Pradhan *et al.*, 2009] but the broadness of the peak could be intepreted as the dipolar relaxation [Sidebottom *et al.*, 2000] that exhibit a distribution of relaxation times. In order to clarify the type of relaxation, M'' versus M' is then plotted according to Mohomed *et al.* (2005). Fig. 7.10 and 7.38 clearly shows a depressed semicircle with a center that lies below the real axis indicating a coupling of conductivity relaxation and dipolar relaxation [Starkweather and Avakian, 1992]. This coupling effect was reported in the literature. Fu *et al.*, (1991) reported a merge of two separate peaks from M'' versus log f plot as the Li salt concentration increased in the PPG-Li salt system. They concluded that a coupling between ion motion and polymer segmental motion has occurred. Jeevanandam and Vasudevan (1998) also reported the same coupling effect in PEO-sodium salt system. In the present work, therefore the ionic motion is most probably coupled with the polymer segmental motion. Temperature dependance conductivtiy studies shall verify this coupling effect.

The temperature dependence of conductivity graphs are plotted for various salt content (Fig. 7.15, 7.17, 7.19 and 7.21) and EC content (Fig. 7.43, 7,45 and 7.47), respectively. Smooth curves with high regression value of polynomial trendlines are obtained, showing a VTF type of relationship. Thus, the linear fits using VTF equation are then carried out as shown in Fig. 7.22 and 7.48. For all the samples, (T_g - T_0) is calculated to be within the range of 40 to 50 K. It is good to note that the room temperature is well above T_g at the rubbery-state of the current systems. This so-called viscoelastic behavior corresponds to the anisotropic liquid at the microscopic scale. Thus the polymer chains have sufficient mobility to enable large scale reorganization of the chains to occur.

VTF equation is based on the theory of free volume. Free volume is not the inevitable gap in between molecules but it is the extra vacant space created by an oscillating molecules. When the temperature increases, the amplitude of chain oscillation also increases. In PE system, this enlarges the free volume and could speed up the polymer segmental motion (assumption has been made that the critical free volume is larger than that of segmental motion). In the present work, the ions should be mobile at temperatures above T_g. Hence, the conductivity is the cause of mechanical coupling between the ionic motion and the polymer segmental motion [Geiculescu *et al*., 2002; Seki *et al*., 2005] whereby VTF gives the perfect fit.

The coupling effect can be viewed as follows. The dipoles in the polymer chains will vibrate with their natural frequencies governed by the elastic restoring forces exerted by neighboring dipoles. They are bonded to an equilibrium positions and rotational state. When the amorphous domain expands (as verified from XRD and DSC studies) with increasing additives (NH_4SCN or EC), these dipolar molecules should be able to move or orient at ease. The polymer chain becomes more flexible to rotate producing segmental motion [Deepa *et al.*, 2002]. During resonance, under the influence of electric field, cations absorbed sufficient energy to dissociate from the weak bonds (at PCL-NH_4SCN or EC-NH_4SCN) and move to the adjacent sites. This movement occurs concurrently with the dipolar relaxation as the distance between two complex sites will be closer at one stage where the potential barrier for cation hopping is the lowest. It means cations have higher chance to move between coordination sites on one polymer chain (intra-) or with different chain (inter-). This is how the polymer segmental motion facilitates the ionic motion motion [Druger *et al.*, 1983; Ratner, 1987] and why the ionic transport mechanism is the product of coupling between these two motions.

For PCL-NH_4SCN system, an increasing trend of parameter A (the pre-exponential factor) is observed with increasing salt content. This indicates that the number of ions in PCL matrix increases. The value of parameter B is in the range of 10^3 K which is of the same magnitude as literature [Seki *et al.*, 2005; Karan *et al.*, 2008]. This pseudo energy increases with addition of ammonium salt. Referring back to DSC studies in Section 4.2 (Table 4.1), the T_g increases when more salt is added. Therefore, the increase of pseudo energy up to 26 wt.% could be explained by considering the stiffer polymer matrix that requires higher energies to promote segmental motion [Fonseca and Neves, 2002].

When EC is added to PCL-NH_4SCN complexes, a new environment is developed for ion conduction. New set of parameter *A* and *B* values are obtained. The estimated value of *B* is one order lower than that in PCL-NH_4SCN system, in which could be explained by FTIR results. Refer to the proposed scheme in Fig. 6.20, the cation also interacts with the C=O of EC. These new EC-NH_4^+ complex sites imply the existence of additional pathways for cation to migrate from one complex site to another. According to Bandara *et al*. (1998), the cations may prefer to conduct through the new pathways as the medium is less viscous, thus improving the ionic mobility. The effective jump distance is expected to be shorter with lower potential cage barrier. As a result, a lower value of *B* is obtained in PCL-NH_4SCN-EC system. This range of value (10^2 K or 10^{-2} eV or 1 kJ mol^{-1}) was also obtained by other EC or PC plasticized PEO-based systems [Kovac *et al*., 1998; Wang *et al*., 2005c].

However, the parameter *B* is also found to increase when more EC is incorporated. A survey on literature shows that similar increasing trend with increasing plasticizer content was reported by Wang and co-workers (2005c). They added two types of plasticizer (EC and PC) separately in their PEO-$LiClO_4$-filler-plasticizer system. When the temperature is elevated, this pseudo energy is transmitted to the polymer chain, promoting segmental motion. The free volume enlarges allowing polymer matrix to expand.

The investigations carried out throughout the entire duration of the study have been successful in addressing the objectives of this work.