Ceylon Journal of Science : Physical Sciences, 9(1), 82-89 (2002)

ELECTRICAL RELAXATION IN SOME PEO - BASED SOLID POLYMER ELECTROLYTES

L.R.A.K. BANDARA AND M.A.K.L. DISSANAYAKE*

Department of Physics, University of Peradeniya, Sri Lanka

ABSTRACT

Dielectric relaxation spectroscopy has proved to be a very powerful tool for obtaining information on relaxing dipoles in polymer electrolytes. The dielectric response of a PEO based plasticized polymer electrolyte systems was studied in the broad frequency range from 5Hz to 1.8GHz and in the temperature range from –25 °C to 80 °C. At high frequencies a dielectric relaxation is observed for pure PEO as well as for the salt containing systems in the GHz region that is assumed to be due to segmental motion of the polymer chains. In the salt containing systems, this relaxation is shifted to lower frequencies relative to that of pure PEO, and is attributed to transient cross-linking. At considerably lower frequencies another dielectric response peak was detected in all samples containing salts. These loss peaks seen at higher temperatures are believed to be due to ion pairs and can only be observed in salt containing samples. However, the effect of the plasticizer on this relaxation is complex. According to the experimental results, it is clear that considerable amounts of ion pairs are present in these electrolyte materials. If the relaxation frequency can be taken as a probe of the local flexibility of the polymer chain we may thus conclude that the conductivity increase is parallel to the increase in the extent of local flexibility.

---

1. INTRODUCTION

The structure of the polymer is important for the ionic conductivity in polymer electrolytes due to the interaction with the ions and the mobility of the segments of the polymer chain. Poly(ethylene oxide) (PEO), the most widely studied polymer host, has a particular efficiency in co-ordinating cations, due to the partial distance and orientation of the ether oxygen atoms in the polymer chain. The multiphase nature of PEO is most often regarded as a major problem in real working systems, since the ion conduction has been shown to take place mainly in the amorphous phase [1]. Over the past several years, efforts have been made to increase the ambient temperature conductivity by decreasing the crystallinity and increasing the segmental mobility of the polymer by the incorporation of salts and plasticizers into PEO.

The ionic conductivity of polymer electrolytes is dependent of a number of parameters that influence the concentration and the mobility of the charge carriers. As for liquid aprotic solvents with low permittivity, ion association is an important factor for the ionic conductivity and it has been shown those "free" ions, ion pairs and triplets exist in polymer electrolytes [2,3]. If a broad frequency range can be investigated dielectric relaxation spectroscopy becomes a very useful tool in obtaining information on relaxing dipoles in polymer electrolytes [4-9].

Dielectric studies are not generally performed on polymer electrolytes above the glass transition temperature (Tg) because of the long-range motion of charges associated with ionic conductivity. Polarization in insulators is defined as the induced

---

* laxmand@pdn.ac.lk

dipole moment per unit volume. This can be identified in an ionic conductor as well and usually described due to the fact as dielectric relaxation. The difficulty of studying dielectric phenomena in ionic conductors is that both dipole reorientation and ionic conductivity are detected via energy loss and it is often difficult to separate the two.

One way to observe dielectric relaxations directly in polymer electrolytes is to cool the material below T_g, where the ionic conductivity is very low. However, dielectric phenomena in polymer electrolytes above T_g can be observed directly, if the applied frequency is sufficiently high so that the contribution of the mobile ions to the imaginary part of the dielectric constant is greatly reduced. In this article, the results of the dielectric relaxation spectroscopy on plasticized PEO-based solid polymer electrolytes containing $LiN(CF_3SO_2)_2$ (LiTFSI) salt in a wide frequency range (5 Hz to 1.8×10^9 Hz) and a temperature range (-20 °C to 80 °C) are presented and discussed in detail.

2. EXPERIMENTAL

Polymer electrolytes, $(PEO)_9LiN(CF_3SO_2)_2$ and $(PEO)_9LiN(CF_3SO_2)_2$ incorporating with poly(perfluoro ethylene methylene oxide) (PPFEMO) with weight ratio PPFEMO / PEO = 1 were prepared using the solvent casting technique. Desired amounts of high purity grade of PEO (Aldrich, M_w - 5×10^6 g mol^{-1}) were complexed with the salt $LiN(CF_3SO_2)_2$ (Aldrich) by dissolving in acetonitrile. The polymer and the salt were mixed together with PPFEMO to obtain plasticized samples in the form of thin solid films of about 100 μm thickness, incorporating the finely dispersed PPFEMO.

Electrical conductivity of the samples was measured by using the complex impedance technique. The measurements were performed over the frequency range of 5Hz to13MHz, using a computer controlled HP4192A, impedance analyzer, with an applied signal of 0.1 V. The impedance data were collected at intervals of 5 °C in the temperature range of -16 °C to 85 °C. The electrodes used were stainless steel. Thermal properties of the systems were determined by performing Differential Scanning Calorimetry (DSC) measurements with a Mettler-Toledo DSC 30 Low Temperature Cell.

Dielectric measurements were performed using a Hewlett-Packard HP4291 High Frequency Impedance Analyzer together with a Novocontrol BDS 2100 sample cell and a BDS 2200 RF extension line. The frequency range covered by this equipment is 1 MHz – 1.8 GHz. The temperature of measurements was varied in the range –25 °C to 80 °C (controlled better than within ±0.1 °C) and the impedance data were collected at intervals of 5 °C. For temperatures above 0 °C, the sample temperature was controlled by pumping water from a water-bath through a metal cylinder surrounding the sample. Below 0 °C, an expansion chamber was used, enabling measurements at temperatures down to about –25 °C. The sample temperature was measured with a chromel-alumel thermocouple placed close to the sample. In the entire frequency range, the dielectric behaviour of the systems was studied by converting the measured impedance data into the complex permittivity. Before the measurements were taken, the instrument was calibrated by using the Hewlett-Packard standard calibrating kit.

3. ELECTRICAL CHARACTERIZATION OF POLYMER ELECTROLYTES

An understanding of the fundamental relationships between the real part of the dielectric function (ε_r') and its imaginary part or the loss index (ε_r'') as a function of frequency and temperature is necessary, in order to understand the electrical properties of polymers. The results of dielectric measurements are often represented in terms of the real and imaginary parts of the complex dielectric function ($\varepsilon_r^* = \varepsilon_r' - j\varepsilon_r''$) which can be determined from the complex impedance through the following equations:

$$\varepsilon' = \frac{-Z''}{\omega C_0 (Z'^2 + Z''^2)}$$

$$\varepsilon'' = \frac{Z'}{\omega C_0 (Z'^2 + Z''^2)}$$

In response to an externally applied ac field, amorphous polymers generally undergo a dielectric relaxation process, referred to as the α-relaxation, which is characterized by large-scale segmental motions (e.g. ~5-10 or more repeat units) that are associated with the glass transition. Although it is well known that significant ionic conductivity in amorphous polymer electrolytes occurs only above T_g, some of the most compelling evidence for the specific role that the α-relaxation plays in the ion transport process comes from dielectric relaxation and conductivity measurements done below T_g.

A problem when performing this type of analysis is that for an ion conducting material the measured dielectric function not only contains contributions from the dielectric relaxation processes but also from ionic transport processes. As a result, the measured dielectric loss, ε_r'', consists not only of contributions from the dipoles in the materials but also contributions from the dc conductivity, σ_{dc}, as given by the following equation.

$$\varepsilon_r'' = \varepsilon_d'' + \frac{\sigma_{dc}}{\omega \varepsilon_o}$$

This means that in high conductive materials such as in polymer electrolytes, the term, σ_{dc}, is dominating at least at moderately high frequencies. The dc conductivity contribution can be subtracted from the measured dielectric function in order to study the relaxations in the system even though this subtraction may be difficult or impossible at low frequencies. The corrected relative permittivity, $\varepsilon_r''_{corr}$ is thus given by,

$$\varepsilon_r''_{corr} = \frac{Z'}{\omega C_o \left(Z'^2 + Z''^2\right)} - \frac{\sigma_{dc}}{\omega \varepsilon_o}$$

4. RESULTS AND DISCUSSION

It is well known that conductivity of plasticized polymer electrolytes is much higher than that of unplasticized polymer electrolytes. According to earlier studies [10], it has been shown that the plasticizer PPFEMO incorporated PEO-LiTf system shows high conductivity suitable as a practical solid electrolyte. The solid electrolyte, PEO-LiTFSI system with the same plasticizer shows even higher conductivities at room temperature and it was found that the ambient temperature conductivity of this system $(PEO)_9LiTFSI$ / PPFEMO with wt. ratio PPFEMO / PEO = 1, was around 3×10^{-5} S cm^{-1}. The system also exhibits stable mechanical properties. The conductivity of the PPFEMO added $(PEO)_9LiTf$ system with wt. ratio PPFEMO / PEO = 1, was 9.6×10^{-7} S.cm^{-1} at 22 °C. The DSC measurements in the range -120 °C to 180 °C showed a glass transition at -45 °C for the sample $(PEO)_9LiTFSI$ with wt. ratio PPFEMO / PEO = 1, more than 6 °C above that for the unplasticized system $(PEO)_9LiTFSI$.

Gray *et al.* [5] have studied the dielectric properties of PEO and PEO-$LiClO_4$ salt complexes. For pure PEO a high frequency relaxation peak has been observed around 6.3 GHz at 65 °C and this peak was assumed to be due to the relaxations arising from long range segmental motion of the polymer chains. We have also detected the same peak for pure PEO e.g. at 0.2 GHz and -20 °C. The fundamental difficulty when investigating the dielectric properties of electrolyte is the influence of ion conduction. Mobile species such as ions in electrolytes will contribute strongly, specially at low frequencies, to the measured dielectric function, ε_r^*, and often make it difficult to detect the dielectric relaxation due to reorientation of "true" dipoles whose centres are fixed in position.

According to the results of Gray *et al.* [9], for the ion co-ordinated polymer, a week relaxation has been observed in the MHz region. This was evident only in salt-containing systems and that also when the loss due to ionic conductance was separated from the total loss. This become more clearly defined as the salt concentration increased. According to our study, for the system PEO-LiTFSI, we have observed the same behaviour and assume that these peaks are related to the presence of ion-pairs in the electrolytes. For highly viscous solid materials such as PEO based solid polymer electrolytes, it is reasonable to expect that the relaxation due to ion pairs should occur in the MHz region for polymer electrolytes at ambient temperatures, despite the fact that the ion pair relaxation in low permittivity liquid electrolytes is detected at frequencies of the order of 1 GHz [4]. In ion conducting materials, observed relaxation peaks might be caused by a number of processes involving dipolar relaxation. For ion conducting polymers similar peaks occur in polypropylene glycol (PPG) complexed with triflate salts, and it has been suggested that theses peaks are due to cation-anion pairs [11]. If the same interpretation is valid for the plasticized amorphous polymer systems studied in this work, then it is clear that these low frequency peaks are due to the formation of ion pairs.

For the two samples with high salt concentrations, $PEO_9LiTFSI$ and $PEO_9LiTFSI$ / PPFEMO with wt. ratio PPFEMO / PEO = 1, two types of relaxation peaks were detected. The real and the imaginary parts of the dielectric function of the sample $PEO_9LiTFSI$ are shown in Fig. 1 (a) & (b), respectively, within the temperature region of 20 °C to 80 °C.

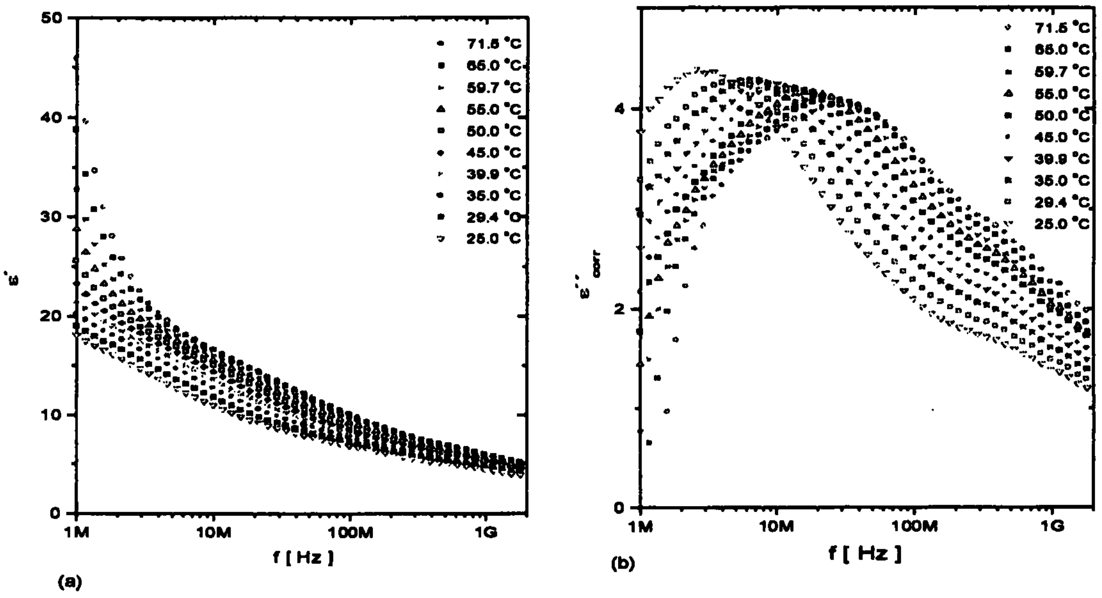

Fig. 1 Dielectric spectrum for $PEO_9LiTFSI$ sample. (a) Real part of the dielectric constant and (b) Corrected imaginary part of the dielectric function.

These electrolytes are completely amorphous and ion pair peak is detected as a distinct peak in the MHz region in the above temperature range. This peak has a high dielectric strength and dominates the dielectric response in this frequency range. In addition to this peak, another relaxation peak appears at higher frequencies (in the GHz region) which become more clear at very low temperatures (not shown in the figure). The real and imaginary parts of the dielectric function of the sample $PEO_9LiTFSI$ / PPFEMO with wt. ratio PPFEMO / PEO = 1, are shown in Fig. 2 (a) & (b) respectively. The dielectric spectrum of the plasticized sample, $PEO_9LiTFSI$ / PPFEMO with wt. ratio PPFEMO / PEO = 1, is similar to the unplasticized sample but shows a shift in the relaxation frequencies at different temperatures. In the two cases the peak positions show a temperature dependence and the relaxation frequency increases with increasing the temperature.

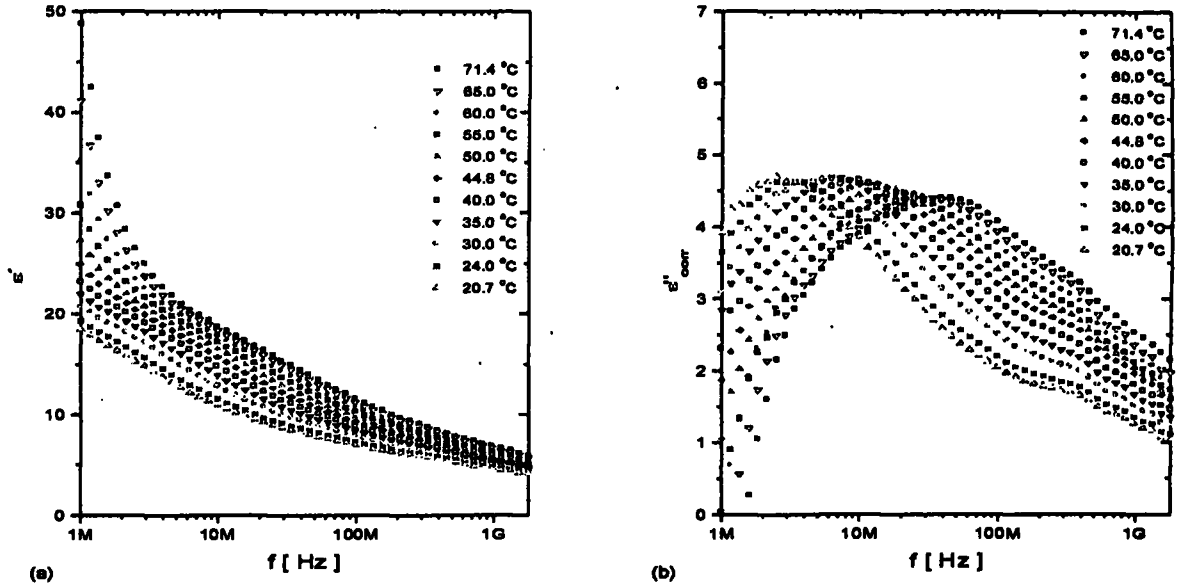

Fig. 2 Dielectric spectrum for $PEO_9LiTFSI$ / PPFEMO with wt. ratio PPFEMO / PEO = 1 sample; (a) Real part and (b) Corrected imaginary part of the dielectric function.

To obtain a high ionic conductivity in a material a large number of charge carriers with high mobility are needed. The dissolved ions can associate into ion pairs, triplets and higher aggregates. The formation of electrically neutral ion pairs will of course impair the electrical conductivity and it is therefore of importance to be able to detect and study such entities. The ion pairs have permanent dipole moments, which are stronger than those of the other types of aggregates. Considering that the host polymer has a comparably low permittivity, the ion pairs are expected to be detectable in dielectric measurements.

The frequency dependence of ε_r'' and ε_r' are shown in Fig. 3 (a) and (b) respectively and ε_{corr}'' vs. *log-f* plot for electrolyte samples in (c), at 60 °C. The plot of the pure PEO sample does not show any loss peak. As pointed out in the introduction, the dielectric loss associated with the glass transition (α-relaxation) is masked by the conductivity for materials containing mobile ions. Therefore, the apparent rapid increase in ε_r'' with decreasing frequency (relative to the pure PEO), shown in Fig 2 (a) for both the salt-polymer complex and for the plasticized electrolytes reflects the effect of the ionic conductivity.

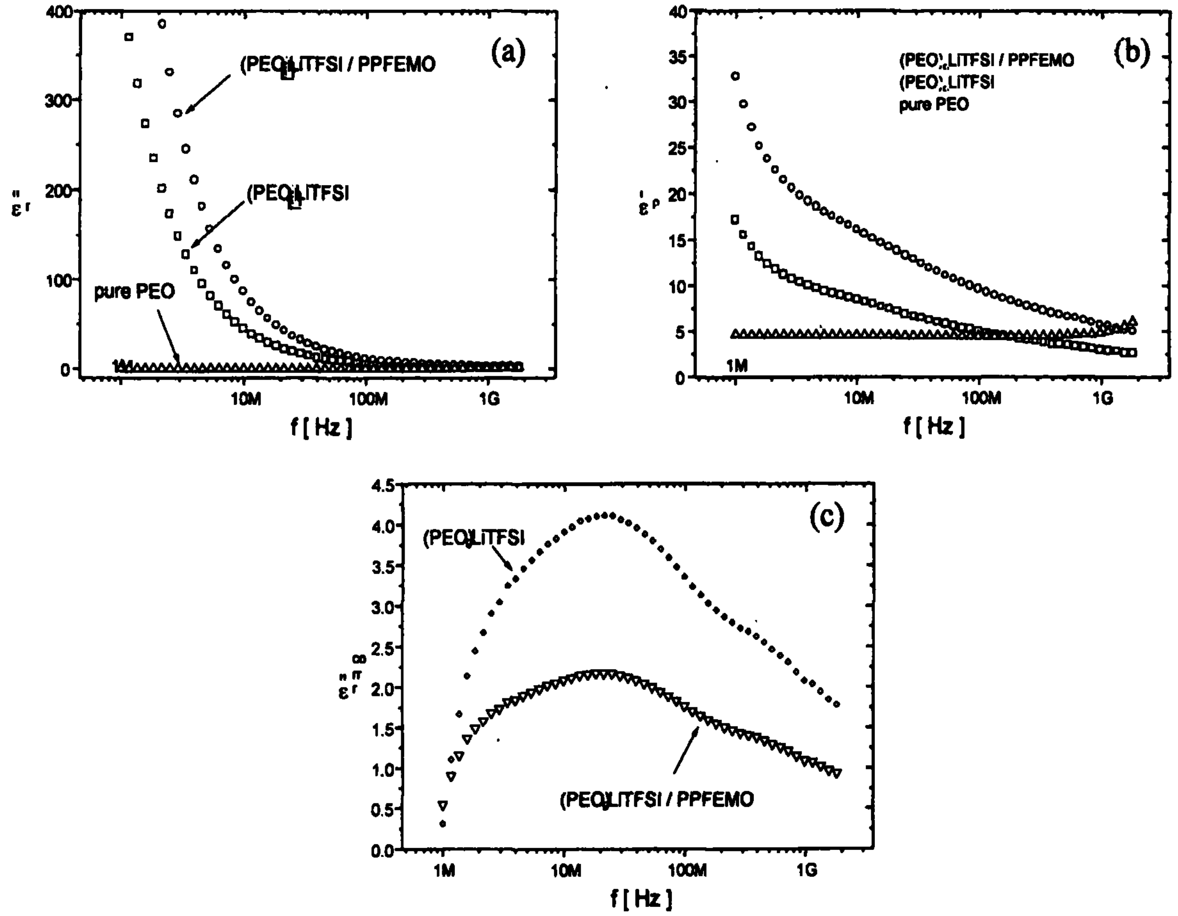

Fig. 3 Permittivity of pure PEO, (PEO)$_9$LiTFSI and (PEO)$_9$LiTFSI / PPFEMO with wt. ratio PPFEMO / PEO = 1, at 60 °C: (a) ε_r' vs. *log-f* plot, (b) ε_r'' vs. *log-f* plot, (c) ε_{corr}'' vs. *log-f* plot for electrolyte samples.

The dielectric behaviour presents a strong departure from the Debye regime; it is well known that this departure contains information about dissipative phenomena in the dipole re-orientation mechanism and dipole-dipole correlation. The addition of a plasticizer, changes the dielectric relaxation time and the loss peak maxima in much the same way as that due to increasing temperature. When the plasticizer is added, the relaxation time becomes shorter as the glass transition temperature and the "internal viscosity" decrease. Plasticizer may also reduce the tendency for the polymer to crystallize.

It is believed that the effect of increasing plasticizer content at constant temperature is equivalent to the effect of increasing temperature at constant amount of plasticizer, both leading to increased segmental mobility of the polymeric chains. The question remains, how the different relaxation processes are affected by temperature and plasticizers at molecular level. With respect to this point important information may be obtained by looking at both aspects of a relaxation process, *i.e.* the temperature and plasticizer dependence of its characteristic frequency and the changes of the shape of the response in frequency induced by temperature and by plasticizers.

The major effect of adding a salt to PEO is to modify the polymer chain structure. Both the loss maximum ($\varepsilon_r''_{max}$) and the permittivity (ε_r') increases with temperature and decreases with salt concentration [12]. In this case, the decreases in ε_r' suggests a stiffening of the matrix on increasing the salt concentration. The above two results can also be observed in Fig. 4, for two samples with constant salt concentration, after the addition of the plasticizer PPFEMO, which reduces both ε_r' and the loss maxima of the dielectric spectrum. However, in this case as the total number of ion pairs is proportional to $\varepsilon_r''_{max}$, it can be seen that the addition of plasticizer also reduces ion pair formation. In order to emphasise the correlation between both sets of data the VTF conductivity curve is plotted in Fig. 4 (a), and the peak frequencies associated with the ion pair relaxation in Fig. 4 (b).

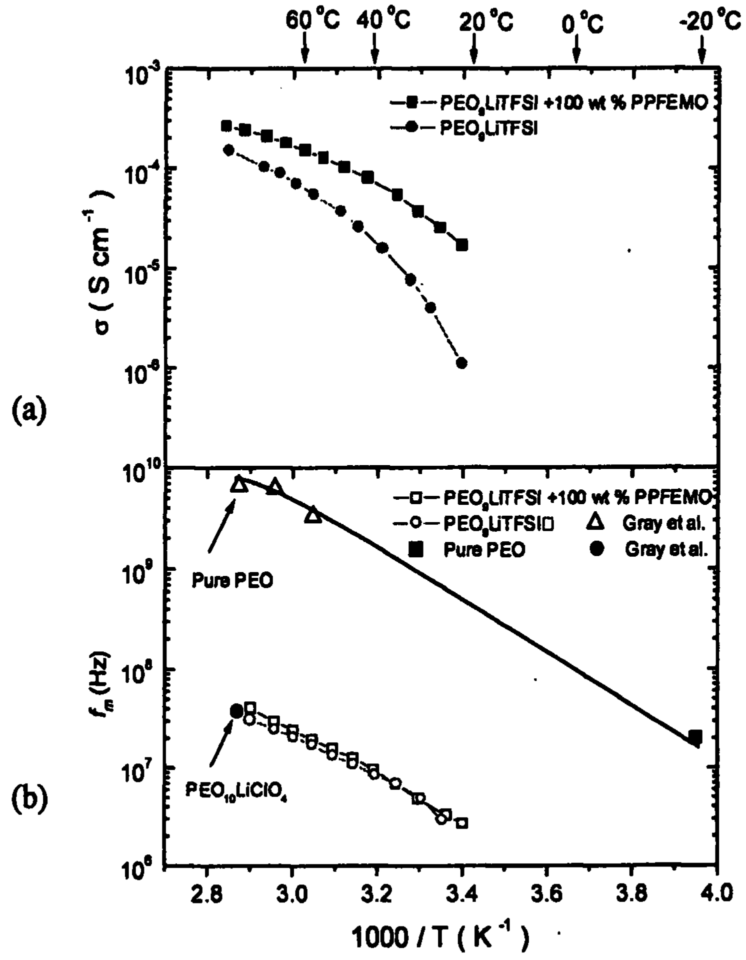

Fig. 4 The temperature dependence of (a) the ionic conductivity and (b) relaxation peak positions (frequencies), for $PEO_9LiTFSI$ and $PEO_9LiTFSI$ / PPFEMO with wt. ratio PPFEMO / PEO = 1, samples (Some results of Gray *et al.* [5] are also included).

In Fig. 4, the logarithm of the relaxation frequency (obtained from the peak frequency in the $\varepsilon_r''_{corr}$ vs. *log-f* plots) is plotted against *1/T* together with some results from earlier dielectric measurements [5] for $PEO_{10}LiClO_4$ system.

The ion-pair relaxation shows a temperature dependence, which can be described by the VTF equation similar to the temperature dependence of the conductivity. However, the effect of the addition of the plasticizers is more clear in the conductivity curves (Fig. 4 (a)) than in the relaxation spectra which show only a slight increase in relaxation frequencies. *Log-σ* vs. *1/T* curve for the plasticized sample seems to have almost the same activation energy as the corresponding log σ vs. *1/T* curve. This can be explained by considering the local flexibility of the polymer electrolyte. Specially, for polymer electrolytes, relaxation frequency can be taken as a probe of the local flexibility of the polymer chain and in this case, the increase in the local flexibility due to the addition of the plasticizer is not quite as large as the increase in conductivity . This implies that plasticizers increase the number of charge carriers available for ion transport and this can be clearly observed especially at low temperatures. In another word, in the plasticized sample, the ion pair relaxation seems to couple with the conduction process. On the other hand these two processes independently affect the unplasticized sample.

5. ACKNOWLEDGEMENTS

We acknowledge the financial support provided by the International Programs in the Physical Sciences (IPPS), Uppsala University, Sweden and the Post-Graduate Institute of Science (PGIS), University of Peradeniya, Sri Lanka.

REFERENCES

1. C. Berthier, W. Gorecki, M. Minier, M.B. Armand, J.M. Chabagno, P. Rigaud, *Solid State Ionics* **11** (1983) 91.
2. P.G. Bruce, C.A. Vincent, *Faraday Discuss. Chem. Soc.* **88** (1989) 43.
3. I. Albinsson , P. Jacobsson, B.-E. Mellander, J.R. Stevens, *Solid State Ionics* **53-56** (1992) 1044.
4. B. -E. Mellander, I. Albinsson, *Solid State Ionics: New Developments*, World Scientific, Singapore (1996) 83-95.
5. F.M. Gray, C.A. Vincent, M. Kent, J. *Polym. Sci. B: Polym. Phys.* **27** (1989) 2011.
6. I. Albinsson, *PhD Thesis*, Chalmers University of Technology and Gothenburg University, Sweden, 1994.
7. J.J. Fontanella, M.C. Wintersgill, J.P. Calame, C.G. Andeen, *Solid State Ionics* **8** (1983) 333.
8. D.R. Figueroa, J.J. Fontanella, M.C. Wintersgill, J.P. Calame, C.G. Andeen, *Solid State Ionics* **28/30** (1988) 1023.
9. M.C. Wintersgill, J.J. Fontanella, J.P. Calame, D.R. Figueroa, C.G. Andeen, *Solid State Ionics* **11** (1983) 151.
10. M. Furlani, L.R.A.K. Bandara, B.-E. Mellander, *Electrochimica Acta* **43** (1998) 1517.
11. I. Albinsson, B.-E. Mellander, J.R. Stevens, *Solid State Ionics* **72** (1994) 177.
12. F.M. Gray, C.A. Vincent, M. Kent, *Solid State Ionics* **28/30** (1988) 936.