

**ARTICLE****Development of Green Polymer Electrolyte Through Hot Press Method****Nidhi Asthana Mrigank Mauli Dwivedi Kamlesh Pandey\***

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## ABSTRACT

To develop the green polymeric membrane electrolyte, Polycaprolactone (PCL) was used as a host and the Ionic liquid (IL)(1-Ethyl-3-methylimidazolium tosylate) as a dopant. The IL is a source of mobile charges in the polymer electrolyte system. The composite membrane has been prepared by Hot Press method and then we characterised this membrane for ionic transportation. Formation of nanocomposite system has been ascertained from their XRD pattern. Interaction phenomenon was studied by ATR based FTIR and Laser Raman spectroscopic technique. Variation of conductivity with composition and temperature was studied with the aid of impedance spectroscopy data.

**1. Introduction**

The use of synthetic polymer materials has caused significant environmental problems. Therefore, biopolymers and its composite materials are becoming important due to their better compatibility and biodegradability<sup>[1]</sup>. Poly  $\epsilon$ -caprolactone (PCL) is one among them with immense potential as biomaterial for various biomedical applications<sup>[2-3]</sup>. It is semi crystalline polymer with a low melting point ( $T_m \sim 60^\circ\text{C}$ ) and glass transition temperature ( $T_g \sim -60^\circ\text{C}$ )<sup>[4]</sup>. It can be prepared by either ring opening polymerization of  $\epsilon$ -caprolactone using a variety of anionic, cationic, and co-ordination catalyst or via free radical ring opening polymerization of 2-methyl -1-3-dioxapane<sup>[5]</sup>. Polycaprolactone (PCL), non-toxic synthetic aliphatic polyester is especially suit-

able for drug delivery devices, because it is completely degradable inside the body. As a type of polymer, it is susceptible to be degraded by many types of bacteria<sup>[6-7]</sup>. PCL degrades at slower rate and therefore it is originally used in drug delivery devices. The most popular application of PCL based biodegradable membrane is in biomedical tissue engineering due to its attractive biocompatibility and easy processability. It also possesses superior rheological and viscoelastic properties<sup>[8-10]</sup>. PCL is now enjoying a wide range of application from packaging to biomedical implants<sup>[11-12]</sup>. The porous structure can actively support the cell function by regulating the interaction between the cells and drug diffusion in a body. It also shows excellent property to produce fine fibres through the melt, wet and electro spinning process for device application. Very few attempts have been focused to develop the compostable

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electrochemical devices like battery using biodegradable polymer electrolyte with PCL as polymer host<sup>[13-18]</sup>. This type of development leads to minimize the electrolyte hazards waste. It also provides the alternatives to maintaining sustainable development of ecologically alternative technology<sup>[19]</sup>. The green polymer composites recently become more popular due to its need for innovations in development of materials from biodegradable polymer and reduction in the volume of harmful gases release in to the atmosphere. The green polymer composites have attracted the tremendous research interest because of its source like Agricultural resources. It also improves the manufacturing and recycling process with the better environmental compatibility<sup>[20]</sup>. To enhance the ionic conductivity, doping of inorganic / organic salts is an innovative technique. It leads to improve the mechanical stability, membrane permeability and porosity. Recently the use of ionic liquid (IL) (i.e. 1-Ethyl -3-methylimidazolium tosylate) as a salt/filler replaces the inorganic/organic salt / filler, providing the eco-friendly membrane for the device application. An ionic liquid is generally defined as a salt in which the ions are poorly coordinated, with a substantially low melting point (below 100°C)<sup>[21]</sup>. In general, ILs has negligible vapour pressure, non volatile, non inflammable and atmospheric pollution free characteristic. It is thermally stable which is better in chemical processes that require heat input also. These unique characteristics make them useful for many applications and meet the criteria of “Green Chemistry”. Recently, Ionic liquids are become hot contender due to some of their important properties like large electrochemical window and capacity of elimination hazards associated with the composite membrane. It has the dual properties as ion supplying materials or like the plasticizer which collectively enhance the ionic conductivity<sup>[22-24]</sup>. Imidazolium based ionic liquid is most widely studied salt. It shows better miscibility with the polymer and provides better porous structure<sup>[25-28]</sup>. In this work, 1-Ethyl -3-methylimidazolium tosylate (Ionic liquid) was used as dopant in PCL-based polymer composite electrolyte membrane. The membrane was characterized by the study of the structural and electrical properties using different experimental tools like- X-ray diffraction (XRD), SEM, C-V measurement, FTIR, Laser Raman and AC Impedance spectroscopy.

## 2. Materials and Methods

Nanocomposite polymer electrolyte films were prepared by well known “Hot Press Method”. Polycaprolactone [(PCL) (MW~14,000 sigma Aldrich)], Ionic liquid (1-Ethyl-3-methylimidazolium tosylate) (282.36g/mol) (Aldrich, AR grade) were used as polymer matrix and salt respec-

tively. The composite film was prepared by casting it in stainless steel dye and synthesized by hot press method. For the hot press membrane synthesis, we used 55-60°C temperature and 2Kg/cm<sup>2</sup> pressure conditions in a specially designed stainless steel die. The possible schematic structure of synthesized polymer composite membrane is shown in Figure 1.

Structural behaviour of [(100-x) PCL-x IL {where x=3%, 10% and 20%}] system was evaluated by XRD pattern and recorded between 2θ=20°-60° at room temperature using Phillips X-pert diffractometer. The SEM image was obtained by JOEL, Electron Probe Micro Analyzer model JXA-8100. For making the surface electrically conductive, the sample was coated with graphite to a thickness ~20 nm using JEOL vacuum evaporator model JEE-420. The coated sample was randomly scanned and photographs were taken with SEM. To determine the electrochemical window, C-V measurement was performed on C-H Workstation (C-H instrument model CH608). The infrared spectrum was recorded on Bruker Alpha (Germany) FTIR with ATR spectrophotometer in a range 4000 – 600 cm<sup>-1</sup> at room temperature. Raman spectra were collected with Uniram Confocal Raman Spectrophotometer with laser source at 785nm with variable power in the spectra range (0-2000cm<sup>-1</sup>). The electrical conductivity was evaluated from complex impedance plot obtained using computer controlled Hioki (JAPAN)-LCZ HI Tester (model 3520-01) in the frequency range of 1Hz to 100KHz.

## 3. Results and Discussion

The XRD pattern of Pure PCL, [0.97 PCL-0.03(1-Ethyl-3-methylimidazolium tosylate)] and [0.80 PCL -0.20 (1-Ethyl-3-methylimidazolium tosylate)] composite membranes are shown in Figure 2. The XRD spectrum of pure PCL shows few crystalline peaks with semi crystalline nature. Two crystalline peaks at about 23.8° and 21.3°, indicating highly ordered chain folding characteristics. The less ordered amorphous regions in which the polymer chains are randomly arranged are thought to be initial sites of hydrolysis. The addition of Ionic Liquid (20wt %) reduces the crystallinity. The disappearance of doublet at 23.8° with broadening of 21.3° shows the modification of the matrix due to the incorporation of Ionic liquid in composite membrane.

The degree of crystallinity of the samples were calculated from the X-ray diffraction pattern, based on the following equation:<sup>[29]</sup>

$$X_c = \frac{A_c}{A_c + A_a}$$

where  $X_c$  is degree of crystallinity,  $A_c$  is crystallized

area on the X-ray diffractogram and  $A_a$  is amorphous area on the X-ray diffractogram. The degree of crystallinity of pure PCL is found to be  $\sim 91\%$  and after the composite formation it reduces to  $\sim 35\%$ . The dispersion of IL enhances the relative broadness of the characteristic peaks, indicating the increase in amorphisity. The increase in amorphisity of electrolyte is clearly observed due to possible interaction of PCL and IL as shown in schematic structure of composite material (shown in material and method section). The free flow of ions enhances the overall ionic conductivity of the membrane. The average crystallite size of the [0.80 PCL -0.20 (1-Ethyl-3-methylimidazolium tosylate)] composite membranes was evaluated by the Scherer's formula<sup>[30]</sup> and was found to be  $\sim 49$  nm.

To study the surface morphology and estimation of particle size, the SEM image of hot press synthesized pure PCL membrane and 80PCL- 20IL electrolyte membrane are shown in Figure 3. The heterogeneous nature of the composite electrolyte clearly indicates the interaction of ionic liquid with the polymeric host. On the inspection of surface morphology the distribution of nano size crystallite is observed, which supports the average size calculation of crystallite in the XRD results.

The FTIR spectra of pure PCL and [0.80 PCL -0.20 (1-Ethyl-3-methylimidazolium tosylate)] nanocomposite membranes are shown in Figure 4. The main FTIR peaks of PCL at  $2865\text{ cm}^{-1}$  and  $2943\text{ cm}^{-1}$  correspond to symmetric and asymmetric vibrations of  $\text{CH}_2$  group and the  $\text{C}=\text{O}$  vibration of ester occurs at  $1727\text{ cm}^{-1}$ . The  $\text{CH}_2$  band vibration of the polymer is present at  $1369\text{ cm}^{-1}$ ,  $1420\text{ cm}^{-1}$  and  $1450\text{ cm}^{-1}$ . The Ester  $\text{C}-\text{O}-\text{O}$  vibrations occur at  $1190\text{ cm}^{-1}$  and  $1240\text{ cm}^{-1}$ . The peak at  $1107\text{ cm}^{-1}$ ,  $1045\text{ cm}^{-1}$  and  $960\text{ cm}^{-1}$  are due to  $\text{O}-\text{C}$  vibrations with the  $\text{CH}_2$  rocking vibrations occurring at  $731\text{ cm}^{-1}$ <sup>[31]</sup>. To study the effect of IL in the nanocomposite membrane, we compare the specific area of FTIR (i.e.  $2260\text{ cm}^{-1}$  to  $2400\text{ cm}^{-1}$ ). The enlarged view of this area is also shown in the inset of Figure 4. Here we observe that peak area increases by 200% after the addition of 3% IL (1-Ethyl-3-methylimidazolium tosylate) and by 350% after the addition of 20% IL (1-Ethyl-3-methylimidazolium tosylate). This indicates that the number of more mobile charge carriers are generated due to dissociation of IL (1-Ethyl-3-methylimidazolium tosylate) and it is responsible for the quantitative change of transmittance parameter in the FTIR measurement<sup>[32]</sup>. It also indicates the better interaction of polymer salt in the nanocomposite electrolyte. The Raman study of Pure PCL and [0.80 PCL -0.20 (1-Ethyl-3-methylimidazolium tosylate)] composite membranes are shown in Figure 5.

The Raman spectrum of pure PCL exhibits three well defined peaks at  $1295\text{ cm}^{-1}$  ( $\text{CH}_2$  wagging mode) at  $1430$

$\text{cm}^{-1}$  ( $\text{CH}_2$ scissoring mode) and  $1722\text{ cm}^{-1}$  ( $\text{C}=\text{O}$  stretching mode) a small peak at  $1151\text{ cm}^{-1}$  is assigned to the stretching vibration of ethereal  $\text{C}-\text{O}-\text{C}$ , a series of peaks between  $1033\text{ cm}^{-1}$  and  $1107\text{ cm}^{-1}$ , which are assigned to the skeleton stretching and a typical finger print in the region between  $500\text{ cm}^{-1}$  and  $1000\text{ cm}^{-1}$ <sup>[33]</sup>. A comparative study show that peak area and height are reduced in the low wave number side support the better interaction in composite electrolyte. The peak around  $65\text{ cm}^{-1}$ , it could be assigned to rafting motion i.e. oscillating hindered translations of central ion inside cage made by the neighbouring ions<sup>[34]</sup>. The peak around the  $100\text{ cm}^{-1}$  wave number is giving the signature of imidazolium ion<sup>[35]</sup>. The peak around the  $1089\text{ cm}^{-1}$  show the less intensity and with two clear peaks at  $1068\text{ cm}^{-1}$  and  $1041\text{ cm}^{-1}$ . Similarly, the peak at  $1109\text{ cm}^{-1}$ ,  $1298\text{ cm}^{-1}$  and  $1444\text{ cm}^{-1}$  are  $1725\text{ cm}^{-1}$  become more intense after complexation. To check the optimum ratio for the best electrical conductivity, the variation in conductivity with varying composition of ionic liquid in [(100-x) PCL-xIL] (where  $x=3\%$  10%, 20%) composite electrolyte system was recorded and shown in Figure 6. Here it is clear that conductivity is unchanged initially upto 3% of ionic liquid composition then it starts decreasing and again increasing trend is obtained. The decrease in conductivity in the mid concentration range is possibly due to short range polymer-ion interaction i.e. small number of free charge carrier release due to dissociation of ionic liquid dissolved in electrolyte medium after this again increase is due to long range columbic force leading to re-dissociation of ions giving better conductivity. The maximum conductivity is obtained in 20% IL composition system. Beyond this concentration the synthesis and handling of film is difficult due to rubbery nature of the film. This type of behaviour could be explained on the basis of free volume model. The increase in conductivity depends on increase of number of charge carriers, which are facilitated from the salt during the increase of temperature<sup>[36]</sup>. During the temperature elevation in conducting measurement, the pseudo energy transmitted to the polymer matrix and expands the polymer matrixes, which promote the segmental motion. In present case the observed change is not much significant and incomplete range of measured temperature the conductivity is almost unchanged. The variation of bulk electrical conductivity (calculated by the cole-cole plot) with temperature of [0.80PCL-0.20 (1-Ethyl-3-methylimidazolium tosylate)] is presented in Figure 7(a). In the temperature dependence conductivity initially it is found that increase in conductivity is due to removal of adsorbed water on the polymeric composite film, beyond this the conductivity remains almost constant. This type of straight temperature dependent nature

of nano composite polymer electrolyte (NCPE) is peculiar nature of hot press synthesized polymer electrolyte system<sup>[37]</sup>. In the Temperature dependence of conductivity for the [0.80 PCL -0.20 (1-Ethyl-3-methylimidazolium tosylate)] polymer electrolyte the Vogel–Tamman–Fulcher (VTF) equation<sup>[38]</sup> is used for the linear fit and is given as:

$$\ln \sigma T^{0.5} = \ln A - \frac{B}{T - T_0}$$

where A is the pre-exponential factor which depends on the number density of charge carriers, B is the pseudo activation energy in unit of K for the redistribution of free volume, T is absolute temperature and T<sub>0</sub> is the quasi-equilibrium glass transition temperature at which free volume disappears or ionic conduction becomes frozen. T<sub>0</sub> is usually 60K, is equal or lower than glass transition temperature (T<sub>g</sub>). For the synthesised electrolyte system, calculated values of constant A and B is 1.5 x 10<sup>-1</sup> and 3462 respectively. Figure 6 presents a good fit of conductivity to the VTF equation with regression value of ~ -0.9784.

The variation of conductivity with frequency and temperature of [0.80 PCL -0.20 (1-Ethyl-3-methylimidazolium tosylate)] electrolyte system is shown in Figure 7(b). The change in conductivity shows an increasing trend with increase in temperature but it decreases with increasing frequency and then enhancement. The initial decrease in conductivity, similar to earlier discussion, is due to removal of surface adsorbed water (moisture) and then conductivity slowly increases with temperature and frequency. The decrease in conductivity at higher frequency region is due to short range interaction of ion with electrolyte. This can also be explained on the basis of electrical relaxation occurring in the lower frequency range. The variation of dielectric constant (ε') and loss (ε'') with frequency of [0.80 PCL -0.20 (1-Ethyl-3-methylimidazolium tosylate)] electrolytes are shown in Figure 8. In both the cases low frequency relaxation was observed, which is the indication of electrode polarization. The C-V measurement of hot press synthesized electrolyte membrane is shown in Figure. 9. From the figure, electrochemical stability of the membrane was found to be ± 0.8V.

#### 4. Conclusion

Polymeric membranes of PCL: Ionic Liquid were synthesized by “Hot Press Method” and characterized by XRD diffraction, FTIR, Laser Raman spectroscopy and Impedance spectroscopy. Based on experimental results it was concluded that the membrane showed better performance regarding to shrinkage, mechanical and thermal resistance. It also showed that an increase in ionic liquid

concentration in the membrane leads to higher Ionic conductivity because more carriers are available for the transport. Regarding the effect of temperature, the nature of electrical conductivity is explained on the VTF nature. Dielectric relaxation behaviour shows the low frequency dispersion. The optimal condition for the developed green polymeric membrane with composition 0.80 (PCL) - 0.20 (1-Ethyl-3-methylimidazolium tosylate), having the best electrical conductivity. This membrane is stable in electrochemical window +0.8V to -0.8V and thermal window from RT to 80°C. Therefore, it can be highlighted that the use of polymer/ ionic liquid facilitated the ionic transport in membranes and it can be considered a potential alternative for the device application.

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#### Supplements

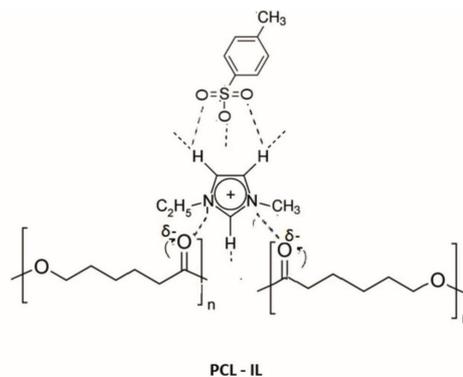


Figure 1. Possible schematic structure of synthesized polymer composite membrane

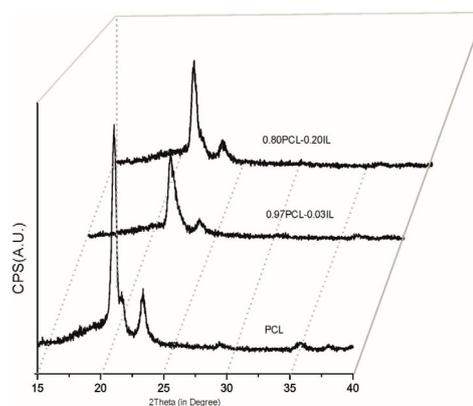


Figure 2. XRD spectra of the PCL and different PCL+IL composite system

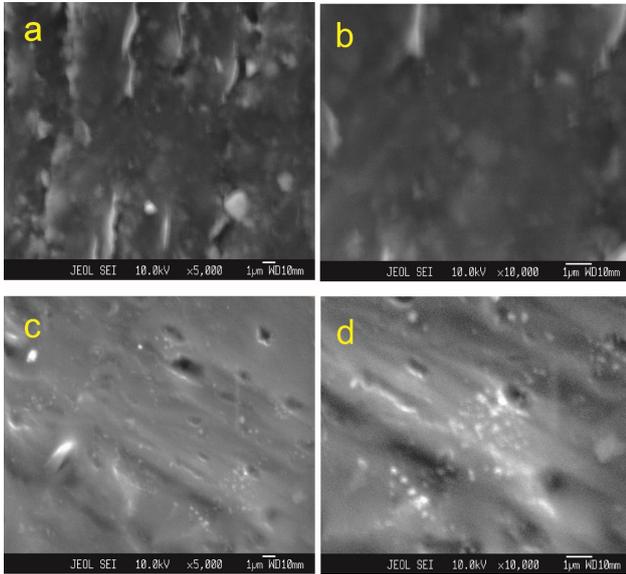


Figure 3. SEM image of (a) & (b) PCL membrane, (c) & (d) 80PCL-20IL electrolyte at two Magnifications

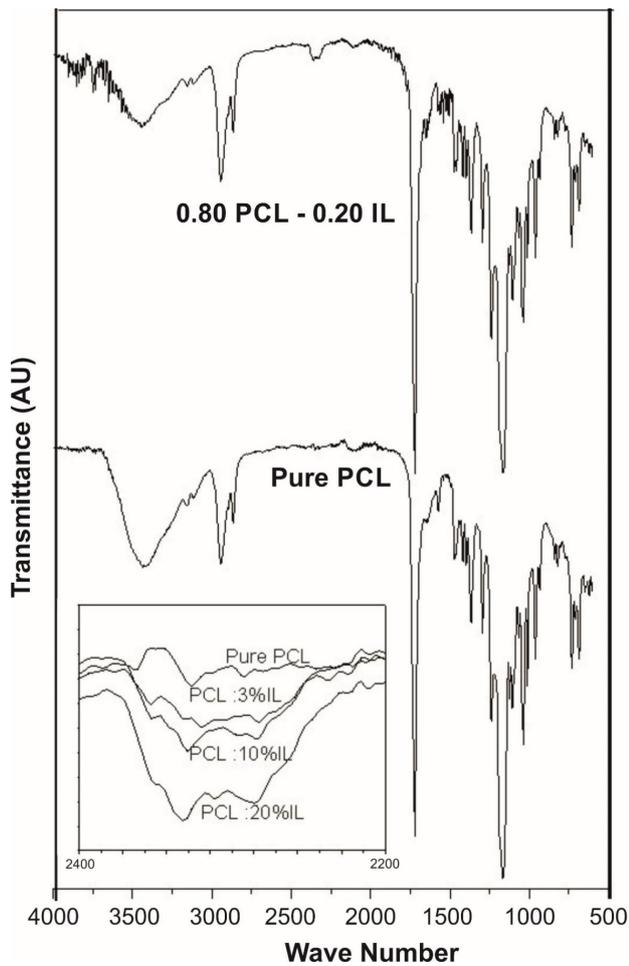


Figure 4. FTIR spectra of different constituent in polymer composite membrane

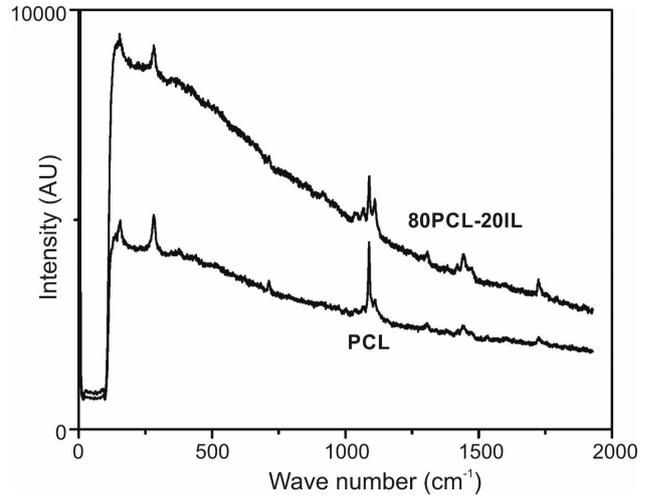


Figure 5. Raman Study of different constituent of polymer composite membrane

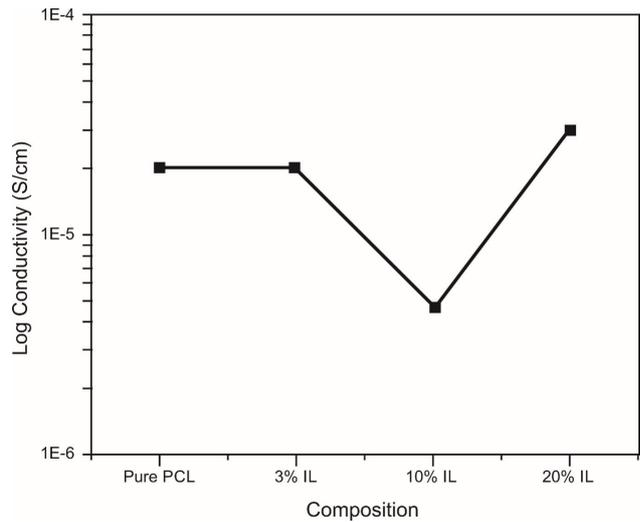


Figure 6. Variation of conductivity with different IL composition in polymer composite

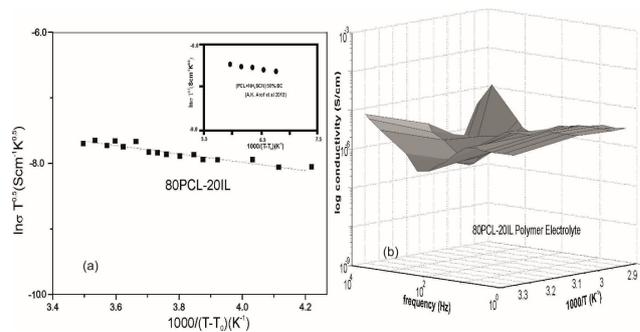
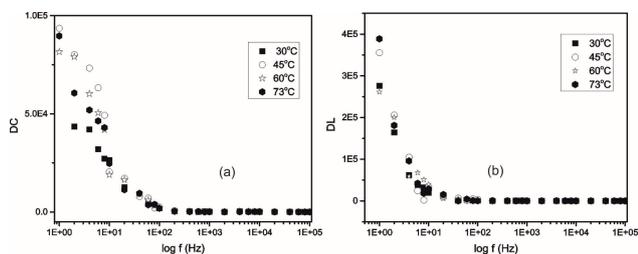
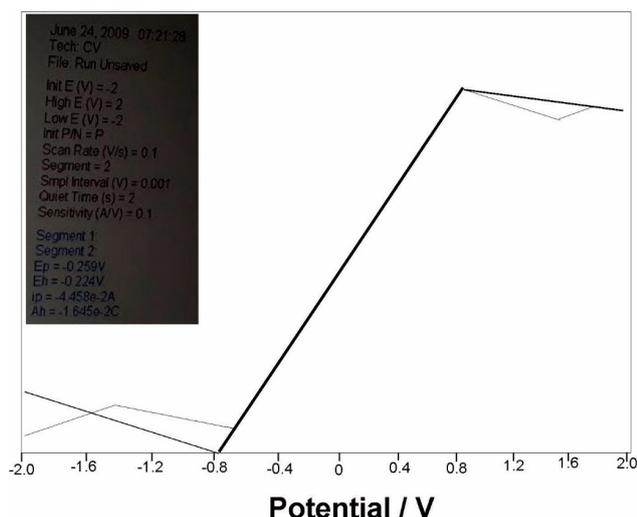


Figure 7(a). Variation of  $\ln \sigma$  with Temperature and (b): variation of conductivity with frequency and temperature in polymer composite membrane



**Figure 8.** Change in dielectric constant ( $\epsilon'$ ) and loss ( $\epsilon''$ ) with frequency of 80PCL-20IL electrolytes at different temperatures



**Figure 9.** C-V Plot of 0.80PCL -0.20IL composite electrolyte

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