3.0 RESULTS AND DISCUSSION I - ELECTRICAL PROPERTIES

3.1 AC-Impedance Spectroscopy

3.1.1 Effect of mixed salt systems

Organic polymers are generally insulators. They show very low room temperature ionic conductivity (10^{-12} - 10^{-18} S/cm) due to some contaminants such as solvents or ions. Ionic conduction in polymers is considered to be caused by the diffusion of the ion through their free volumes [120-121]. Many polymers dissolve salts to form mixtures which support ionic conductivity. The salt component must have a relatively low lattice energy and may form crystalline polymer-salt complexes at high salt concentrations [85].

The general formula of the polymer electrolytes that were prepared is [x $LiBF_4$ + (1-x)$LiCF_3SO_3$][PVC] where x ranges from 0 to 1 mole fraction. Figure 3.1 to 3.11 shows the complex impedance plots for these samples from which the bulk impedance values were extracted and used to calculate the electrical conductivity values.

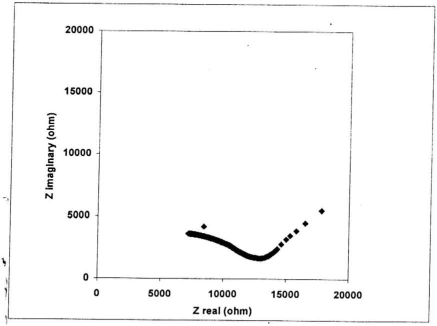

Figure 3.1 : Impedance spectrum of [x $LiBF_4$ + (1-x)$LiCF_3SO_3$][PVC] complex with x=0.

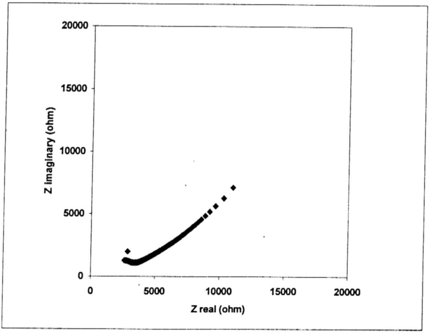

Figure 3.2 : Impedance spectrum of [x $LiBF_4$ + (1-x)$LiCF_3SO_3$][PVC] complex with x=0.1.

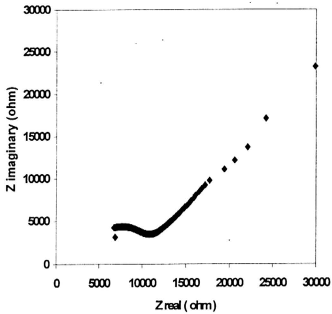

Figure 3.3 : Impedance spectrum of [x $LiBF_4$ + (1-x)$LiCF_3SO_3$][PVC] complex with x=0.2.

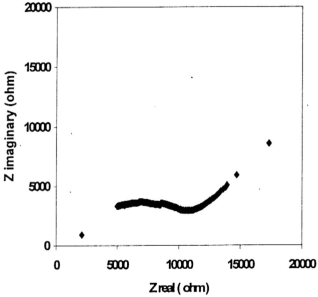

Figure 3.4 : Impedance spectrum of [x $LiBF_4$ + (1-x)$LiCF_3SO_3$][PVC] complex with x=0.3.

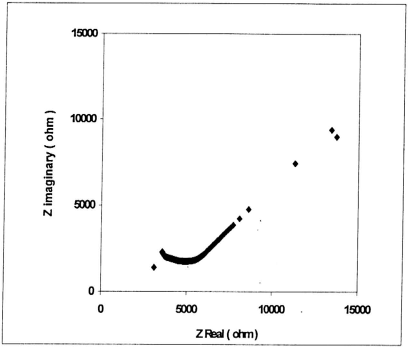

Figure 3.5 : Impedance spectrum of [x $LiBF_4$ + (1-x)$LiCF_3SO_3$][PVC] complex with x=0.4.

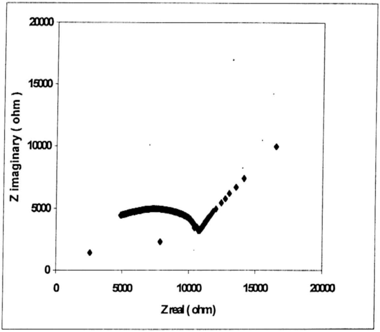

Figure 3.6 : Impedance spectrum of [x $LiBF_4$ + (1-x)$LiCF_3SO_3$][PVC] complex with x=0.5.

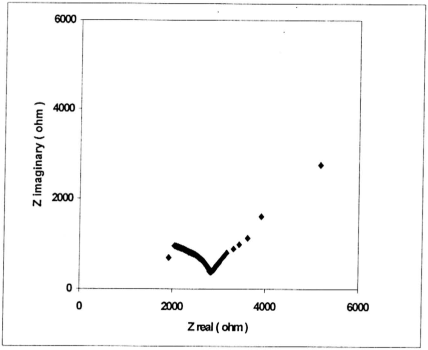

Figure 3.7 : Impedance spectrum of [x $LiBF_4$ + (1-x)$LiCF_3SO_3$][PVC] complex with x=0.6.

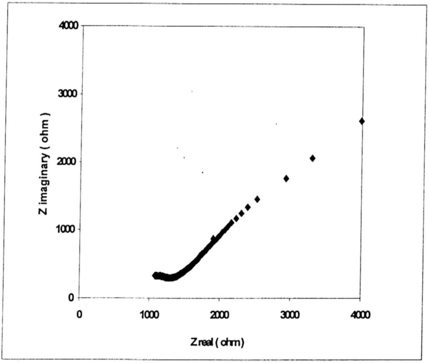

Figure 3.8 : Impedance spectrum of [x $LiBF_4$ + (1-x)$LiCF_3SO_3$][PVC] complex with x=0.7.

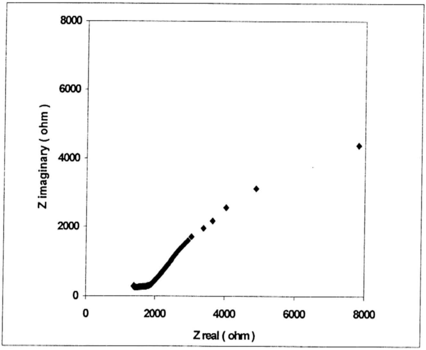

Figure 3.9 : Impedance spectrum of [x $LiBF_4$ + (1-x)$LiCF_3SO_3$][PVC] complex with x=0.8.

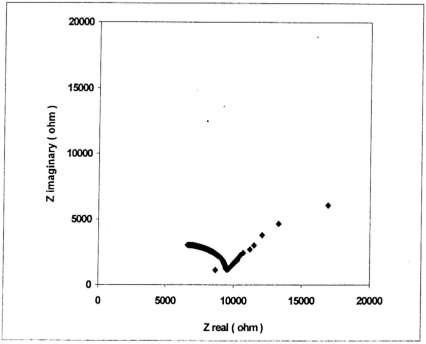

Figure 3.10 : Impedance spectrum of [x $LiBF_4$ + (1-x)$LiCF_3SO_3$][PVC] complex with x=0.9.

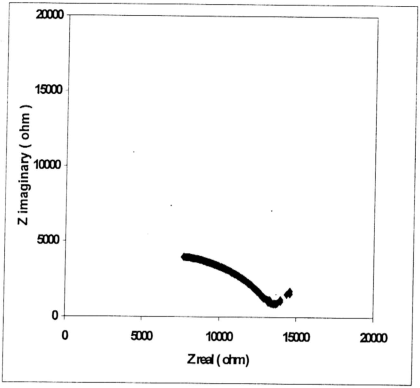

Figure 3.11 : Impedance spectrum of [x $LiBF_4$ + (1-x)$LiCF_3SO_3$][PVC] complex with x=1.0.

The above impedance plots show a typical impedance behaviour being a semicircular portion at high frequency followed by a spike (residual tail) at low frequency. These results suggest that the migration of ions may occur through the free volume of matrix polymer, which can be represented by a resistor. The immobile polymer chains become polarized in the alternating field, which can be represented by a capacitor. The ionic migration and bulk polarization are physically in parallel, and therefore, the portion of the semicircle can be observed at high frequencies [122].

Table 3.1 provides the concentration of the polymer complexes with their name, weight fraction and the resulting ionic conductivity values.

X	Composition	Conductivity (S/cm)	Name of the complex
0	PVC : $LiCF_3SO_3$ (50:50)	1.65×10^{-6}	LT02
0.1	PVC : $LiCF_3SO_3$: $LiBF_4$ (50 : 45 : 5)	1.07×10^{-6}	LT03
0.2	PVC : $LiCF_3SO_3$: $LiBF_4$ (50 : 40 : 10)	2.89×10^{-7}	LT04
0.3	PVC : $LiCF_3SO_3$: $LiBF_4$ (50 : 35 : 15)	6.41×10^{-7}	LT05
0.4	PVC : $LiCF_3SO_3$: $LiBF_4$ (50 : 30 : 20)	2.91×10^{-7}	LT06
0.5	PVC : $LiCF_3SO_3$: $LiBF_4$ (50 : 25 : 25)	2.58×10^{-7}	LT07
0.6	PVC : $LiCF_3SO_3$: $LiBF_4$ (50 : 20 : 30)	2.47×10^{-6}	LT08
0.7	PVC : $LiCF_3SO_3$: $LiBF_4$ (50 : 15 : 35)	5.15×10^{-6}	LT09
0.8	PVC : $LiCF_3SO_3$: $LiBF_4$ (50 : 10 : 40)	2.92×10^{-6}	LT10
0.9	PVC : $LiCF_3SO_3$: $LiBF_4$ (50 : 5 : 45)	1.26×10^{-6}	LT11
1.0	PVC : $LiBF_4$ (50 : 50)	1.04×10^{-6}	LT12

Table 3.1 : Room temperature conductivity of [x $LiBF_4$ + (1-x)$LiCF_3SO_3$][PVC] complex with x ranges from 0 to 1.

Figure 3.12 shows the variation of conductivity as a function of mole fraction of $LiBF_4$ at room temperature. The conductivity of the mixed salt electrolytes are relatively higher than that of either pure salt electrolyte [123-124]. The conductivity plot appears to go through a maximum for the composition of x=0.7 [PVC:$LiCF_3SO_3$:$LiBF_4$ (50 : 25 : 25)]. The conductivity value of $LiCF_3SO_3$ doped PVC is significantly higher than the value obtained for $LiBF_4$ doped PVC. This is because $LiCF_3SO_3$ has a larger anion and lower lattice energy compared to $LiBF_4$. Salts having low lattice energy are generally expected to promote greater dissociation of the salt, thereby providing a higher concentration of ions.

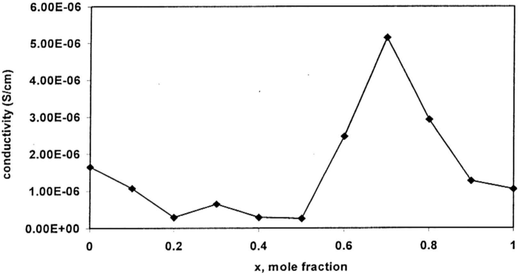

Figure 3.12 : Variation of conductivity as a function of $LiBF_4$ in the [x $LiBF_4$ + (1-x)$LiCF_3SO_3$][PVC] system.

The implications of a mixed anion/cation effect in polymer electrolytes are different from that in glasses. Glasses are basically cationic (Li^+ , Na^+ , K^+ , Ag^+) conductors 'only' while in polymers , both cations (Li^+ , Na^+ , K^+ , Ag^+) and anions ($CF_3SO_3^-$, BF_4^-) are simultaneously mobile [125-126]. In terms of the conduction mechanism, these data can be divided into two regions, one corresponding to $x < 0.7$ and the other corresponding to $x > 0.7$. It would appear that in the $x < 0.7$ region, the segmental motion of the polymer chain and the number of charge carriers are controlled by the $LiCF_3SO_3$ salt content whereas the $LiBF_4$ salt content controls the conduction process in the sample for which $x > 0.7$. According to B.V.R.Chowdari *et.al.*[127], it is possible that the two competing factors, segmental mobility which affects the mobility of charge carriers and the mobile charge carrier concentration which depends on the nature of inorganic salt and its interaction with the polymer chain, are optimized for the composition $x = 0.7$, resulting in higher conductivity.

From the above studies, it can be clearly observed that there is a possible complexation between the salts and the polymer system. Because of this complexation between the salts and the polymer, the conductivity of the polymer electrolyte changes with different concentration of salt content. The composition with $x = 0.7$, which gives the maximum ionic conductivity from the present study is taken and fixed for further studies.

3.1.2 Effect of Mixed salt and EC

The highest ionic conductivity which has been obtained from the PVC - $LiCF_3SO_3$ - $LiBF_4$ complex is quite low for any particular use in batteries. In order to enhance the ionic conductivity at ambient conditions, .one of the approaches is to incorporate a plasticizer to make the matrix more liquid-like [128].

In the present study, we have employed Ethylene Carbonate (EC) which has a high dielectric constant as the plasticizer. Table 3.2 provides the information regarding the polymer electrolytes composition and the name used for the particular composition.

Composition	Name
PVC : $LiCF_3SO_3$: $LiBF_4$: EC (45 : 13.5 : 31.5 : 10)	EC 1
PVC : $LiCF_3SO_3$: $LiBF_4$: EC (40 : 12 : 28 : 20)	EC 2
PVC : $LiCF_3SO_3$: $LiBF_4$: EC (35 : 10.5 : 24.5 : 30)	EC 3
PVC : $LiCF_3SO_3$: $LiBF_4$: EC (30 : 21 : 9 : 40)	EC 4
PVC : $LiCF_3SO_3$: $LiBF_4$: EC (25 : 7.5 : 17.5 : 50)	EC 5
PVC : $LiCF_3SO_3$: $LiBF_4$: EC (20 : 6 : 14 : 60)	EC 6

Table 3.2 : Polymer electrolyte composition with their name

The complex impedance plots for the above polymer electrolyte complexes are illustrated in Figure 3.13 to 3.18.

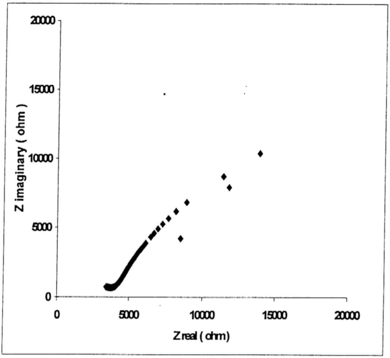

Figure 3.13 : Complex impedance plot for EC 1

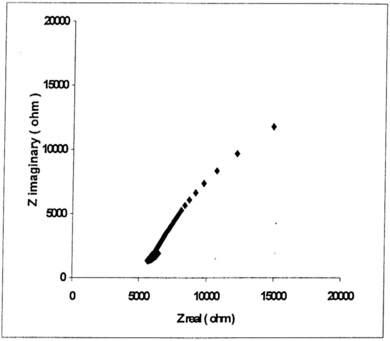

Figure 3.14 : Complex impedance plot for EC 2

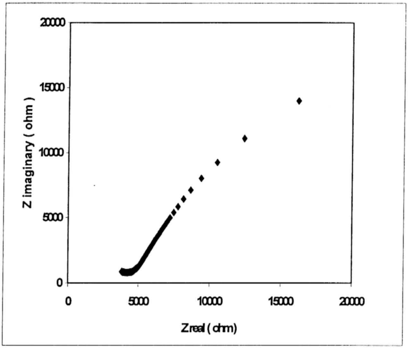

Figure 3.15 : Complex impedance plot for EC 3

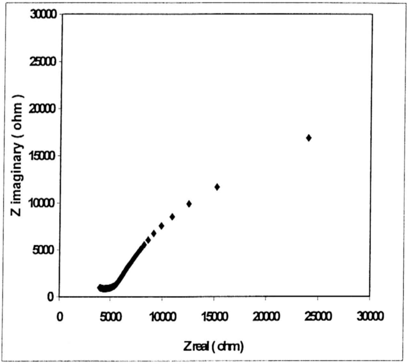

Figure 3.16 : Complex impedance plot for EC 4

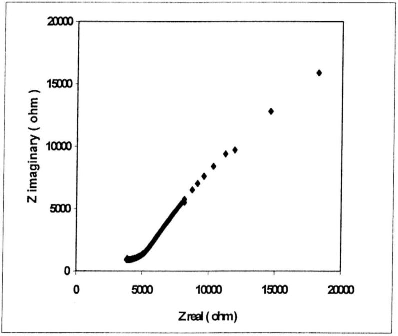

Figure 3.17 : Complex impedance plot for EC 5

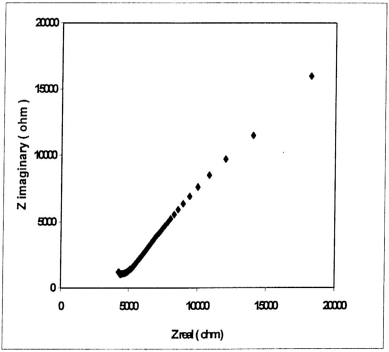

Figure 3.18 : Complex impedance plot for EC 6

The ionic conductivity value for the above complexes are shown in table 3.3. Figure 3.19 presents a variation of the ionic conductivity as a function of EC weight fraction into PVC : $LiCF_3SO_3$: $LiBF_4$ (50 : 15 : 35) system. It is found that, although the conductivity increased, it is still in the order of 10^{-6} S/cm.

Name of the complex	Conductivity (S/cm)
EC 1	5.65×10^{-6}
EC 2	5.71×10^{-6}
EC 3	5.85×10^{-6}
EC 4	6.33×10^{-6}
EC 5	6.25×10^{-6}
EC 6	5.86×10^{-6}

Table 3.3 : Ionic conductivity values and name of polymer electrolytes

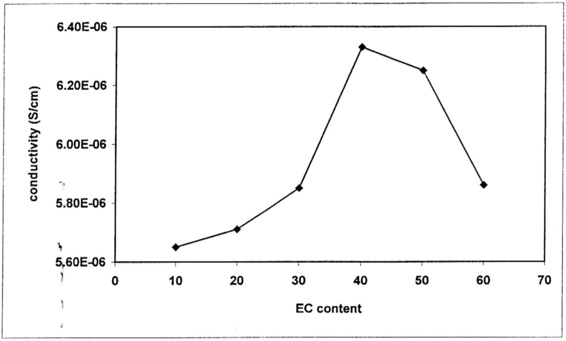

Figure 3.19 : Conductivity of PVC - $LiCF_3SO_3$ - $LiBF_4$ - EC complexes as a function of EC content at 25°C.

The plasticizer, (EC) , itself is amorphous and upon addition to another polymer will increase the amorphous nature of the system and hence the ionic conductivity. However, the addition of more than 40 wt% of EC decreases the electrical conductivity of the polymer. This is attributed to the formation of linkages between the plasticizer itself, thus causing it to crystallize, resulting in the decrease in electrical conductivity [129].

3.1.3 Effect of the γ - irradiation technique

One serious problem encountered with the polymer complexes is that at ambient temperature, the polymer has a tendency to crystallize. Their ionic conductivity is reduced because it has been recognised that the ionic conduction preferentially occurs in the amorphous phase [83]. One of the approaches taken to suppress the crystallinity is by crosslinking, so as to obtain a host polymer consisting mainly of amorphous nature. [65, 130].

In this work, γ -irradiation technique was selected to increase the amorphous nature of the PVC structure while it is in the powder form. The composition of material used in this study is PVC : $LiCF_3SO_3$: $LiBF_4$:EC (30 : 9 : 21 : 40), which gave the highest ionic conductivity in previous work.

γ -irradiation technique is simple and feasible if an x-ray source is available. Different dose rates were given each month and the calculation of the decay is as follows [131]:

Dose rate for January 1997, $D_o = 0.45131$ Gys $^{-1}$

$$\text{Decay constant, } \lambda = \frac{\ln 2}{T_{1/2}}$$

where,

$T_{1/2}$ = half life

Half life for Co 60 is 1.663×10^8 s

$$\text{Decay constant, } \lambda = \frac{0.69315}{1.663 \times 10^{8}}$$

$$= 4.1681 \times 10^{-9}$$

From the decay formula,

$$D = D_o e^{-\lambda t}$$

1 month = 2592000 s

$$\text{Dose rate after 1 month} = D_o e^{-\lambda (2592000) 1}$$

$$= 0.44646 \text{ Gys}^{-1}$$

Dose rate for 21 months is as shown in the figure below .

n	Month	Dose rate (Gys $^{-1}$) $D = D_o e^{-\lambda (2592000) n}$
1	Feb. '97	0.44646
2	Mar. '97	0.44166
3	Apr. '97	0.43692
4	May '97	0.43222
5	June '97	0.42758
6	July '97	0.42298
7	Aug. '97	0.41844
8	Sept. '97	0.41394
9	Oct. '97	0.40949
10	Nov. '97	0.40509
11	Dec. '97	0.40074
12	Jan. '98	0.39643
13	Feb. '98	0.39217
14	Mar. '98	0.38796
15	Apr. '98	0.38379
16	May '98	0.37967
17	June '98	0.37559
18	July '98	0.37155
19	Aug. '98	0.36756
20	Sept. '98	0.36361
21	Oct. '98	0.35970

Table 3.4 : Dose rate at different months

Thus, in October '98, when this part of the experiment was conducted, the radiation dose rate was 0.3597 Gys $^{-1}$. From this value, the radiation dose for different radiation time was calculated. The electrical conductivity of the polymer electrolytes with different radiation doses are summarised in Table 3.5.

Sample name	Radiation Dose (Gy)	Conductivity (S/cm)
RD 1	2.59×10^3	7.56×10^{-6}
RD 2	5.18×10^3	1.90×10^{-5}
RD 3	7.77×10^3	2.86×10^{-4}
RD 4	1.04×10^4	4.51×10^{-4}
RD 5	1.30×10^4	4.31×10^{-4}
RD 6	1.55×10^4	2.07×10^{-5}

Table 3.5 : Electrical conductivity of polymer electrolytes with different radiation dose.

Figure 3.20 to Figure 3.25 shows the typical impedance plot of all the above examples.

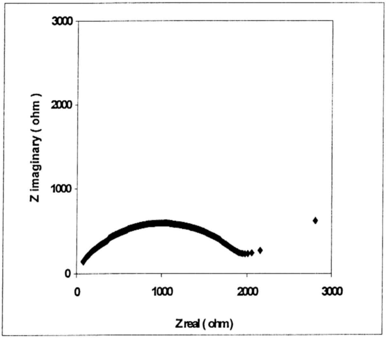

Figure 3.20 : Typical impedance spectra for RD 1

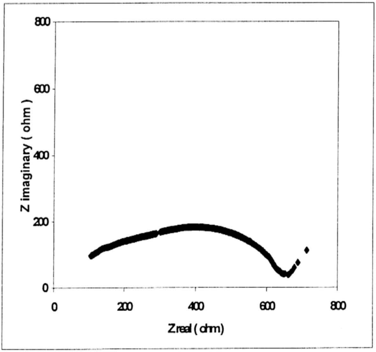

Figure 3.21 : Typical impedance spectra for RD 2

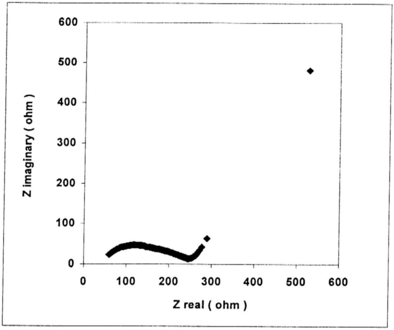

Figure 3.22 : Typical impedance spectra for RD 3

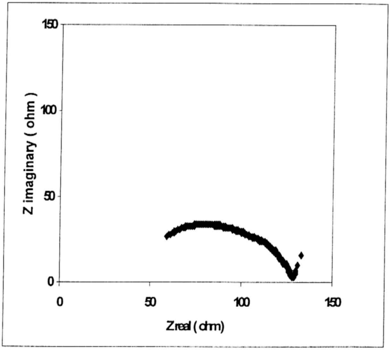

Figure 3.23 : Typical impedance spectra for RD 4

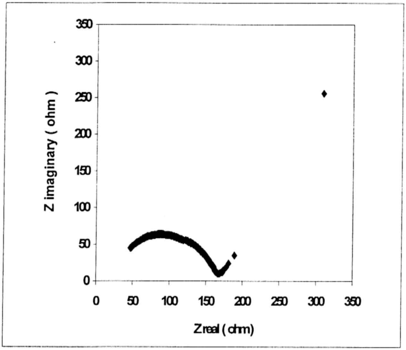

Figure 3.24 : Typical impedance spectra for RD 5

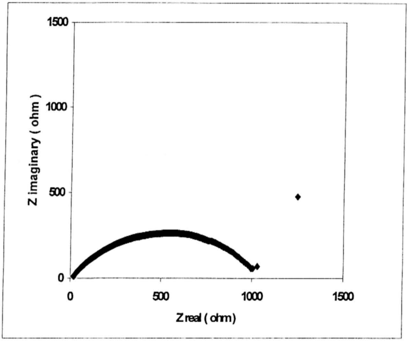

Figure 3.25 : Typical impedance spectra for RD 6

The radiation dose dependence of ionic conductivity at ambient temperature for electrolytes is depicted in Figure 3.26.

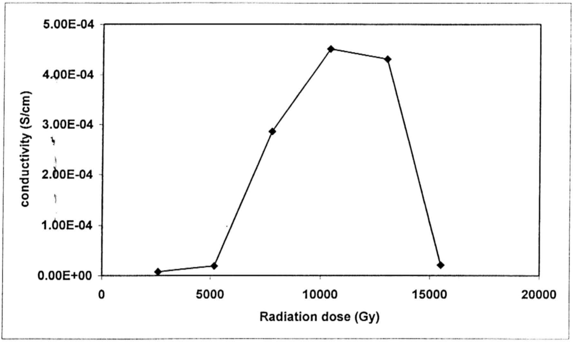

Figure 3.26 : Radiation dose dependence of ionic conductivity of PVC : $LiCF_3SO_3$: $LiBF_4$:EC (30 : 9 : 21 : 40)

With the increase in radiation dose, the electrical conductivity value increases at first and then decreases. The maximum electrical conductivity value of 4.51 x 10^{-4} S/cm is exhibited at a dose of 1.04 x 10^4 Gy. Usually γ-irradiation creates free radicals as acceptor sites for chemical moieties. According to Y.Song *et.al.*[65], the increase of conductivity is due to the segmentation of the polymer network and an increase in the amorphous nature. Whereas, in the very low dose range, the network formation is rather poor. On the other hand, the network would become too dense if the dosage is excessive. This will result in a decrease of the conductivity.

3.1.4 Effect of Mixed Plasticizers (EC and PC)

In order to improve upon the existing conductivity of PVC based polymer electrolytes, plasticizers were added. The plasticizers used in this study are a combination of EC (Ethylene Carbonate) and PC (Propylene Carbonate). Table 3.6 gives us the information regarding the polymer electrolyte composition and the name of each particular composition.

Composition	Name
PVC : $LiCF_3SO_3$: $LiBF_4$: EC : PC (27 : 8.1: 18.9 : 36 : 10)	PC 1
PVC : $LiCF_3SO_3$: $LiBF_4$: EC : PC (24 : 7.2 : 6.8 : 32 : 20)	PC 2
PVC : $LiCF_3SO_3$: $LiBF_4$: EC : PC (21 : 6.3 : 14.7 : 28 : 30)	PC 3
PVC : $LiCF_3SO_3$: $LiBF_4$: EC : PC (18 : 5.4 : 12.6 : 24 : 40)	PC 4
PVC : $LiCF_3SO_3$: $LiBF_4$: EC : PC (15 : 4.5 : 10.5 : 20 : 50)	PC 5
PVC : $LiCF_3SO_3$: $LiBF_4$: EC : PC (12 : 3.6 : 8.4 : 16 : 60)	PC 6
PVC : $LiCF_3SO_3$: $LiBF_4$: EC : PC (9 : 2.7 : 6.3 : 12 : 70)	PC 7

Table 3.6 : The composition of polymer electrolytes and their name

Figure 3.27 to figure 3.33 shows the complex impedance plots of all the above polymer electrolytes from where we can calculate the ionic conductivity values.

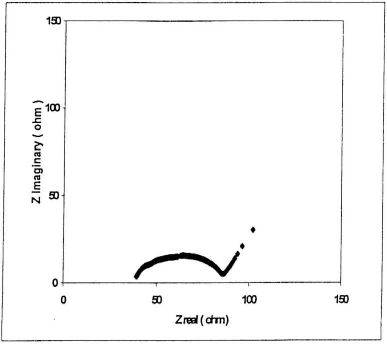

Figure 3.27 : Complex impedance plot for PC 1

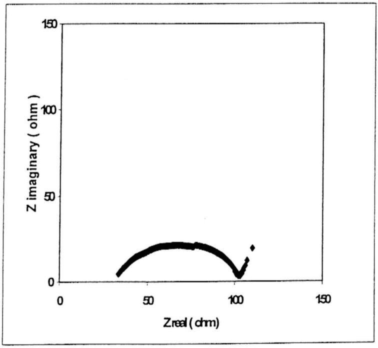

Figure 3.28 : Complex impedance plot for PC 2

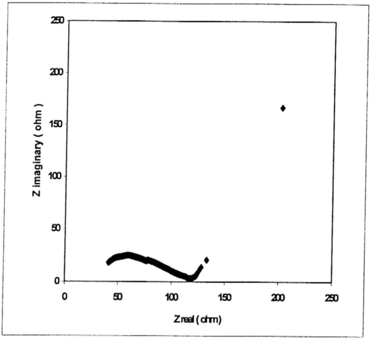

Figure 3.29 : Complex impedance plot for PC 3

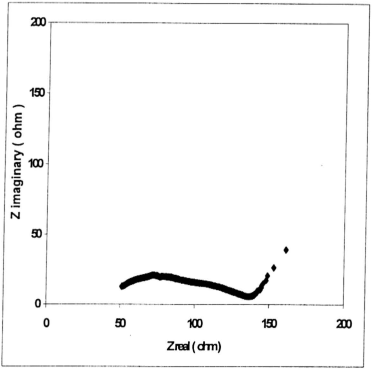

Figure 3.30 : Complex impedance plot for PC 4

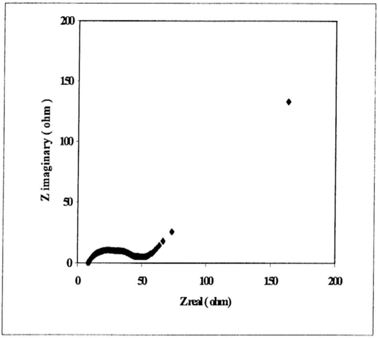

Figure 3.31 : Complex impedance plot for PC 5

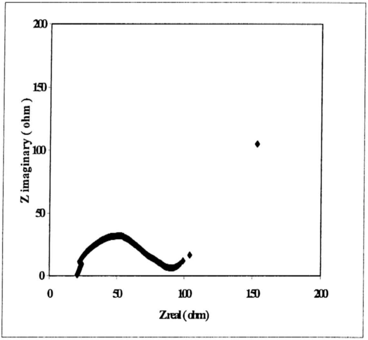

Figure 3.32 : Complex impedance plot for PC 6

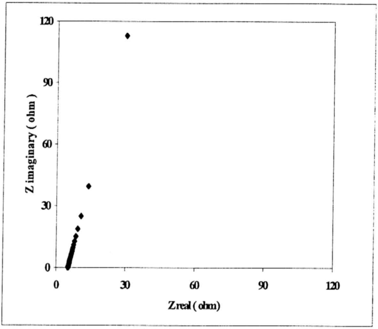

Figure 3.33 : Complex impedance plot for PC 7

It is noted that the semicircle observed at high frequency completely disappears in the polymer electrolytes with 70 wt% of PC (sample PC 7). This result suggests that, only the resistive component of polymer electrolyte can be considered, when the amount of plasticizing solution is high.

As the plasticizer content increases, it is possible to construct a local effective pathway in liquid phase for ionic conduction. As a result, ions can transport quickly in the liquid phase as the electric potential alternates between positive electrode and negative electrode in an a.c. field. Therefore, no capacitance effect occurred in the polymer electrolytes with the highest content of plasticizers [122].

Name	Conductivity at 25°C (S/cm)
PC 1	3.63×10^{-4}
PC 2	6.67×10^{-4}
PC 3	7.00×10^{-4}
PC 4	7.09×10^{-4}
PC 5	1.03×10^{-3}
PC 6	1.14×10^{-3}
PC 7	2.60×10^{-3}

Table 3.7 : Ionic conductivity values of PVC : $LiCF_3SO_3$: $LiBF_4$: EC : PC complexes.

Figure 3.34 shows the change of ionic conductivity with the content of PC. It can be observed that the addition of PC significantly improved the ionic conductivity.

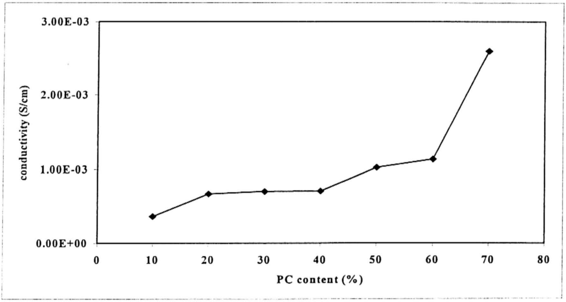

Figure 3.34 : Ionic conductivity of polymer electrolytes as a function of PC content.

The addition of a suitable amount of a mixture of PC and EC to the polymer - salts complexes increase the room temperature conductivity to 10^{-3} S/cm. The cause for overall conductivity enhancement in the case of adding EC and PC in the above polymer electrolytes may be explained as follows.

EC and PC have high dielectric constant. This high dielectric constant plasticizers, dissociate more salts and can form a local solvent channel for ionic conduction, which is a major medium governing the ionic conductivity. This will increase the ionic carrier number. Thus, the ionic conductivity of the material is increased [122, 132-133].

The mobility of charge carriers is apparently increased as a result of addition of plasticizers. These low viscosity solvents reduce the viscosity of the polymer electrolytes, thereby facilitating the ionic charge carriers to move in the polymer backbone [132, 134].

However, an addition of PC beyond 70 wt% causes poor mechanical strength. The poor mechanical property prevented the preparation of dimensionally stable films necessary for practical use. Therefore, the amount of PC is maintained below 70 wt% to ensure acceptable mechanical properties.

3.1.5 Complex Admittance Analysis

When it is difficult to determine the bulk impedance directly from the complex impedance plot, we can obtain the reciprocal of the bulk impedance from the complex admittance plot. Complex admittance is reciprocal to complex impedance [135]. Figure 3.35 to figure 3.38 shows the complex admittance plots for some of the highest conducting polymer complexes.

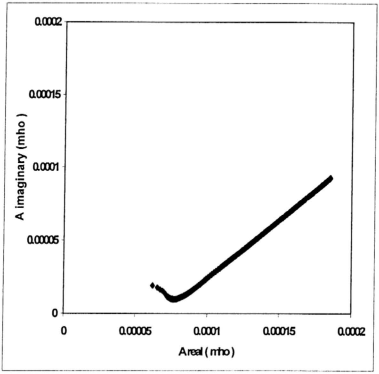

Figure 3.35 : Complex admittance plot for LT 02

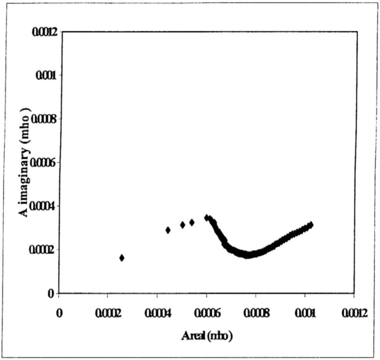

Figure 3.36 : Complex admittance plot for LT 09

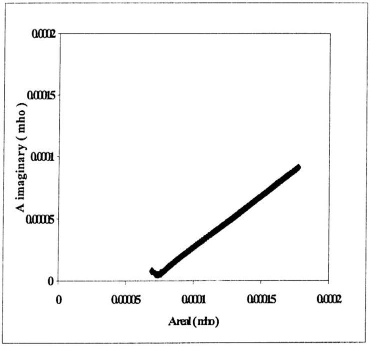

Figure 3.37 : Complex admittance plot for LT 12

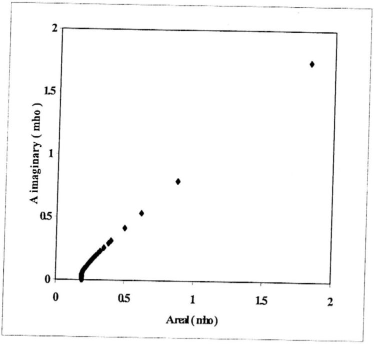

Figure 3.38 : Complex admittance plot for PC 7

The intercept on the real impedance axis in the complex impedance plot is approximately the same as the reciprocal of the intercept on the real admittance axis in the complex admittance plot. From Table 3.8, it can be observed that the electrical conductivity values are almost same as that calculated from the impedance plots.

Sample	Conductivity (S/cm)
LT 02	1.66×10^{-6}
LT 09	5.41×10^{-6}
LT 12	1.08×10^{-6}
PC 7	2.73×10^{-3}

Table 3.8 : Room temperature conductivity values from the complex admittance plots.

3.1.6 Ion Conduction Mechanism

In order to understand the mechanism of ionic conduction, the temperature dependence of ionic conductivity studies were carried out. The temperature dependant ionic conductivity for polymer electrolytes consisting of PVC, $LiCF_3SO_3$, $LiBF_4$, EC and PC were studied in the temperature range between room temperature (25°C) and 100°C. Table 3.9 gives the data on conductivity-temperature studies for sample PC 5 and PC 7. Figure 3.39 depicts the Arrhenius plots of logarithmic conductivity versus inverse temperature for these complexes.

Temperature, T (K)	1000/T	log σ (PC 5)	log σ (PC 7)
298	3.36	-2.9872	-2.5850
313	3.19	-2.9788	-2.4868
323	3.10	-2.9431	-2.4260
333	3.00	-2.8125	-2.4112
343	2.92	-2.7986	-2.3969
353	2.82	-2.7520	-2.3335
363	2.75	-2.7496	-2.3019
373	2.68	-2.6925	-2.2774

Table 3.9 : Temperature and conductivity values for polymer electrolyte complexes

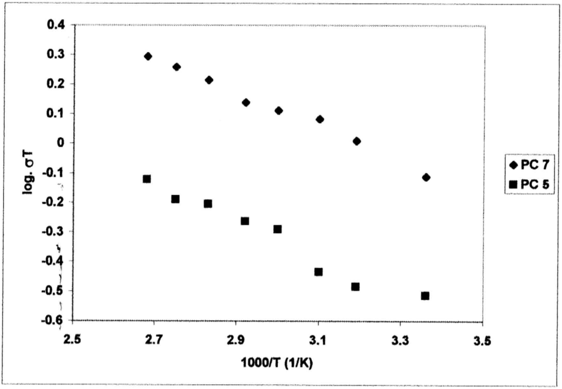

Figure 3.39 : Temperature dependence of ionic conductivity for samples PC 5 and PC 7.

Figure 3.39 shows that the conductivity values do not show any abrupt jump indicating the fact that these electrolytes exhibit a completely amorphous structure [63]. The increase in conductivity with temperature can be linked to the decrease in viscosity and hence, increased chain flexibility [136].

The regression value for sample PC 5 and PC 7 is 0.93 and 0.98 respectively. Since the regression value is ~ 1, the conductivity-temperature data obeys the Arrhenius rule and can be written according to the classical Arrhenius relationship. If the conductivity-temperature data follows the Arrhenius relationship, the possibility of cation transport is quite similar to that occurring in ionic crystals, where ions jump into neighbouring vacant sites and hence increase the ionic conductivity to a higher value [33].

The activation energy (E_a), which is a combination of the energy of defect formation and the energy of defect migration can be calculated from the plots. The activation energy for samples PC 5 and PC 7 are 0.42 eV and 0.37 eV respectively. The activation energy for the lithium ion transport is significantly low for the present polymer electrolytes. This is due to the fact that the completely amorphous nature of the polymer electrolytes facilitate the fast Li - ion motion in the polymer network and it further provides a higher free volume in the polymer electrolyte system upon increasing the temperature [63]. For devices operating over a wide temperature range, it is desirable to have a uniform conductivity. Thus, systems with the low values of activation energies are desirable [132,137-138]. It can be observed that sample PC 7 has higher ionic conductivity and lower activation energy compared to sample PC 5.

3.1.7 Conductivity – Frequency Dependence

Different methods of data representations are normally used to get a complete knowledge of the relaxation processes. In this study, the conductivity (σ) of the polymer electrolyte complexes were analysed with respect to the frequency. The logarithmic plots of the conductivity variations as a function of frequency for polymer electrolytes giving high ionic conductivity (at 25°C) for different system and for sample PC 7 at different temperatures are shown in Figure 3.40 and 3.41 respectively.

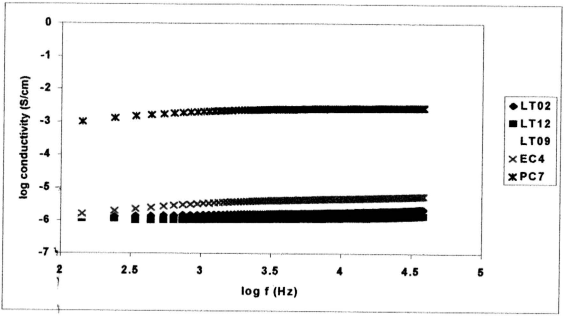

Figure 3.40 : Frequency dependent conductivity spectra for samples LT02 , LT12, LT09, EC 4and PC 7

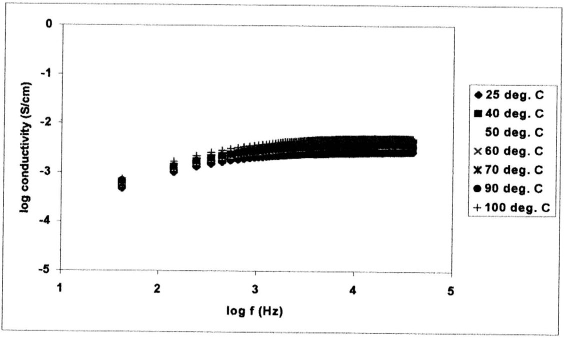

Figure 3.41 : Frequency dependent conductivity at various temperatures for sample PC 7.

The observed frequency dependent curve can be divided into a low frequency dispersion region (f < 1 kHz) and an almost frequency independent plateau region at higher frequency. This non-debye type of nature which cannot be expressed by a single relaxation equation has been accounted for by Jonscher's universal power law,

$$\sigma(\omega) = \sigma(o) + A\,\omega^{s}, \qquad 0 < s < 1$$

where σ (o) is the d.c limit of conductivity and A and s are temperature dependent constants [139].

From Figure 3.41, one can observe that the low frequency dispersion region and the plateau region increases with temperature. This low frequency dispersion, which is shown in the plots, may be due to the interfacial impedance or space-charge polarization [140]. As the frequency decreases, more and more charge accumulation occurs at the electrode and electrolyte interface, which leads to a drop in conductivity at low frequency. In the high frequency region, the mobility of charge carriers is high and hence the conductivity increases with frequency [141].

3.1.8 Modulus Studies

The real (M') and imaginary (M'') parts of modulus formalism measured at different frequencies for various polymer electrolyte complexes are shown in Figure 3.42 to 3.45.

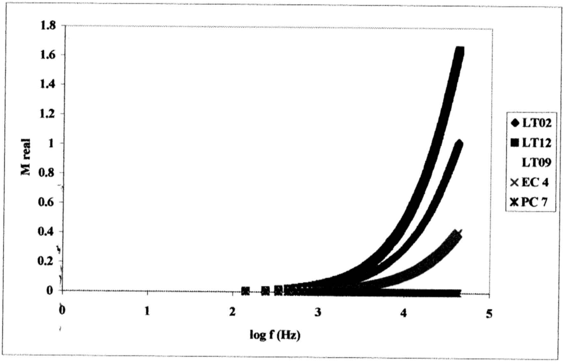

Figure 3.42 : The real part of modulus (M') as a function of frequency for samples LT02 , LT09, LT12, EC 4 and PC 7.

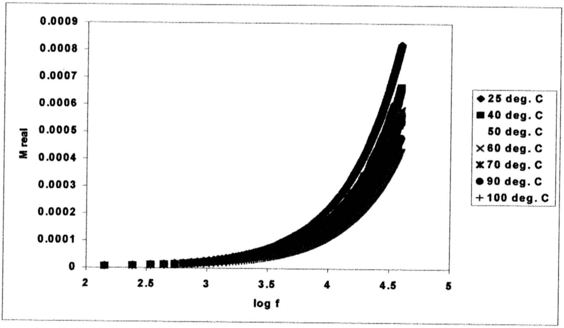

Figure 3.43 : The real part of modulus (M') as a function of frequency for sample PC 7 at different temperatures.

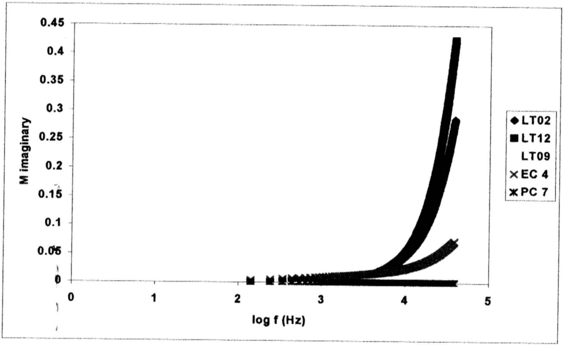

Figure 3.44 : The imaginary part of modulus (M'') as a function of frequency for samples LT02 , LT09, LT12, EC 4 and PC 7.

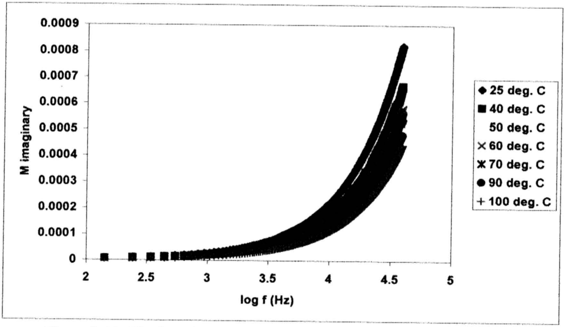

Figure 3.45 : The imaginary part of modulus (M'') as a function of frequency for sample PC 7 at different temperatures.

The M' and M'' show an increase at the high frequency end. The possible presence of peaks in the modulus formalism at higher frequencies for all the polymer system and temperature indicates that the polymer electrolyte films are ionic conductors. The peaking curve at higher frequencies may be attributed to the bulk effect. The heights of peaks decrease with increase in temperature suggesting a plurality of relaxation mechanisms [142].

At low frequencies, M' and M'' approach to zero indicating the fact that the electrode polarization phenomena makes a negligible contribution. The plots also gives a long tail at lower frequencies. This long tail is probably due to the large capacitance associated with the electrodes [140].

3.1.9 Dielectric Relaxation Studies

Dielectric relaxation studies were examined in the same frequency range for similar samples at equally similar conditions. The frequency dependence of dielectric relaxation curves are shown in Figure 3.46 to 3.49.

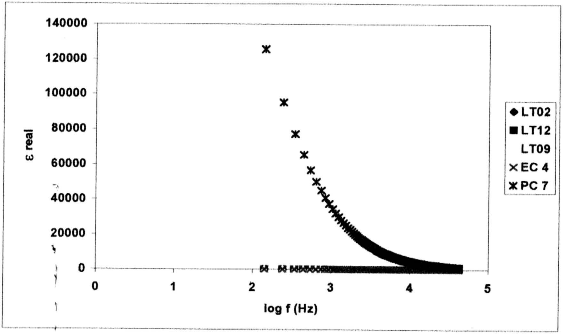

Figure 3.46 : Typical plots of the variation of real (ε') part of dielectric constant with frequency for samples LT02, LT09, LT12 ,E 4 and PC 7.

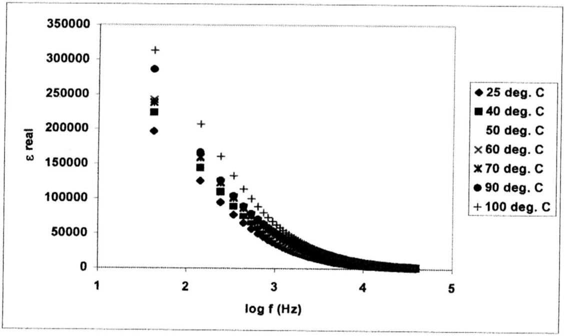

Figure 3.47 : Typical plots of the variation of real (ε') part of dielectric constant with frequency for sample PC 7 at different temperatures.

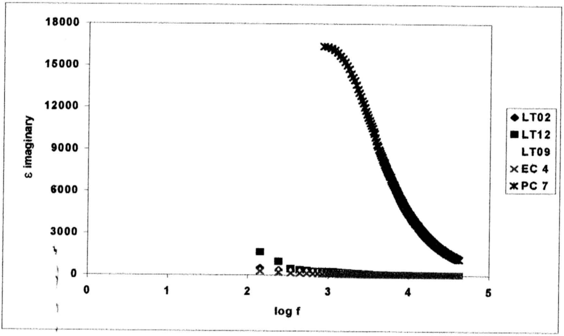

Figure 3.48 : Typical plots of the variation of imaginary (ε'')part of dielectric constant with frequency for samples LT02, LT09, LT12 , E 4 and PC 7.

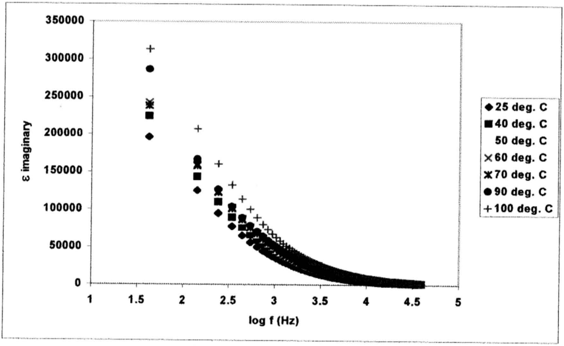

Figure 3.49 : Typical plots of the variation of imaginary (ε'') part of dielectric constant with frequency for sample PC 7 at different temperatures.

Both the real (ε') and imaginary (ε'') parts of the dielectric constant rise sharply towards low frequencies and the rise is displaced to higher frequencies. The rather sensitive and sharp rise of the components of the dielectric constant is due to the electrode polarization effects [143]. At high frequencies, the periodic reversal of the electric field occurs so fast that there is no excess ion diffusion in the direction of the field. The polarization due to the charge accumulation decrease, leading to the observed decrease in the value of ε' and ε''.

3.2 Transference Number Measurement

Transference number measurement was performed using Wagner's polarization technique in order to know the major conducting species in polymer electrolytes. The polarization current was collected until it gets saturated. The value of transference number was obtained by normalizing the polarization current with the initial current at t=0.

Figure 3.50 and 3.51 shows the plots of change in current with time for a PVC-$LiCF_3SO_3$ polymer electrolyte and PVC - $LiBF_4$ polymer electrolyte respectively. These electrolytes are sandwiched between carbon conducting cement. The value of cation transference number (t_+) for PVC-$LiCF_3SO_3$ complex was obtained as 0.4 whereas for PVC - $LiBF_4$ complex, a value of 0.32 was obtained. This means that the major conducting species in the above polymer electrolytes are anions. The major conducting species for PVC-$LiCF_3SO_3$ complex is the $CF_3SO_3^-$ anion and for PVC - $LiBF_4$ complex, it is the BF_4^- anion. Other reports have obtained lithium ion transference number as 0.40-0.50, with lithium triflate being a salt [144], 0.30 with $LiBF_4$ salt [30], 0.10-0.20 with $LiClO_4$ salt [144] and 0.03-0.08 with LiTFSI salt [145].

These low values are considered to be caused by the preferential solvation of the chlorine dipoles to Li^+, resulting in the co-operative motion of the cation and the polymer segment, whereas the corresponding anions are weakly solvated, allowing the motion to be independent of the segmental motion [145-146]

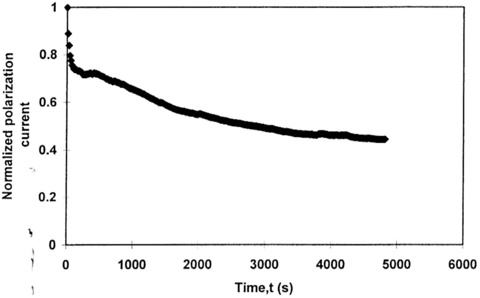

Figure 3.50 : Normalized current versus time for PVC - $LiCF_3SO_3$ complex

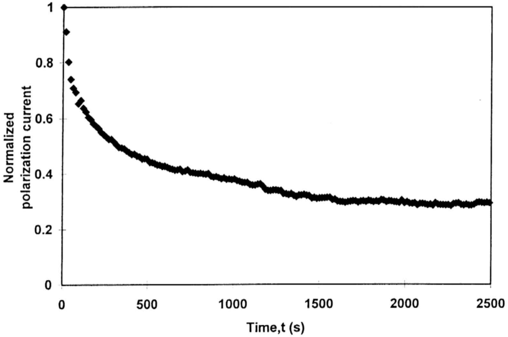

Figure 3.51 : Normalized current versus time for PVC - $LiBF_4$ complex

The normalized polarization current versus time curve for PVC - $LiCF_3SO_3$ - $LiBF_4$ complex polymer electrolyte is presented in Figure 3.52. From this mixed anion complex figure, the cation transference number (t_+) was calculated as 0.46.

This increase in cation transference number is due to decrease in crystallinity of the above complex compared to the single salt system. This decrease in crystallinity in mixed anion system is also confirmed by x-ray diffraction studies.

In the mixed anion region a trend exists in which lower crystallinity corresponds to higher cation transference number. It is a common belief , as stated in the polymer electrolyte literature, that ions move in the amorphous region. It appears that the amorphous region can sustain bulk cation and anion mobility while anions may show substantial mobility in the crystalline region also over and above their mobility in the amorphous region. This is an obvious consequence of the fact that the net anion transference number is (t_-) larger for higher crystallinity [125,147].

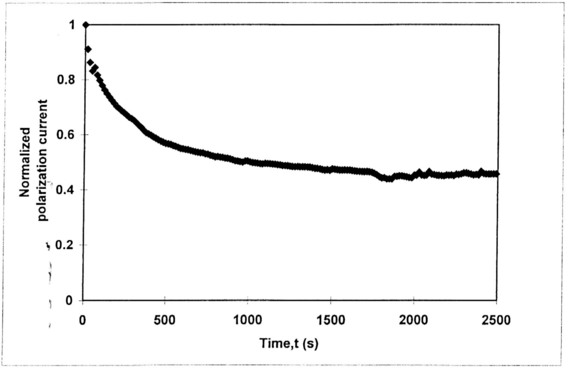

Figure 3.52 : Normalized current versus time for PVC - $LiCF_3$ SO_3 - $LiBF_4$ complex.

Figure 3.53 shows the transference measurement curve of plasticized PVC - $LiCF_3$ SO_3 - $LiBF_4$ complex. The plasticizers used are EC and PC. The cation transference number (t_+) for this complex is 0.5 which is higher than the previous complexes. Thus, we can conclude that the cationic part of the ionic transport will be high since the plasticizers have the ability to solvate the cations and to support their mobility in the electric field [129,148-149]. In addition, the plasticized polymer electrolytes have more amorphousity than the unplasticized polymer electrolytes.

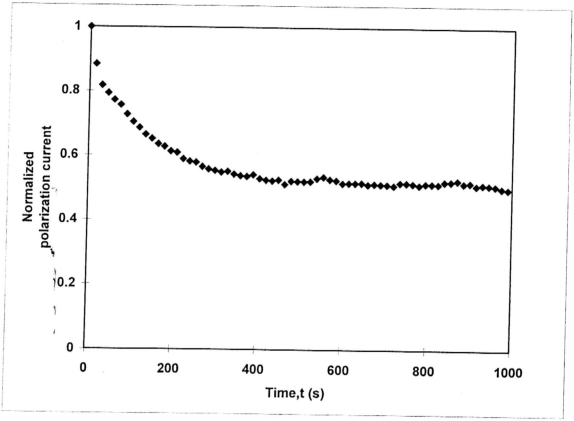

Figure 3.53 : Normalized current versus time for PVC - $LiCF_3SO_3$ - $LiBF_4$ - PC - EC complex