Analysis of Lithium Ion Conducting P(VdCl-co-AN-co-MMA)-LiClO$_4$-DMF Tri Block Copolymer Electrolytes

Inbavalli D	S. Selvasekarapandian	C Sanjeeviraja
Research and Development Centre, Bharathiar University, Coimbatore-641 046, TAMILNADU	Materials Research Centre, Coimbatore-641 045, TAMILNADU	Department of Physics, Alagappa University, Karaikudi-630 003, TAMILNADU
R Baskaran	**Junichi Kawamura**	**Yoshitake Masuda**
Institute of Multi Disciplinary Research for Advanced Materials, Tohoku University, Sendai, JAPAN	Institute of Multi Disciplinary Research for Advanced Materials, Tohoku University, Sendai, JAPAN	National Institute of Advanced Industrial Science and Technology (AIST), Nagoya 463-8560, JAPAN

ABSTRACT *The lithium ion conducting tri block copolymer electrolytes based on Poly(vinylidene chloride-co-acrylonitrile-co-methyl methacrylate)(P(VdCl-co-AN-co-MMA):Lithium per chlorate (LiClO$_4$) (P(VdCl-co-AN-co-MMA):LiClO$_4$) and Poly(vinylidene chloride-co-acrylonitrile-co-methyl methacrylate)P(VdCl-co-AN-co-MMA):Lithium per chlorate (LiClO$_4$):Dimethyl formamide (DMF) P(VdCl-co-AN-co-MMA):LiClO$_4$:DMF of different compositions were prepared by solution casting technique. Structural and surface morphological characterizations were studied by X-ray diffraction (XRD) analysis and Scanning Electron Microscopy (SEM) measurements respectively. The interaction of Li+ ion with the copolymer and DMF has been studied by FTIR Analysis. The conductivity behaviors of copolymer:salt and copolymer:salt:plasticizer complexes were studied by employing ac impedance measurements. The highest bulk conductivity was found to be 1.36 x 10-6 S cm-1 at 303 K for the plasticized sample. The conductance, modulus, dielectric behavior and relaxation parameters of the samples have also been presented and discussed.*

1. INTRODUCTION

The science and technology challenges that need to be overcome are significant and now revolve towards greener environment, which has resulted in the rapid expansion of lithium battery industry. Today lithium ion batteries are canonical power source for all portable electronics, undoubtedly represent the most promising ubiquitous energy storage media ever invented [1,2].

The invention of the lithium-ion battery has been one of the most significant advances in electrochemical energy-storage technology. These batteries store the highest amount of energy per unit mass among the various types of rechargeable battery and are widely employed in portable electronic devices [3]. Ion-conducting polymer membranes (i.e., polymer electrolytes) are essential components of modern rechargeable lithium batteries and are now being produced as thin, compact films to enable good interfacial contact with electrodes [4]. Ionic transport occurs mainly through coupling between the ions and polymer segmental motion, and early work, using poly(ethylene oxide) (PEO) as the host polymer, showed that ionic conduction takes place mainly in the amorphous regions of the polymer–salt complexes. An understanding of the relationship between ionic conductivity and degree of solvation of lithium salts as well as the influences of the anions on the physical state of the mixtures is crucial to the effort to discover new and more effective electrolyte systems [5].

The effects of the addition of either propylene carbonate (PC) or dimethyl formamide (DMF) as plasticizers, to a cross linked amorphous polyether polymer electrolyte might enhance the ionic conductivity as both plasticizers have a relatively high dielectric constant and low viscosity however, they have different coordinating ability [6]. It has been shown that PVdF/ethylene carbonate (or PC)/Li salt polymer gel electrolytes lose carbonate solvent by evaporation, when they are exposed to an open atmosphere [7]. This solvent loss causes variation of electrolyte composition as well as low ionic con-

ductivity. GPE still does not make a popular choice for commercial application and lacks in terms of mechanical integrity and the reactivity of its interface with lithium metal electrode [8]. Thus, a polymer gel electrolyte with high ionic conductivity and little or no volatility is desired.

For the present study, the plasticizer DMF has been selected because of its low freezing and high evaporation temperatures, as well as its large dielectric constant [9] which will easily dissociate the salt into ions thereby easily enhancing the ionic conductivity. The interactions of DMF as a plasticizer have been investigated by Whang et al [10]. Bishop et al have reported on the effect of ion association in a system comprising a random copolymer of ethylene oxide and propylene oxide with LiCF$_3$SO$_3$ as the salt and DMF as the plasticizer.

In the present study the new copolymer P(VdCl-co-AN-co-MMA) has been doped with various concentrations of LiClO$_4$ and for the same system, the plasticizer DMF has been added for various compositions and the conductivity behavior of all the copolymer complexes has been analyzed. The presence of large number of polar groups such as oxygen, nitrogen and chlorine in the copolymer (Fig.1) has been a great advantage to enhance the ionic mobility. And it is interesting to note that so far no works has been reported on this copolymer which has further enhanced the curiosity to learn about the conductivity behavior of this new tri block copolymer electrolyte.
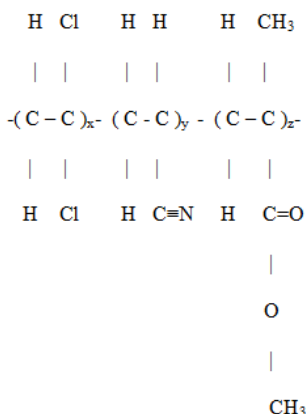
2. EXPERIMENTAL DETAILS

P(VdCl-co-AN-co-MMA)(Himedia) and LiClO$_4$ (Himedia) were dried by heating under vacuum at 100°C and 120°C for 12 h and 10 h respectively and tetrahydrofuran (THF, S.d. Fine. Chem. Ltd.) was used as the solvent. Copolymer electrolytes of P(VdCl-co-AN-co-MMA): LiClO$_4$ and the plasticized electrolytes of P(VdCl-co-AN-co-MMA):LiClO$_4$:DMF in different weight ratios have been prepared by solution-casting technique. Appropriate weights of P(VdCl-co-AN-co-MMA) and LiClO$_4$ (Table 1) were dissolved in THF. The solution was then

stirred continuously until the mixture became homogeneous viscous liquid. Similarly appropriate weights of P(VdCl-co-AN-co-MMA) and LiClO$_4$ (Table 1) were dissolved in THF followed by the addition of DMF. The solution was then stirred continuously until the mixture became homogeneous viscous liquid. These solutions of different compositions were poured into identical Petri glass dishes of 10 cm diameter. The films were dried in a vacuum chamber at room temperature for 24 h. The copolymer films were further dried in a vacuum chamber at 60°C for 5 h to remove any traces of solvent (THF) and was then stored in sealed containers in a desiccator. Gel-like and solvent-free polymer electrolyte films with thickness of (1–2) mm were obtained.

The Cu-K$_\alpha$ line was used for XRD measurements by the usual θ-2θ scan. SEM micrographs of samples were observed with a field emission scanning electron microscope (FE-SEM;JSM-6335F,JEOLLtd.). The electrical conductivity, conductance, modulus, dielectric behavior and relaxation parameters studies were carried out on the copolymer electrolyte films by using a computer-controlled HIOKI model 3532 LCZ meter of frequency range 42 Hz–5MHz at 303 K.

Fig. 1 Structure of Poly(vinylidene chloride-co-acrylonitrile-co-methylmethacrylate)

H   Cl   H   H   H   CH$_3$

 | | | | | |

-(C – C)$_x$- (C - C)$_y$ - (C – C)$_z$-

 | | | | | |

H   Cl   H   C≡N   H   C=O

                                    |

                                    O

                                    |

                                    CH$_3$

TABLE 1
COMPOSITIONS OF THE COPOLYMER AND THE SALT:

SAMPLE COMPOSITION	USED HEREAFTER AS
P(VdCl-co-AN-co-MMA) - Pure Copolymer	P(VdCl..)
70m% P(VdCl-co-AN-co-MMA):30m% LiClO$_4$	70m% P(VdCl..):30m% LiClO$_4$
50m% P(VdCl-co-AN-co-MMA):50m% LiClO$_4$	50m% P(VdCl..):50m% LiClO$_4$
45m% P(VdCl-co-AN-co-MMA):45m% LiClO$_4$+10m% DMF	45m% P(VdCl..):45m% LiClO$_4$:10m% DMF
25m% P(VdCl-co-AN-co-MMA):25m% LiClO$_4$+50m% DMF	25m% P(VdCl..):25m% LiClO$_4$:50m% DMF

To understand the mechanism of ion transport in the copolymer electrolytes, for the above system i.e. P(VdCl..):LiClO$_4$:DMF, the characterization techniques such as X-ray Diffraction (XRD) Analysis, Fourier Transform Infra Red (FTIR) Spectroscopy, Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM) and AC Impedance studies have been carried out and the obtained results have been analysed and compared with that of P(VdCl..):LiClO$_4$.

2.1 X-RAY DIFFRACTION ANALYSIS
XRD measurements were conducted to examine the nature of crystallinity of the copolymer electrolytes and to investigate the occurrence of complexation. XRD studies were performed using the XRD - RIGAKU – RINT - 2000 with Cu-K

alpha for 2theta measurements and the obtained XRD patterns of pure P(VdCl..), P(VdCl..):LiClO$_4$ complexes and P(VdCl..):LiClO$_4$:DMF complexes of different compositions have been depicted in Figs.2(a-e). The XRD pattern of pure LiClO$_4$ showed intense, sharp peaks at angles 2 = 21.78°, 27.5°, 32.99° and 36.58° and they revealed the crystalline nature of the ionic salt [JCPDS: 30-0751] [11]. The pure copolymer showed two broad diffraction peaks at 32.34° and 38.56° and another two sharp peaks at 24.88° and 15.8° as seen in Fig 2(a).

For the P(VdCl..):LiClO$_4$ complexes as shown in Fig. 2(b-c), it was found that the incorporation of LiClO$_4$ into the copolymer matrix has caused slight increase in the amorphous nature of the sample which was observed from the increase in broadness and decrease in intensity of the peaks with respect to that of the pure copolymer. This result can be interpreted by considering the Hodge et al. criterion, which has established a correlation between the intensity of the peak and the degree of crystallinity [12]. The amorphous nature has produced greater ionic diffusivity leading to high ionic conductivity. Also it was observed that in the XRD patterns of P(VdCl..):LiClO$_4$ there were no peaks corresponding to pure LiClO$_4$.

The diffractograms of P(VdCl..):LiClO$_4$:DMF complexes have been presented in the Figs. 2(d-e). It was seen that the broadness and the intensity of the same peaks mentioned above have been further increased and decreased respectively when compared with that of the P(VdCl..):LiClO$_4$ complexes. This increase in amorphous nature has enhanced the ionic conductivity of P(VdCl..):LiClO$_4$:DMF complexes.
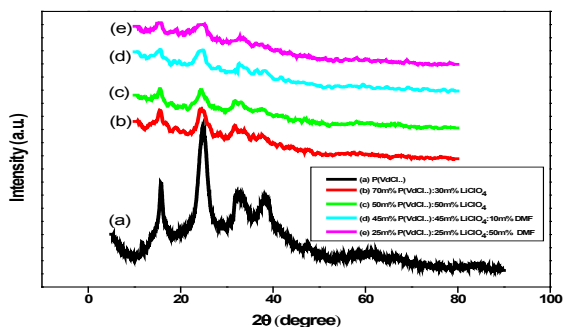
Fig. 2 XRD Diffractograms of (a). (P(VdCl..), (b). 70m% P(VdCl..):30m% LiClO$_4$ (c). 50m% P(VdCl..):50m% LiClO$_4$, (d). 45m% P(VdCl..):45m% LiClO$_4$:10m% DMF & (e). 25m% P(VdCl..):25m% LiClO$_4$:50m% DMF

2.2 MORPHOLOGICAL CHARACTERISTICS
Scanning electron micrographs (SEM) of pure P(VdCl..), P(VdCl..):LiClO$_4$ complexes and P(VdCl..):LiClO$_4$:DMF copolymer electrolyte films have been shown in Figs. 3(a-e). Fig 3(a) showed smooth and non porous morphology of pure P(VdCl..) copolymer. For 70m% P(VdCl..):30m%LiClO$_4$, many minute pores has beeen seen from the Fig. 5.2(b). When the LiClO$_4$ concentration has been increased to 50m%, the number of pores and its size has been increased as evident from Fig. 3(c).

In the micrograph of 45m% P(VdCl..):45m% LiClO$_4$:10m% DMF, a large number of ring like structure with high porosity with small pores in between the ring like structures can be seen from the Fig. 3(d) which might be due to the addition of plasticizer DMF. The size of these small pores and the ring like structure has been further increased was seen for 25m% P(VdCl..):25m% LiClO$_4$:50m% DMF which is evident from Fig. 3(e) with the increase in DMF content. This large amount of pores in the porous membrane and the increase in the size of the pores and ring like structure has enlarged the contact areas between copolymer and solvent such that the

electrolyte solution was well retained in the membrane by copolymer–solvent interactions which inturn has enhanced the conductivity [13]. Hence the conductivity was more for the copolymer complex 25m% P(VdCl..):25m% $LiClO_4$:50m% DMF which was in good agreement with the SEM micrographs.
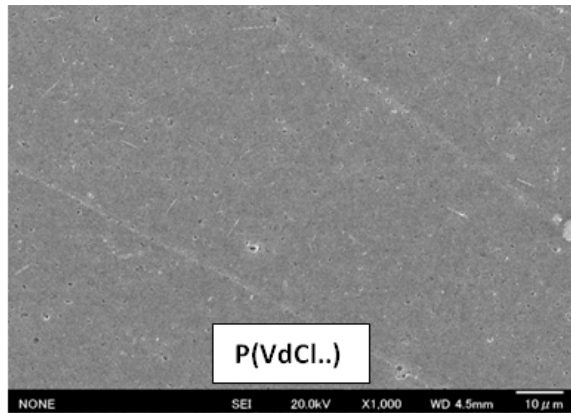

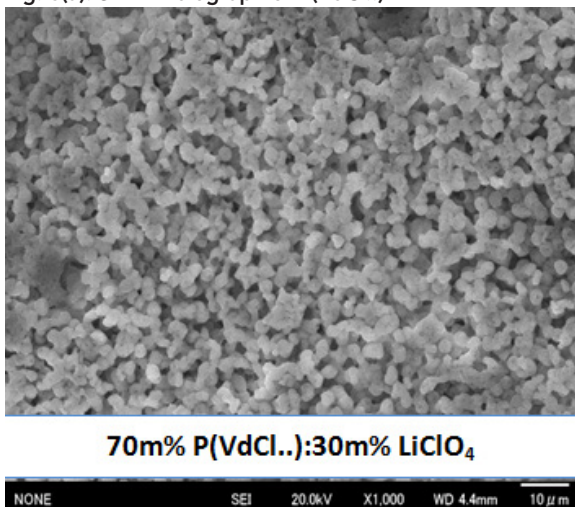
Fig. 3(a). SEM Micrograph of P(VdCl..)

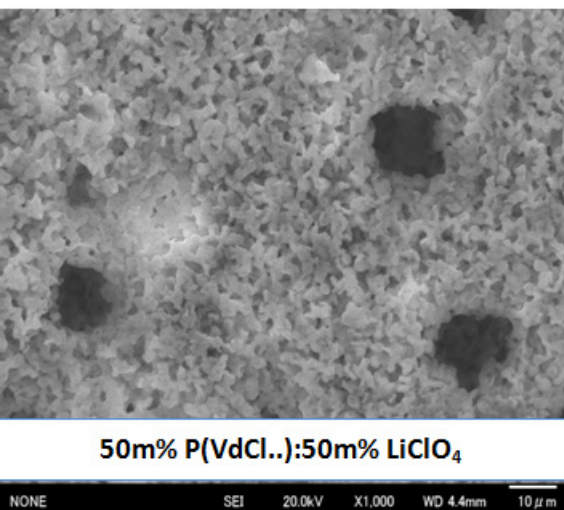Fig. 3(b) SEM Micrograph of 70m% P(VDCl) : 30m% $LiClO_4$

Fig. 3(c) SEM Micrograph of 50m% P(VDCl) : 50m% $LiClO_4$
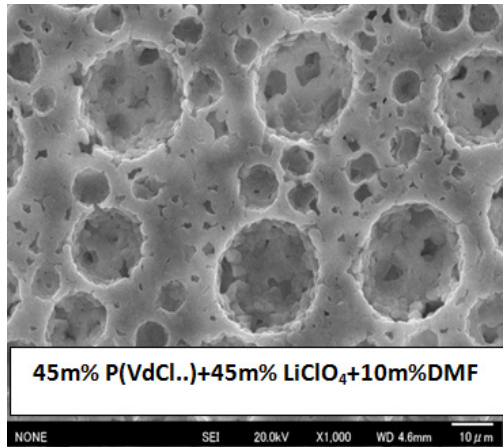
Fig. 3(d). SEM Micrograph of
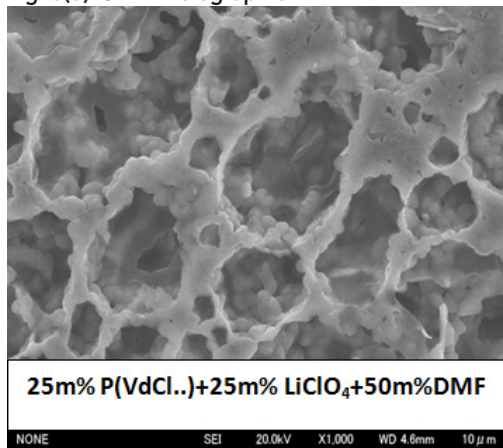
Fig. 3(e). SEM Micrograph of 25m% P(VdCl..):25m% $LiClO_4$:50m% DMF

2.3 FTIR SPECTROSCOPY:

FTIR analysis has been a powerful tool for identifying the nature of bonding and different functional groups present in a sample by monitoring the vibrational energy levels of the molecules, which were essentially the fingerprint of different molecule. It was used to characterize the chain structure of the copolymers. For the present study, the IR spectra of (a). (P(VdCl..), (b). 70m% P(VdCl..):30m% $LiClO_4$ (c). 50m% P(VdCl..):50m% $LiClO_4$, (d). 45m% P(VdCl..):45m% $LiClO_4$:10m% DMF & (e). 25m% P(VdCl..):25m% $LiClO_4$:50m% DMF were taken using Thermo Nicolet (Avatar Model) Spectrometer in the range (4000 – 400cm^{-1}) with a resolution of 1cm^{-1} and the obtained IR spectra has been shown in Fig.4.

Fig. 4 FTIR Spectra of (a). P(VdCl..), (b). 70m% P(VdCl..):30m% $LiClO_4$ (c). 50m% P(VdCl..):50m% $LiClO_4$,

(d). 45m% P(VdCl..):45m% LiClO$_4$:10m% DMF & (e). 25m% P(VdCl..):25m% LiClO$_4$:50m% DMF

In the Fig 4(a) for P(VdCl..), an absorption peak at 735.18 cm^{-1} has been observed which might be assigned to C-Cl stretching vibration of the copolymer [14]. The band appearing at 814.15 cm^{-1} might be assigned to characteristi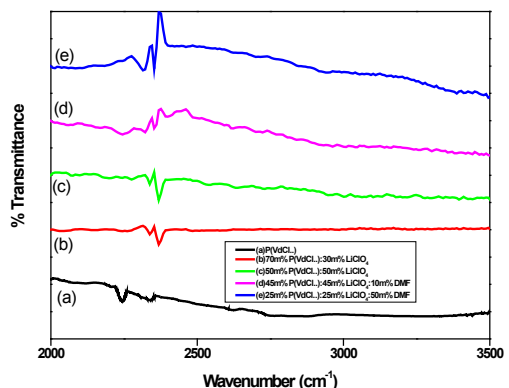c frequency of vinylidene group of P(VdCl..) [15]. The vibrational peak at 1258.11 cm^{-1} might be assigned to C-N stretching of pure PAN [15]. The vibrational peak observed at 1440.60 cm^{-1} has been assigned to H-C-H bend of the copolymer [16]. The characteristic vibrational peak which has been observed at 1696.80 cm^{-1} has been ascribed to C=O stretch of the ketonic group. Another doublet of the same peak has been observed at 1719.61 cm^{-1} [16] which might be due to repeated group of the ketone in the copolymer since P(VdCl..) was a tri block copolymer. The peak at 2289.92 cm^{-1} represented the functional group of C≡N stretch of the nitriles [14] which has been the most characteristic features of the nitriles. There was also another additional vibrational peak observed at 2335.98 cm^{-1}.

For the copolymer complexes, with the addition of LiClO$_4$ as showed in FTIR spectra of Fig. 4(b) and Fig. 4(c) it was seen that the vibrational peak observed at 2335.98 cm^{-1} in P(VdCl..) has been split into 2337.65 cm^{-1} and 2368.58 cm^{-1} for 70m% P(VdCl..):30m% LiClO$_4$ and the same doublet has been shifted to 2336.81 cm^{-1} and 2366.90 cm^{-1} respectively for 50m% P(VdCl..):50m% LiClO$_4$ as observed from Fig. (c). The peak at 2289.92 cm^{-1} of P(VdCl..) has been shifted to 2269.95 cm^{-1} for 70m% P(VdCl..):30m% LiClO$_4$ due to the interaction between Li$^+$ and C≡N of the copolymer [17] and the same peak has been shifted to 2273.30 cm^{-1} for 50m% P(VdCl..):50m% LiClO$_4$ with further addition of LiClO$_4$. These shifts in the functional group of the copolymer complexes has confirmed the definite complexation between P(VdCl..) and LiClO$_4$.

For the copolymer complexes, with further addition of DMF as showed in FTIR spectra of Fig. 4(d) and Fig. 4(e) it was seen that the vibrational peak observed at 2335.98 cm^{-1} in P(VdCl..) has been split into 2320.93 cm^{-1} and 2316.75 cm^{-1} for 45m% P(VdCl..):45m% LiClO$_4$+10m% DMF and the same doublet has been shifted to 2321.75 cm^{-1} and 2357.20 cm^{-1} for 25m% P(VdCl..):25m% LiClO$_4$+50m% DMF. The peak at 2289.92 cm^{-1} of P(VdCl..) has been shifted to 2310.90 cm^{-1} for 45m% P(VdCl..):45m% LiClO$_4$+10m% DMF due to the interaction between Li$^+$ and C≡N of the copolymer with DMF [17] and the same peak has been shifted to 2318.42 cm^{-1} for 25m% P(VdCl..):25m% LiClO$_4$+50m% DMF with further addition of DMF. The O=C-N deformation mode of DMF at 659 cm^{-1} [18] has not been observed in the copolymer complexes as showed in Fig. (d) and (e) which might be due to the definite complexation of DMF with the copolymer. These shifts in the functional group of the copolymer complexes has confirmed the complexation and interaction of P(VdCl..) and LiClO$_4$ with DMF.

Possible Interaction of Lithium ion in the Tri block Copolymer Electrolyte

2.4 DIFFERENTIAL SCANNING CALORIMETRY ANALYSIS

DSC was employed to determine the thermal behavior of P(VdCl..):LiClO$_4$ complexes and P(VdCl..):LiClO$_4$:DMF plasticized complexes with respect to that of the pure copolymer P(VdCl..). The Figs. 5(a), 5(b-c), 5(d-e) showed DSC thermograms obtained for pure P(VdCl..), P(VdCl..):LiClO$_4$ complexes and P(VdCl..):LiClO$_4$:DMF gel copolymer electrolytes of different compositions and the obtained results has been shown in the Table 2. From the Fig. 5(a), it was seen that the T$_g$ of the pure copolymer P(VdCl..) was 144.7°C.

With the addition of LiClO$_4$, the T$_g$ has been increased to 146.2°C and 147.6°C for 70m% P(VdCl..):30m% LiClO$_4$ and 50m% P(VdCl..):50m% LiClO$_4$ respectively. This increase in T$_g$ might be due to the interaction of Li$^+$ ion with the copolymer P(VdCl..). Similarly for the plasticized systems, with the addition of LiClO$_4$ and DMF the T$_g$ has increased significantly to 153.1°C and 153.6°C for 45m% P(VdCl..):45m% LiClO$_4$:10m% DMF and 25m% P(VdCl..):25m% LiClO$_4$:50m% DMF respectively as evident from the thermograms seen in Figs. 5(d-e). This increase in T$_g$ might be due to the restriction of the molecular movement of the DMF by the copolymer chains due to which the molecules get trapped within the cages formed by the polar groups in the copolymer P(VdCl..)[19].

TABLE 2

SAMPLE COMPOSITION	T$_g$ (in °C)
P(VdCl..)	144.7
70m% P(VdCl..):30m% LiClO$_4$	146.2
50m% P(VdCl..):50m% LiClO$_4$	147.6
45m% P(VdCl..):45m% LiClO$_4$:10m% EC	153.1
25m% P(VdCl..):25m% LiClO$_4$:50m% EC	153.6

T$_g$ obtained from DSC Analysis for P(VdCl..):LiClO$_4$ and P(VdCl..):LiClO$_4$:DMF copolymer systems

(a) P(VdCl..)

(b) 70m% P(VdCl..):30m% LiClO$_4$

(c) 50m% P(VdCl..):50m% LiClO₄

(d) 45m% P(VdCl..):45m% LiClO₄:10m% DMF
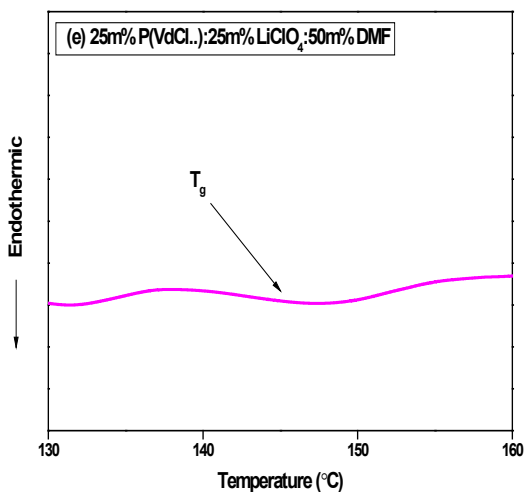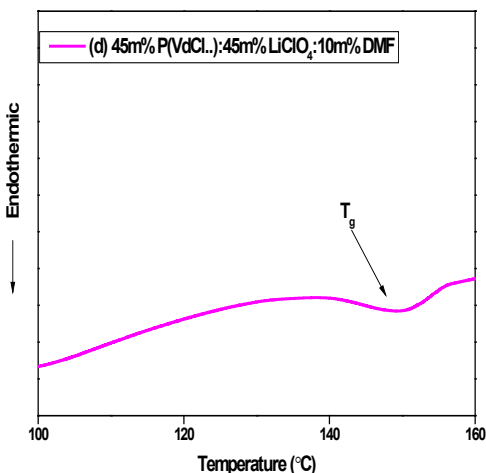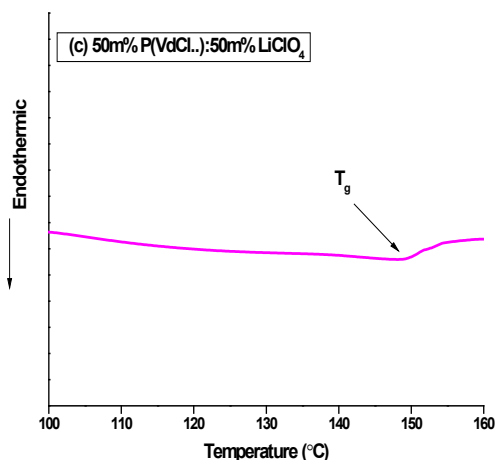

(e) 25m% P(VdCl..):25m% LiClO₄:50m% DMF

Fig. 5 DSC thermograms of DSC thermograms of (a). P(VdCl..), (b). 70m% P(VdCl..):30m% LiClO₄ (c). 50m% P(VdCl..):50m% LiClO₄, (d). 45m% P(VdCl..):45m% LiClO₄:10m% DMF & (e). 25m% P(VdCl..):25m% LiClO₄:50m% DMF

2.5 AC IMPEDANCE ANALYSIS

The ionic conductivity of the P(VdCl..):LiClO₄ systems

and P(VdCl..):LiClO₄:DMF plasticized system was derived from the complex impedance plots. The Nyquist plots for P(VdCl..):LiClO₄ and P(VdCl..):LiClO₄:DMF copolymer electrolyte samples of different compositions at 303 K have been presented in Figs. 6(a-d). The plots consisted of a high-frequency depressed semicircle represented by a frequency-dependent capacitor C_g parallel to a bulk resistor (R_b) and a low frequency spike represented by a constant phase element CPE. The high-frequency part of impedance plots can be related to bulk relaxation processes according to Armstrong's model of a solid electrolyte [20]. The low-frequency spur resulted from the electrode/electrolyte interface properties. It was noted that the semicircle depression has been decreased with the increase in LiClO₄ as seen from Figs. 6(a-c).

The EQ software program developed by Boukamp [21, 22] was used to extract the bulk electrical resistance (R_b) of the copolymer electrolytes from the impedance plot of the low-frequency side intercept on the Z' axis. The ionic conductivity was calculated using the equation

$$\sigma = L/R_b A \ (S \ cm^{-1}) \ \text{---------------------------- Equation (1)}$$

where 'L' and 'A represented the thickness and surface area of the copolymer electrolyte film respectively.

From the impedance spectra of 70m% P(VdCl..):30m% LiClO₄ and 50m% P(VdCl..):50m% LiClO₄ as seen from Figs. 6(a-b), it was observed that the value of the bulk resistance decreases with increase in LiClO₄ content which in turn has enhanced the ionic conductivity. It was seen from the Table 3 that the ionic conductivity for 70m% P(VdCl..):30m% LiClO₄ and 50m% P(VdCl..):50m% LiClO₄ was 4.89 x 10⁻⁹ S cm⁻¹ and 1.21 x 10⁻⁷ S cm⁻¹ respectively. As the LiClO₄ content has been increased from 30m% to 50m%, there was increase in conductivity due to the increase in charge carrier concentration.

Also from Table 3, the conductivity value for 45m% P(VdCl..):45m% LiClO₄:10m% DMF and 25m% P(VdCl..):25m% LiClO₄:50m% DMF was found to be 1.00 x 10⁻⁶ S cm⁻¹ and 1.36 x 10⁻⁶ S cm⁻¹ respectively. There has been considerable increase in conductivity when compared with that of the P(VdCl..):LiClO₄ system which might be due to the enhancement of the ionic mobility and number of carrier ions due to the plasticizing effect of DMF as many previous workers have already reported [23,24].
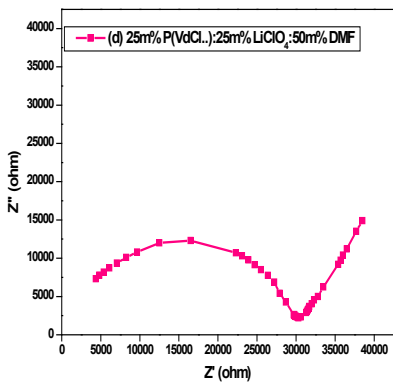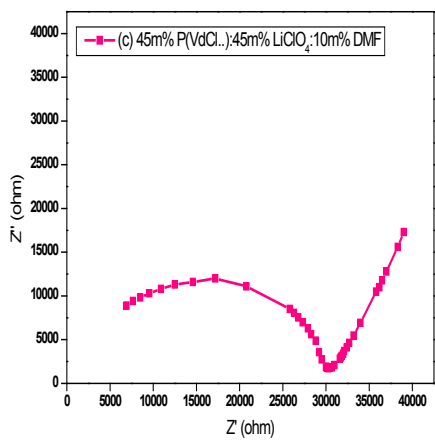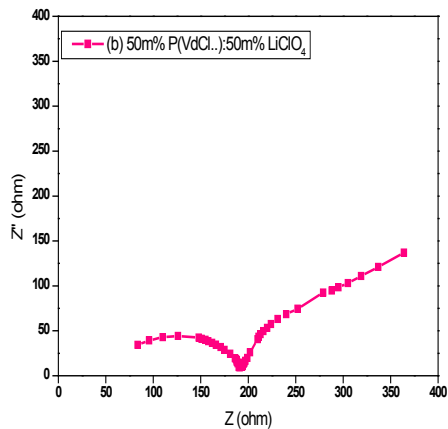

(a) 70m% P(VdCl..):30m% LiClO₄
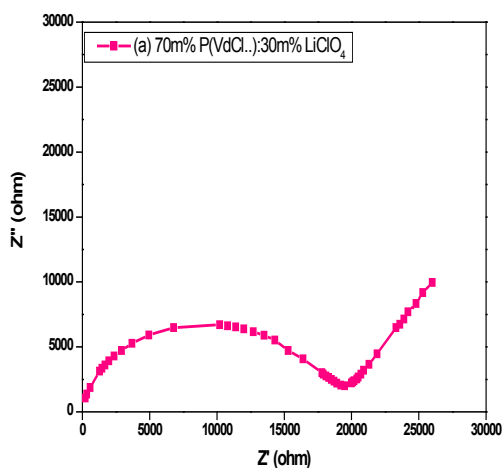
Fig. 6 Nyquist Plots of (a) 70m% P(VdCl..):30m% LiClO$_4$ (b). 50m% P(VdCl..):50m% LiClO$_4$, (c). 45m% P(VdCl..):45m% LiClO$_4$:10m% DMF & (d). 25m% P(VdCl..):25m% LiClO$_4$:50m% DMF at 303 K

TABLE 3
Ionic conductivity from Nyquist plot of P(VdCl..): LiClO$_4$ & P(VdCl..): LiClO$_4$:DMF copolymer complexes

VARIOUS COMPOSITIONS OF CO-POLYMER ELECTROLYTES	σ FROM NYQUISTPLOT (S cm^{-1})
70m% P(VdCl..):30m% LiClO$_4$	4.89 x 10^{-9}
50m% P(VdCl..):50m% LiClO$_4$	1.21 x 10^{-7}
45m% P(VdCl..):45m% LiClO$_4$:10m% DMF	1.00 x 10^{-6}
25m% P(VdCl..):25m% LiClO$_4$:50m% DMF	1.36 x 10^{-6}

2.6 CONDUCTANCE SPECTRAL ANALYSIS
The logarithmic plots of the conductivity as a function of angular frequency for P(VdCl..):LiClO$_4$ & P(VdCl..):LiClO$_4$:DMF copolymer complexes have been shown in the Fig. 7. As seen from Fig. 7, the conductance spectra showed three regions, low frequency dispersion region due to the electrode polarization effects, frequency independent plateau region in the mid frequency range representing the d.c. conductivity and dispersive region at high frequencies for both the P(VdCl..):LiClO$_4$ & P(VdCl..):LiClO$_4$:DMF copolymer complexes.

The d.c conductivity was calculated using Jonscher's power law and it was found to vary with angular frequency ω which is given by,

$$\sigma_{a.c} = \sigma_{d.c} + A\,\omega^n \text{----------------------------- Equation (2)}$$

where $\sigma_{a.c}$, $\sigma_{d..c}$ represented a.c and d.c conductivity respectively and A and n represented the temperature dependent parameters. The calculated d.c conductivity has been shown in Table 4.
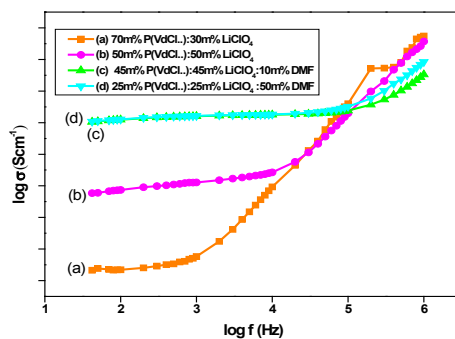
Fig. 7 Conductance Spectra of (a) 70m% P(VdCl..):30m% LiClO$_4$ (b). 50m% P(VdCl..):50m% LiClO$_4$, (c). 45m% P(VdCl..):45m% LiClO$_4$:10m% DMF & (d). 25m% P(VdCl..):25m% LiClO$_4$:50m% DMF at 303 K

From the Table 4, it was seen that for P(VdCl..): LiClO$_4$ complexes, high conductivity has been found for 50m% P(VdCl..):50m% LiClO$_4$ which can be attributed to the increase in charge carrier concentration and the mobility of ions [25]. In the P(VdCl..):LiClO$_4$:DMF system, the highest conductivity has been found for 25m% P(VdCl..):25m% LiClO$_4$:50m% DMF which was due to the plasticizing effect of DMF.

At low frequencies, the ionic conductivity was high enough to produce the buildup of charges at the electrodes which has reduced the effective applied field and hence has enhanced the conductivity. At high frequencies, the period of applied field was too short for the charging to occur and the a.c conductivity was generally taken to assume the frequency independent value, which was equal to the d.c conductivity. The extrapolation of the d.c plateau on the log σ axis has given the d.c conductivity [26]. The $\sigma_{d.c}$ values obtained from conductance spectra as seen from Table 4 was in good agreement with the values obtained from Nyquist plot of P(VdCl..): LiClO$_4$.

TABLE 4
Calculated $\sigma_{d.c}$(S cm^{-1}) from Conductance Spectra for the copolymer electrolytes

VARIOUS COMPOSITIONS OF CO-POLYMER ELECTROLYTES	$\sigma_{d.c}$ FROM CONDUCTANCE SPECTRA (S cm^{-1})
70m% P(VdCl..):30m% LiClO$_4$	2.10 x 10^{-8}
50m% P(VdCl..):50m% LiClO$_4$	6.52 x 10^{-6}
45m% P(VdCl..):45m% LiClO$_4$:10m%	7.97 x 10^{-5}
25m% P(VdCl..):25m% LiClO$_4$:50m% DMF	8.39 x 10^{-5}

2.7 MODULUS SPECTRAL ANALYSIS:

The complex electric modulus was first applied to the study of glasses by Macedo et al in studies of the dielectric properties of alkali silicate glass and was given by the equation,

$$M^* = M' + jM'' = j\omega C_0 Z^* \text{ ----------------------- Equation (3)}$$

Here, the real and imaginary parts of the modulus are plotted against logω for different salt concentrations. For both the systems [Fig.8 (I) & Fig.8 (II)], the value of M' and M'' showed an increase at the high frequency end which may be due to the bulk effect of the copolymer electrolyte. At low frequencies M' and M'' approach to zero indicating that the electrode polarization phenomena make a negligible contribution [27].
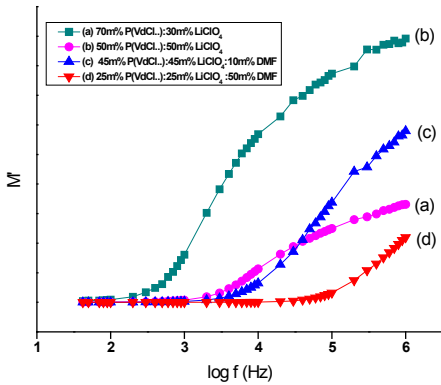
Fig. 8 (I). Modulus Spectra of (a) 70m% P(VdCl..):30m% LiClO$_4$ (b). 50m% P(VdCl..):50m% LiClO$_4$, (c). 45m% P(VdCl..):45m% LiClO$_4$:10m% DMF & (d). 25m% P(VdCl..):25m% LiClO$_4$:50m% DMF at 303 K
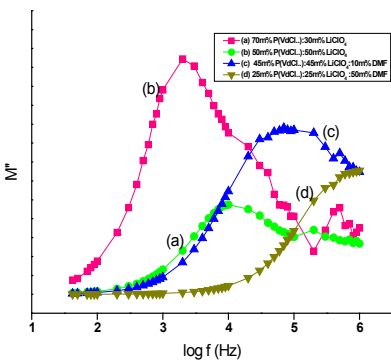
Fig. 8(II). Modulus Spectra of (a) 70m% P(VdCl..):30m% LiClO$_4$ (b). 50m% P(VdCl..):50m% LiClO$_4$, (c). 45m% P(VdCl..):45m% LiClO$_4$:10m% DMF & (d). 25m% P(VdCl..):25m% LiClO$_4$:50m% DMF at 303 K

2.8 DIELECTRIC SPECTRAL ANALYSIS

The complex permittivity (ε') or dielectric constant of a system has been defined defined by

$$\varepsilon^* = \varepsilon' - j\,\varepsilon'' = \varepsilon' - j\,(\sigma/\omega\varepsilon_0) \text{ ----------------------- Equation (4)}$$

where ε', ε'', σ, represented the real and imaginary part of dielectric constant of the material, is the conductivity, ω is the angular frequency and ε$_0$ is the permittivity of the free space. The Figs 9(a) & 9(b) showed ε' Vs log f and ε'' Vs log f plots for P(VdCl..):LiClO$_4$ & P(VdCl..):LiClO$_4$:DMF copolymer complexes respectively. It was seen from the Fig. 9(a) and 9(b) that for both the P(VdCl..):LiClO$_4$ & P(VdCl..):LiClO$_4$:DMF systems, the dielectric permittivity has risen sharply towards low frequencies which was due to the electrode polarization effects [28]. The low frequency dispersion region has been attributed to the contribution of charge accumulation at the electrode-electrolyte interface. At high frequencies, due to

high periodic reversal of the field at the interface, the contribution of charge carriers (ions) towards the dielectric constant decreases with increasing frequency. Hence ε' decreases with increasing frequency.

From the Fig. 9(b), it was observed that the dielectric loss (ε'') has becomes very large (~40 x10^3) at lower frequencies due to free charge motion within the material [29]. These values do not correspond to the bulk dielectric processes but were due to the free charges build up at the interface between the material and the electrodes. At very low frequencies there was time for charges to build up at the interfaces before the field changes the direction and this has contributed to very large apparent values of ε''. This phenomenon has lead to the so called "conductivity relaxation" [30].

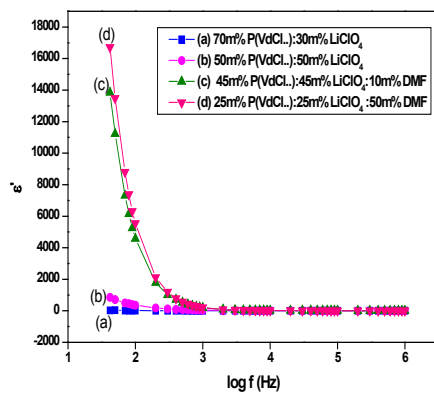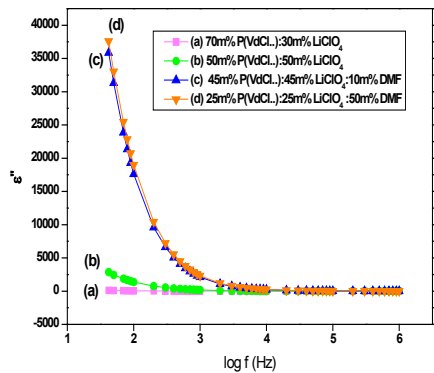**Fig. 9(a). Dielectric Spectra of (a) 70m% P(VdCl..):30m% LiClO$_4$(b). 50m% P(VdCl..): 50m% LiClO$_4$, (c). 45m% P(VdCl..):45m% LiClO$_4$:10m% DMF & (d). 25m% P(VdCl..):25m% LiClO$_4$:50m% DMF at 303 K**

Fig. 9(b). Dielectric Spectra of (a) 70m% P(VdCl..):30m% LiClO$_4$ (b). 50m% P(VdCl..): 50m% LiClO$_4$, (c). 45m% P(VdCl..):45m% LiClO$_4$:10m% DMF & (d). 25m% P(VdCl..):25m% LiClO$_4$:50m% DMF at 303 K

2.9 LOSS TANGENT SPECTRAL ANALYSIS

The dielectric relaxation parameter of the copolymer complexes P(VdCl..):LiClO$_4$ & P(VdCl..):LiClO$_4$:DMF have been obtained from the plot of Tan δ as a function of frequency

$$\text{Tan } \delta = \varepsilon''/\,\varepsilon' \text{ ----------------------- Equation (5)}$$

The variation of Tan δ with frequency has been presented in Fig. 10 for all the copolymer complexes P(VdCl..):LiClO$_4$ & P(VdCl..):LiClO$_4$:DMF at 303 K. It has been observed that for all the copolymer complexes as showed in Fig.10, Tan δ has increased with increasing frequency, reached a maximum and then decreased with further increase of frequency. For the maximum dielectric loss, the loss tangent peak was described the relation

$$\omega\tau = 1 \text{ ----------------------------Equation (6)}$$

where τ and ω represented the relaxation time and angular frequency of the applied electric field respectively [31]. The relaxation parameters for all the copolymer complexes at 303 K has been calculated and tabulated in Table 5.

From Table 5, it was seen that the relaxation time (τ) has decreased from 9.05×10^{-3} s for 70m% P(VdCl..):30m% LiClO$_4$ to 1.67×10^{-3} s for 50m% P(VdCl..):50m% LiClO$_4$. The relaxation time has further decreased from 3.71×10^{-4} s for 45m% P(VdCl..):45m% LiClO$_4$:10m% DMF to 3.09×10^{-4} s for 25m% P(VdCl..):25m% LiClO$_4$:50m% DMF. This decrease in relaxation time τ has enhanced the ionic conductivity. From Table 5, it was noted that the relaxation time was lowest for 25m% P(VdCl..):25m% LiClO$_4$:50m% DMF and hence exhibit highest ionic conductivity which was in good agreement with the result of Nyquist plots.
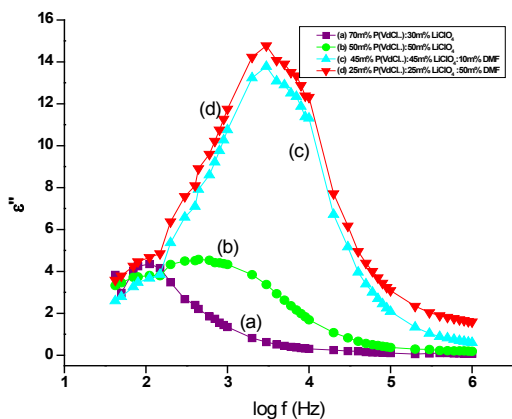

Fig. 10 Loss Tangent Spectra of (a) 70m% P(VdCl..):30m% LiClO$_4$ (b). 50m% P(VdCl..): 50m% LiClO$_4$, (c). 45m% P(VdCl..):45m% LiClO$_4$:10m% DMF & (d). 25m% P(VdCl..):25m% LiClO$_4$:50m% DMF at 303 K

TABLE 5 Calculated Dielectric relaxation parameters for the copolymer complexes

SAMPLE COMPOSITION	RELAXATION FREQUENCY log ω_m (Hz)	ω_m (Hz)	RELAXATION TIME τ (s)
70m% P(VdCl..):30m% LiClO$_4$	2.0434	1.105×10^2	9.05×10^{-3}
50m% P(VdCl..):50m% LiClO$_4$	2.7076	6.000×10^2	1.67×10^{-3}
45m% P(VdCl..):45m% LiClO$_4$:10m% DMF	3.4304	2.695×10^3	3.71×10^{-4}
25m% P(VdCl..):25m% LiClO$_4$:50m% DMF	3.5103	3.238×10^3	3.09×10^{-4}

3.0 CONCLUSION

The tri block copolymer electrolytes of P(VdCl..):LiClO$_4$ and P(VdCl..):LiClO$_4$:DMF complexes of various compositions have been prepared by solution casting method. The XRD studies revealed the increase in amorphous nature of P(VdCl..):LiClO$_4$:DMF complexes and thereby produced greater ionic diffusivity when compared with that of P(VdCl..):LiClO$_4$ complexes. The SEM micrographs revealed increase in porosity and size of the pores for the P(VdCl..):LiClO$_4$ complexes. There was further increase in the porosity and the size of the pores along with the presence of ring like structures for the P(VdCl..):LiClO$_4$:DMF complexes.

From the FTIR Spectra, the vibrational peak at 2335.98 cm^{-1} in P(VdCl..) has been split into 2321.61 cm^{-1} and 2352.70 cm^{-1} for 45m% P(VdCl..):45m% LiClO$_4$:10m% DMF and the same doublet has been shifted to 2320.93 cm^{-1} and 2316.75 cm^{-1} respectively for 25m% P(VdCl..):25m% LiClO$_4$:50m% DMF. Similarly, the peak at 2289.92 cm^{-1} [1] of P(VdCl..) has been shifted to 2321.75 cm^{-1} and 2357.20 cm^{-1} for 45m% P(VdCl..):45m% LiClO$_4$:10m% DMF and 25m% P(VdCl..):25m% LiClO$_4$:50m% DMF respectively. These shifts in the functional group of the copolymer complexes has confirmed the definite complexation and interaction of P(VdCl..) and LiClO$_4$ with DMF.

DSC measurements revealed increase in T$_g$ with increase in LiClO$_4$ content for P(VdCl..):LiClO$_4$ system because of the interaction of Li$^+$ with the polar groups of the copolymer. The T$_g$ has been further increased for P(VdCl..):LiClO$_4$:DMF complexes due to the restriction of the molecular movement of DMF by the copolymer chains due to which the molecules get trapped within the cages formed by the polar groups in the copolymer P(VdCl..).

The ionic conductivity was found to exhibit increasing trend with increasing salt concentration. For the P(VdCl..):LiClO$_4$ systems, the maximum conductivity was found to be 1.21×10^{-7} S cm^{-1} for 50m% P(VdCl..) : 50m% LiClO$_4$. But the highest conductivity of 1.36×10^{-6} S cm^{-1} was obtained for 25m% P(VdCl..):25m% LiClO$_4$:50m% DMF for the plasticized system. The low frequency dispersion of dielectric constant for both the P(VdCl..):LiClO$_4$ and P(VdCl..):LiClO$_4$:DMF complexes revealed the space charge effects arising from the electrodes. From the loss tangent spectra, it was found that the relaxation time (τ) was lowest for 25m% P(VdCl..):25m% LiClO$_4$:50m% DMF and hence exhibited high ionic conductivity.

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