## **CHAPTER 7**

## DISCUSSION

Both PEMA and PVdF–HFP have polar functional groups: carbonyl (C=O) and C–O groups in PEMA, and CF<sub>2</sub> and CF<sub>3</sub> groups in PVdF–HFP, which have affinity for positively charged species of inorganic salts, plasticizers and ionic liquids. It is well–known that a polymer can form dative or coordinate bonds with the cations of inorganic salt(s) [Gray, 1997]. Electronegatively–charged atoms can donate its electron to the positively–charged cations from salt to form a new polymer electrolyte complex. In this work, the oxygen (O) atoms in PEMA and fluorine (F) atoms in PVdF–HFP have negatively charged electron pairs that can coordinate with the positively charged Li<sup>+</sup> ions from LiTf salt, partially positively charged carbon (C) atom of the carbonyl (C=O) group belonging to EC and PC, as well as the imidazolium ions (BMI<sup>+</sup>) of BMII and BMITf.

Before we study the blending between PEMA and PVdF–HFP, and the resultant complexation with LiTf, EC, PC, BMII and BMITf, it is useful to understand the interactions that occur within each polymer. In PEMA, the polar C=O and C–O–C<sub>2</sub>H<sub>5</sub> groups contains C atoms which are partially positively charged, and negatively charged O atoms; PVdF–HFP contains polar C–F groups with the C atom being partially positively charged and the F atoms which are partially negatively charged. Attractive forces exist between the polymer chains contained in each polymer. Intermolecular interactions hold polymer chains together to form a macromolecule, and are also formed between two or more polymers in the formation of polymer blends [Chiu et al., 2007].

Hydrogen bonds are usually formed by F–H, O–H, N–H groups with neighbouring polymer chains. Since those groups do not exist in PEMA and PVdF–HFP, only Van der Waals forces, which are weaker than hydrogen (H) bonds, are considered. Intermolecular interactions occur due to the electrostatic interactions between permanent dipoles in molecules. Hence, intermolecular interactions can occur between the partially negative–charged (labeled as  $\delta$ –) O atoms in C=O and C–O–C<sub>2</sub>H<sub>5</sub> groups with the partially positive–charged (labeled as  $\delta$ +) C atom in neighbouring C=O groups in PEMA to form C····O interactions as shown in Figure 4.4 (a). In PVdF–HFP, the partially negative–charged F atoms in CF<sub>3</sub> groups can form intermolecular interactions with neighbouring partially positive–charged C atom of the group in CF<sub>3</sub> groups to form C····F interactions, Figure 4.4 (b).

The blending between PEMA and PVdF–HFP in the weight ratio of 70:30 to form S–0 sample was investigated by FTIR and TGA to determine the changes in the vibrational, structural and thermal characteristics of the polymers and S–0. In order to form a polymer blend, polymers interact with one another to form intermolecular interactions. If PEMA and PVdF–HFP have interacted with each other to form a blend, the IR spectrum of PEMA/PVdF–HFP blend film will show changes in the position, intensity and shape of the IR bands from the original characteristic bands of both polymers. New bands may form and some original bands may disappear. If PEMA and PVdF–HFP are not suitable to form a blend with each other, the IR spectrum of PEMA/PVdF–HFP blend film will show the original vibrational bands of both PEMA and PVdF–HFP. Table 4.3 lists the comparison between IR bands of individual PEMA and PVdF–HFP with the bands in S–0. Shifting of the  $v_a(COC)$ , v(CO) of –COO– and v(CO) of –OC<sub>2</sub>H<sub>5</sub> group of PEMA indicates that the C–O group in PEMA has undergone interaction with PVdF–HFP. The  $v_a(CF_2)$  and the bands due to the  $\alpha$ –phase and amorphous region of PVdF–HFP at 984 and 885 cm<sup>-1</sup> respectively are due to the interaction of PVdF–HFP with PEMA. This indicates that intermolecular forces form between the O atom of C–O group in PEMA and C atoms in CF<sub>3</sub> group of PVdF–HFP, and also between the F atom of CF<sub>3</sub> group in PVdF–HFP and C atom of C=O group in PEMA, which shows the miscibility between the two polymers to form a polymer blend. The schematic diagram of the intermolecular interactions that take place between PEMA and PVdF–HFP in S–0 blend sample is depicted in Figure 4.4 (c).

Results from TGA analysis depicted in Figure 6.1 and Table 6.1 show increased  $T_{\rm d}$  of the three decomposition stages I, II and III of PEMA from 229 to 268 °C, 264 to 328 °C, and 344 to 413 °C, respectively. The increased thermal stability of PEMA could be induced by the interaction between the fluorine atoms in PVdF-HFP with carbon atoms in PEMA through intermolecular interactions to form a polymer blend; the intermolecular interaction between PEMA and PVdF-HFP could have increased the thermal stability of the former polymer. Improved thermal stability of polymer blend system was also achieved by Wu and co-workers (2009) who obtained higher  $T_d$  of  $poly(3-\{2-[2-(2-hydroxyethoxy) ethoxy] ethoxy\}methyl-3'-methyloxetane (PHEMO)$ from 365 °C to about 408 °C when blended with PVdF-HFP. Hence, the presence of PVdF-HFP increased the thermal stability of PEMA in the PEMA/PVdF-HFP blend system. High fluorine-containing polymers contain strong C-F bonds which are involved in intermolecular interactions between carbon and fluorine atoms within PVdF–HFP chains [Montermoso, 1961; Cooper, 1968; Schmiegel and Logothetis, 1984]. This can explain the unchanged high  $T_d$  of PVdF–HFP at 446.6 °C even after being blended with PEMA.

The intermolecular interactions between PVdF–HFP and PEMA as depicted in Figure 4.4 can decrease the intermolecular forces between PVdF–HFP chains, thus lowering the crystallinity imposed by PVdF–HFP in the polymer blend. The schematic diagram of the polymer chains of PEMA and PVdF–HFP in the resultant S–0 sample is shown in Figure 4.4 (c).

After the incorporation of various LiTf content into PEMA/PVdF–HFP (70:30) blend, it is crucial to study the vibrational changes that are evidences that complexation has occurred between the LiTf and the polymer blend. As coordination of Li<sup>+</sup> ions is expected to occur at the O atoms in the C=O and C–O–C<sub>2</sub>H<sub>5</sub> groups of PEMA and at the F atoms in the CF<sub>2</sub> group of PVdF–HFP, the v(C=O),  $v_a$ (COC), v(CO) of –CO– group and v(CO) of –C<sub>2</sub>H<sub>5</sub> group of PEMA and the  $v_a$ (CF<sub>2</sub>) of PVdF–HFP were investigated.

As shown in Figure 4.4 (c), intermolecular interactions occur between the O atoms of PEMA and partially positive–charged carbon atoms of PVdF–HFP, and between the F atoms in CF<sub>3</sub> group of PVdF–HFP and partially positive–charged carbon atoms in PEMA. When LiTf salt is added into PEMA/PVdF–HFP blend system, the positively charged Li<sup>+</sup> ions in LiTf will be attracted to the negatively–charged O atoms in PEMA and F atoms in PVdF–HFP. The interactions that form between Li<sup>+</sup> ions with O atoms in PEMA and F atoms in PVdF–HFP. The interactions that form between Li<sup>+</sup> ions with O atoms in PEMA and F atoms in PVdF–HFP are known as coordinate bonds. When Li<sup>+</sup> ions are coordinated to the C=O and C–O–C groups of PEMA, C=O····Li<sup>+</sup> and C–O····Li<sup>+</sup> interactions occur, which caused some intermolecular forces between PEMA and PVdF–HFP to break. The same phenomenon is also expected to occur when Li<sup>+</sup> ions coordinate to F atoms in PVdF–HFP. Besides breaking intermolecular interactions that occur

within PEMA and PVdF–HFP may also be disrupted to create coordination sites for Li<sup>+</sup> ions.

Figures 4.5 and 4.6 show shifting of the v(C=O) and  $v_a(COC)$  band, respectively which indicates that Li<sup>+</sup> ions can occur at the O atoms in both the C=O and the C–O–C groups of PEMA. So, it is of our interest to investigate which oxygen is more preferred for coordination with Li<sup>+</sup> ions. Figure 4.5 (d) shows the v(C=O) band of PEMA with increased intensity but did not show significant wavenumber shift from 1722 cm<sup>-1</sup> upon the addition of lithium salt while the  $v_a(COC)$  band demonstrated a significant shift (+ $\Delta \approx 10$  cm<sup>-1</sup>). This suggests that Li<sup>+</sup>...O interaction tends to occur at the C–O group at a larger extent. Li<sup>+</sup> ions coordinate at the oxygen atom located at the C–O–C group rather than at the C=O group of PEMA, as shown in both PEMA/PVdF–HFP–LiTf and 70 wt.% PEMA–30 wt.% LiTf samples Figure 4.5 (d) and (f), respectively.

Ramesh and co–workers (2007) also reported downshift of v(C=O) band of PMMA from 1732 to 1726 cm<sup>-1</sup> and upshift of the  $v_a(COC)$  band from 1150 to 1168 cm<sup>-1</sup> in poly(vinyl chloride) (PVC)/poly(methyl methacrylate) (PMMA)–LiTf complexes, which were attributed to the interaction between Li<sup>+</sup> and the oxygen atoms in PMMA. The larger IR wavenumber shift was obtained for the C–O–C bond (18 cm<sup>-1</sup>) as compared to the C=O group (6 cm<sup>-1</sup>). Sim and co–workers (2010) reported that FTIR studies showed the addition of lithium perchlorate (LiClO<sub>4</sub>) salt into polyacrylate (PAc)/poly(ethylene oxide) (PEO) blend system shifted the ester C–O band, and not the C=O band of the PAc. Although larger IR shift is observed for bands due to C–O–C group as compared to C=O group, none of the researchers have explained this observation.

Complexation of Li<sup>+</sup> ions onto the polar atoms of PEMA and PVdF–HFP could be evidenced from TGA studies. TGA results from Table 7.2 shows the decrease in the  $T_d$  of PEMA and PVdF–HFP upon incorporation of LiTf into PEMA/PVdF–HFP blend:  $T_d$  of stage I of PEMA was reduced from 268 to 256–260 °C while PVdF–HFP decomposed at lower temperatures at 411–418 °C in the presence of LiTf as compared to 447 °C in S–0 sample. The disruption of intermolecular forces between PEMA and PVdF–HFP caused the polymers to degrade at reduced temperatures. Wu and co– workers (2009) also reported on the decrease in the  $T_d$  on PHEMO/PVdF–HFP blend polymer electrolytes with addition of lithium trifluoromethanesulfonimide salt, which was attributed to the coordination of Li<sup>+</sup> ions on the ether oxygen of PHEMO.

As for the plasticized polymer electrolyte systems, there are mixed reviews contributed from researchers as to whether interactions between plasticizers i.e. EC or PC do occur with polymer–salt complexes in polymer electrolyte systems. EC and PC have the tendency to interact via the carbonyl group (C=O) with the polar groups of polymer(s) [Choi et al., 2005; Starkey and Frech, 1997] and also cations from inorganic salts [Osman and Arof, 2003; Cazzanelli et al., 1997; Wang et al., 1996]. The interaction occurs at the partially positively charged carbon (C) atom of the C=O group in the plasticizers. Good interaction between the plasticizer and polymer blend–salt is desired as it can facilitate the transport of free ions in the polymer electrolytes. As both Li<sup>+</sup> ions and the C atom of EC and PC molecules can coordinate to the oxygen atom at the C=O group of PEMA, the coordination of either one species, for example EC or PC will lessen the coordination of Li<sup>+</sup> ions onto the polymer. Incorporation of EC or PC into 70 wt.% [PEMA/PVdF–HFP]–30 wt.% LiTf composition downshifted the v(C=O) of PEMA (as illustrated in Figure 4.14 and 4.22). Since the PEMA····EC (Figure 4.14 (g)) and PEMA····PC (Figure 4.22 (g)) interactions tend to shift the position of the

v(C=O) of PEMA to higher wavenumbers, the downshift of the IR mode in EC– and PC–based electrolytes are due to enhanced coordination of Li<sup>+</sup> ions and not the plasticizer onto the O atom of C=O of PEMA to form Li<sup>+</sup>····O=C bonds. The oxygen atom of the C=O group of PEMA prefers to coordinate with the Li<sup>+</sup> ions rather than with the partially positive carbon atom of EC or PC could be due to Li<sup>+</sup> ions being smaller sized and more electropositive than the plasticizers which are more bulky and therefore Li<sup>+</sup> can reach the coordination site more easily. Li<sup>+</sup> ions from LiTf also coordinated to the partially negatively charged O atoms in EC or PC, as shown in Figures 4.14 (k) and 4.23, respectively. The *v*(C=O) modes belonging to EC or PC exhibit the largest shift in EC–6 and PC–6 samples which indicate that interaction of the respective plasticizer occurred to a large extent in the polymer blend–salt complexes. The *v*(C=O) mode of the plasticizer in PC–6 recorded a shift of 15 cm<sup>-1</sup> (Figure 4.22 (d)) while EC–6 shifted 17 cm<sup>-1</sup> (Figure 4.14 (d)).

In contrast to organic solvents, which in this project are EC and PC, ionic liquids, namely BMII and BMITf do not possess free electron pairs which can solvate the cation, Li<sup>+</sup> from LiTf, other than those on the anion. There are reports by researchers that imidazolium–based ionic liquids can interact with polar groups present in polymers through the imidazolium cation, BMI<sup>+</sup> [Li et al., 2009]. Both BMII and BMITf were shown to interact with the polymers in PEMA/PVdF–HFP–LiTf through the BMI<sup>+</sup> ion. The positively charged carbon atoms at the C(2), C(4) and C(5) positions of the BMI<sup>+</sup> ion are electrostatically attracted to the O atoms in PEMA and F atoms in PVdF–HFP. BMI<sup>+</sup> cations from BMII and BMITf share the same coordinate sites as Li<sup>+</sup> cations from salt. Hence, when more BMI<sup>+</sup> cations from the ionic liquid coordinate to the polar atoms in PEMA and PVdF–HFP, there will be less empty coordination sites for Li<sup>+</sup>. Reduced coordination of Li<sup>+</sup> onto the polymers will cause the tendency of Li<sup>+</sup> ions to associate

with Tf<sup>-</sup> ions to form ion pairs and ion aggregates, hence resulting in high amount of undissociated LiTf as shown in Figures 4.38 and 4.45 for BMII and BMITf–based electrolyte samples. As the content of the ionic liquid is increased, the complexation of BMI<sup>+</sup> onto PEMA and PVdF–HFP decreased which paves way for the coordination of Li<sup>+</sup> onto the polar atoms of the polymers. Upon reduced coordination of BMI<sup>+</sup> of the ionic liquid onto PEMA and PVdF–HFP, more ion pairs and ion aggregates of triflate anions can dissociate into free ions when positively charged Li<sup>+</sup> ions are coordinated to the polar atoms of the polymers. Figure 4.45 shows the decrease in the amount of ion pairs and ion aggregates above 30 and 40 wt.% BMITf. The amount of free ions were observed to increase upon addition of BMITf up to 60 wt.% explains the rise in conductivity as shown in Figure 5.24. As for BMII system, Figure 4.38 shows the decrease in the amount of ion pairs from 5 to 12.5 wt.%, after which it increased.

In BMII and BMITf systems, PVdF–HFP polymer decomposes at lower temperatures than its original  $T_d$  at 412 °C when added with the respective ionic liquid (Table 6.6 and 6.7). Several researchers studying on IL–added PVdF–HFP also reported reduced  $T_d$  of the polymer when incorporated with ionic liquid [Suleman et al., 2013; Nath and Kumar, 2013]. Nath and Kumar (2013) reported that the addition of 1–butyl–3–methylimidazolium bromide (BMIBr) into PVdF–HFP reduced the  $T_d$  of the electrolyte system which may be attributed to the complexation of [BMIM]<sup>+</sup> cations of IL with the polymer that destabilizes the C–H bonds of the polymer. This will lead to increase in the amorphousness of the system, and amorphous materials have lower decomposition temperature compared with crystalline materials.

Although EC has boiling point of 248 °C [Xu, 2004], the thermal decomposition of EC was observed to occur at 89.3 °C as shown in Figure 6.3. The boiling point of PC

is recorded at 242 °C. However, similar to EC, the  $T_d$  of PC starts at lower temperature of 94 °C, Figure 6.4. Decomposition of PVdF–HFP–based GPEs containing PC and DEC was also observed to occur at low temperature at about 80 °C despite the high boiling point of PC and DEC (126 °C) as reported by Saikia and co–workers (2008). TGA studies conducted by Kim and co–workers (2006) in PVdF–HFP–based system also showed that PC vaporized around 80 °C. Ye et al. (2007) also observed the decomposition of EC to occur at a lower temperature around 120 °C.

TGA results listed in Table 6.6 show significant reduction in  $T_d$  of PEMA with increasing BMII content from 281°C in BI-5 sample to 202 °C in BI-20 sample. As compared to other polymer electrolyte systems, BMII-added polymer electrolytes exhibit the lowest  $T_{d}$ . Ionic liquids containing weakly nucleophilic anions are most stable to high temperature decomposition [Ohno and Yoshizawa, 2002; Bonhote et al., 1996]. As compared to BMII, more alkenes are formed rather than haloalkanes due to strong C-F bonds in Tf<sup>-</sup> anion. This explains the lowest thermal stability of the BMII system as compared to other systems. Papaiconomou et al. (2010) also reported that different pyridinium-based ionic liquids which contain the iodide anion decomposed at lower temperatures as compared to those containing the triflate anion. This is because decomposition of ionic liquids is influenced by the nature of the anion. The stability of the ionic liquid is inversely proportional to the tendency to form a stable alkyl-X (where X = F, Cl, Br, I, etc) species. The large  $T_d$  difference of 79 °C can be attributed to the dominant effect of nucleophilic attack on the imidazolium cation by iodide anion [Chan et al., 1977]. On the other hand, the  $T_d$  of BMITf–based electrolytes were observed to increase from 275 °C up to 294 °C upon addition of 60 wt.% of the ionic liquid. Increased thermal stability of polymer electrolytes upon the addition of ionic liquid has been reported for SPEEK/BMImBF<sub>4</sub> system by Yi and co-workers (2011). The phenomenon was attributed to the complexation between the sulfonic acid groups of the polymer and the imidazolium cations which increased the decomposition temperature of SPEEK. In contrast to EC and PC plasticizers, the ILs have an advantage over organic solvents in thermal stability whereby they rarely evaporate before their decomposition points due to their low vapour pressures which are similar to solid salts [Jenkins, 2011]. The  $T_d$  of BMII and BMITf were recorded at 247 °C and 377 °C, respectively (Tables 6.6 and 6.7).

Ion transport properties are dependent on various factors such the amount or concentration of salt and its degree of dissociation, ion pairing and ion aggregation; the dielectric constant of polymer host and/or plasticizer(s) and the mobility of polymer chains and/or ions [Dillip et al., 2008]. Equation (2.1) shows the relationship between mobility, carrier concentration and the ionic conductivity. Using the amount of PEMA, PVdF–HFP, LiTf and additives i.e. EC, PC, BMII or BMITf and % area of free ions obtained from FTIR deconvolution studies, the carrier concentration or number density (n), mobility ( $\mu$ ) and diffusion coefficient (D) of the mobile ions for every system were estimated.

Although a drop in the % area of free ions was observed at 20 wt.% LiTf as obtained from the deconvolution of the  $v_s(SO_3)$  band shown in Figure 4.12, the *n* still increased in that sample as more LiTf amount is present in the S–20 sample, Figure 5.5. The drop of *n* in S–40 can be explained by the decrease in the amount of free ions caused by the combination of Li<sup>+</sup> and Tf<sup>-</sup> ions to form more ion pairs and ion aggregates in Figure 4.12. This is due to the increasing strength of Li<sup>+</sup>....CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> interactions between the Li<sup>+</sup> and CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> which tend to occur as the concentration of salt increases. It is widely accepted that ions of salt are separated by a shorter distance and tend to

combine to form larger ionic species as the concentration of salt is increased [Rey et al., 1998]. With increasing amount of ion pairs and the formation of ion aggregates in S–40, the mobility of the charge carriers is still increased. This indicates that ion pairs can play a role to enhance the transport of ions despite its larger size. Comparing with conductivity studies, the  $\sigma$  of PEMA/PVdF–HFP–LiTf system was observed to increase with addition of LiTf until 40 wt.% as shown in Figure 5.2. This shows that both the *n* and  $\mu$  influence the enhancement of  $\sigma$  upon addition of LiTf up to 30 wt.%. It is well known that viscosity generally increases with salt content [Azeez and Fedkiw, 2010]. This is because the ionic species of the salt can act as crosslinks to coordination sites on adjacent polymer molecules, thus restricting the mobility of polymer chains [Lorimer, 1993]. However, in this work, the increasing  $\mu$  up to 40 wt.% LiTf shows that the viscosity is still not a dominant factor within the salt content studied in this system and does not impede the mobility of polymer–salt samples. In S–40, the  $\mu$  plays the dominant factor which allows more ions to be transported more easily in the PE film, hence increasing its conductivity value.

Usually, larger number of free ions will produce higher ionic conductivity, however this is not the case for the EC–based system. According to Figure 4.20, the % area of ion pairs follows the same trend of the variation of  $\mu$ , Figure 5.11. The ionic conductivity behavior also followed that of the ion pairs and mobility whereby the highest conductivity of  $1.05 \times 10^{-4}$  S cm<sup>-1</sup> was found at 6 wt.% EC, Table 5.4. This indicates that ion pairs can play a role in enhancing the mobility of the charge carriers, which consequently increased the ionic conductivity in this system. Although EC exhibits high dielectric constant ( $\varepsilon = 89.6$ ), the lower % area of free ions as compared to ion pairs in all EC–added samples (Figure 4.20) showed that the dielectric constant does not play a dominant role in determining the conductivity behavior. From Figure 5.11, above 6 wt.% EC, a drop of  $\mu$  and hence its  $\sigma$  occurred despite the increasing % area of free ions as observed in Figure 4.20. The reduction of the  $\mu$  above 6 wt.% could also be caused by the increasing viscosity of EC which caused difficulty for the ions to be transported from one coordination site to another. This indicates the dominant factor of viscosity over the free ion effect in influencing the conductivity of this system at higher EC content. Azeez and Fedkiw (2010) reported the reduction in the ionic conductivity of LiBOB solution after reaching a maximum concentration of EC which was attributed to the increasing viscosity of the system. On the other hand, the minimum *n* value obtained at 6 wt.% EC can be explained by the least amount of free ions due to the combination of Li<sup>+</sup> and Tf<sup>-</sup> ions to form ion pairs; Figure 4.20 shows the maximum amount of ion pairs observed at 6 wt.% EC.

As the ionic conductivity of EC–based system follows the trend of the ion pairs (Figure 4.20), it is suggested that the ion pairs play a role in the transport of Li<sup>+</sup> in the polymer electrolytes. From EIS analysis in section 5.3.1, the temperature dependent studies of the polymer electrolyte incorporated with EC was found to obey the VTF rule. Besides the conventional cation hopping within a polymer chain and between two different polymer chains assisted by polymer segmental motion, Gray (1997) mentioned that cation motion can also occur via ion clusters as shown in Figure 2.6 (c) and (d). Therefore, it is suggested that the ion pairs present in EC–based polymer electrolytes facilitates the movement of Li<sup>+</sup> from one coordination site to another in PEMA, PVdF–HFP and EC via the formation of ionic clusters. Figure 7.1 shows the possible ion transport mechanism of Li<sup>+</sup> in PEMA/PVdF–HFP–LiTf–EC system. With the assistance of polymeric segmental motion, the ionic cluster may move by itself or act as transient center for Li<sup>+</sup> ions. This shows the active role of ion pairs in increasing the ionic conductivities of EC–based system.



Figure 7.1 Possible ion transport mechanism in PEMA/PVdF-HFP-LiTf-EC system involving the formation of ionic clusters

The deconvolution of the  $v_s(SO_3)$  band of LiTf in Figure 4.29 shows that the free ions follow the trend of the ionic conductivity whereby both % area of free ions and  $\sigma$ were highest at 6 wt.% PC with  $\sigma = 1.46 \times 10^{-6}$  S cm<sup>-1</sup> (Table 5.6). The drop of ionic conductivity above 6 wt.% PC could be explained by the reduced *n* and  $\mu$  due to ion association. This indicates that the ionic conductivity is influenced primarily by the amount of free ions in this system. As PC has a lower dielectric constant ( $\varepsilon = 64.4$ ) as compared to EC, it is suggested that the dielectric constant is not the reason for the high % area of free ions as shown in Figure 4.29. Since the ionic conductivity trend of PC–based samples are directly proportional to the amount of free ions, it is suggested that the formation of ion clusters from ion pairs to facilitate ion transport in the electrolytes did not occur or occurred to a much lower extent as compared to EC–based system.

For the BMII–added system, the increase in the % area of ion pairs due to the LiTf salt at 15 wt.% and above of BMII and the formation of ion aggregates in both BI– 17.5 and BI–20 as shown in Figure 4.38 could explain the drop of both *n* and  $\mu$  at high BMII content in Figure 5.22. The *n* decreased because more BMI<sup>+</sup> cations are coordinated to the polymer blend, as evidenced in section 4.4.1.1. This prevents Li<sup>+</sup> from dissociating from ion pairs, and could even caused the combination of free Li<sup>+</sup> and Tf<sup>-</sup> with ion pairs to form ion aggregates. The drop in  $\mu$  at high BMII content is due to the presence of larger sized ion pairs and ion aggregates which blocks the transport of Li<sup>+</sup> ions in the PE film. Another reason for the reduction of  $\mu$  above 15 wt.% BMII could be due to the increasing viscosity of the system with further addition of the IL.

The increase in *n* and  $\mu$  for this system with BMITf content in Figure 5.27 could be explained by the decreasing amount of ion pairs and increasing amount of free ions with BMITf content, Figure 4.45. Dissociation of ion pairs from 10 wt.% BMITf and subsequently, the ion aggregates above 40 wt.% BMITf to form free Li<sup>+</sup> and Tf<sup>-</sup> ions facilitates the migration of charge carriers in the PE film. As observed in the conductivity studies of the system in Figure 5.24, the  $\sigma$  increased upon addition of BMITf up to 60 wt.%. Hence, the conductivity behavior of this system can be attributed to the mobility of the charge carriers since the number density only changed slightly from the order of  $10^{22}$  to  $10^{23}$  cm<sup>-3</sup>. Comparing BMII– and BMITf–containing systems, the ionic liquid range which could be employed to produce increased ionic conductivity for BMITf system at 60 wt.% is higher than that of BMII system at 12.5 wt.%. The viscosity of BMII (963 cP at 25 °C) [Kubo et al., 2002] is much higher than BMITf (60 cP at 20 °C) [Bonhote et al., 1996], which could be the reason why the ionic conductivity dropped after a maximum at 12.5 wt.% BMII due to lower mobility, but continually increased up to 60 wt.% of BMITf.

All polymer electrolyte systems namely PEMA/PVdF-HFP-LiTf, and the systems of 70 wt.% [PEMA/PVdF-HFP]-30 wt.% LiTf incorporated with EC, PC, BMII and BMITf were found to exhibit conductivities which increased with temperature up to 353 K as observed in Figures 5.4, 5.9, 5.15, 5.21, 5.26 respectively. Increase in conductivity with temperature is a common phenomenon of polymer electrolytes and is due to thermally-assisted ion mobility [Ali et al., 2013]. The plots of log  $\sigma$  versus 1000/T for EC and PC systems exhibited curvatures which indicates non-Arrhenian and exhibit the Vogel-Tammann-Fulcher (VTF) behavior. The VTF behavior is attributed to the amorphous component of the polymeric systems [Cohen and Turnbull, 1959; Cohen and Grest, 1980; Bohnke et al., 1993] and has been reported by many researches [Al-Kahlout et al., 2010; Agnihotry et al., 2000; Deepa et al., 2002; M. Deepa, N. Sharma, Agnihotry et al., 2002; Bhide and Hariharan, 2007; Pennarun and Jannasch, 2005]. Ali et al. (2006) also observed VTF behaviour for EC and PC added MG30 samples. The increase in the conductivity with temperature is due to hopping mechanism between coordinating sites, local structural relaxations and polymer segmental motions [Jaipal Reddy et al., 1999]. As the temperature is increased, the polymer chains acquire faster internal modes whereby the bond rotations produce segmental motion and favours inter- and intrachain ion movements [Baskaram et al., 2004]. The increased vibrational energy of the polymer segment pushes against the

hydrostatic pressure imposed by its neighbouring atoms and creates a small amount of space known as free volume. Hence, the free volume around the polymer chain causes the mobility of ions and polymer segments to increase. Consequently, the ionic conductivity is increased.

The estimation of the  $T_0$  values of EC- and PC-based electrolytes allows us to correlate to the glass transition temperature,  $T_g$  of the samples since  $T_0$  values are usually taken to be 50 K lower than  $T_g$  [Wintersgill and Fontanella, 1987]. From Table 5.4, the  $T_0$  values obtained for the EC-added system was found to decrease from 255 K in EC-2 to 244 K in EC-6, after which the  $T_0$  increased to 258 K in EC-10. The trend of  $T_0$  values were observed to follow the conductivity trend whereby EC-6 has the highest ionic conductivity of the system with  $\sigma = 1.05 \times 10^{-4} \text{ S cm}^{-1}$  and the lowest  $T_0$ value. This suggests that the interaction of EC with the polymer blend-salt complex as described in FTIR analysis helps to separate the polymer chain by disrupting the intermolecular interactions within PEMA and PVdF-HFP. This in turn increases the free volume of the polymer and enhances the polymer segmental motion which facilitates ion transport from one coordination site to another. For PC-based system, the  $T_0$  value also decreases from 271 K in PC-2 to 264 K in PC-6. The  $T_0$  value increased in PC-8 and PC-10 samples, Table 5.6. The  $T_0$  trend of PC-based system correlates with the ionic conductivity trend whereby the best conducting sample is PC-6 with  $\sigma$  =  $1.46 \times 10^{-6}$  S cm<sup>-1</sup> exhibits the lowest  $T_0$  value. This indicates that PC-6 has the highest chain flexibility due to increased free volume and enhanced polymer segmental motion, which aids in the transport of ions in the electrolyte. The polymer-salt complex added with EC exhibit higher conductivity over their PC containing counterparts. Maximum ionic conductivity was observed at 6 wt. % at  $1.05 \times 10^{-4}$  S cm<sup>-1</sup> and  $1.46 \times 10^{-6}$  S cm<sup>-1</sup> for the EC and PC added electrolytes, respectively. Accordingly, the  $T_0$  values of EC- based electrolytes (Table 5.4) were found to be lower as compared to PC–added samples (Table 5.6). Hence, the  $T_g$  value of EC–6 sample is expected to be 20 K lower than PC–6. This big difference in  $T_g$  may also account for the large difference in ionic conductivity between EC and PC containing samples.

For PEMA/PVdF-HFP-LiTf, PEMA/PVdF-HFP-LiTf-BMII the and PEMA/PVdF-HFP-LiTf-BMITf polymer electrolyte systems, the log  $\sigma$  versus 1000/T plots displayed linearity which indicates that the conductivity-temperature relationship to obey the Arrhenius model. Both the PEMA/PVdF-HFP-LiTf and PEMA/PVdF-HFP-LiTf-BMII systems displayed two linear sections which indicate two different activation energies beyond a phase transition, Figure 5.4 and 5.21. The increase in  $E_{a1}$ with increasing LiTf content could be due to the formation of ion pairs and/or ion aggregates which impedes the hopping of Li<sup>+</sup> from one coordinating site to another. The presence of rubbery amorphous state eases the transport of  $Li^+$  ions hence the lower  $E_{a2}$ with increasing LiTf content. Decreasing  $E_{a2}$  helps to lower the energy barrier that is needed for Li<sup>+</sup> ions to hop from one coordination site to another, and thus increases the ionic conductivity value from S-10 to S-40, Table 5.2. For BMII-based system, the trend of both  $E_{a1}$  and  $E_{a2}$  values are opposite and could correlate well to the ionic conductivity trend listed in Table 5.8. The smallest  $E_a$  value is obtained for BI-12.5 which exhibits the highest ionic conductivity of  $4.86 \times 10^{-5}$  S cm<sup>-1</sup>. The Li<sup>+</sup> ions in this sample required the lowest energy needed for transportation. For BMITf-based system, the  $E_a$  values obtained from a single linear plot decreases with BMITf content. This correlates well to the ionic conductivity trend which is found to be inversely related to the activation energy. The best conducting BT-60 sample exhibits the lowest  $E_a$  of 0.15 eV.

Among all polymer electrolyte systems prepared in this work, EC–6 sample is the best conducting electrolyte with its maximum conductivity achieving the order of  $10^{-4}$  S cm<sup>-1</sup>. Fabrication of an electrochromic device utilizing EC–6 sample as the Li<sup>+</sup> ion source has been successful and reported in literature [Sim et al., 2012a].