

# <sup>1</sup>H NMR, Thermal, and Conductivity Studies on PVAc Based Gel Polymer Electrolytes

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**ABSTRACT:** The lithium-ion conducting gel polymer electrolytes (GPE), PVAc-DMF-LiClO<sub>4</sub> of various compositions have been prepared by solution casting technique. <sup>1</sup>H NMR results reveal the existence of DMF in the gel polymer electrolytes at ambient temperature. Structure and surface morphology characterization have been studied by X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM) measurements. Thermal and conductivity behavior of polymer- and plasticizer-salt complexes have been studied by differential scanning calorimetry (DSC), TG/DTA, and impedance spectroscopy results. XRD and SEM analyses indicate the amorphous nature of the gel polymer-salt complex. DSC measurements show a decrease in  $T_g$  with the increase in

DMF concentrations. The thermal stability of the PVAc : DMF : LiClO<sub>4</sub> gel polymer electrolytes has been found to be in the range of (30–60°C). The dc conductivity of gel polymer electrolytes, obtained from impedance spectra, has been found to vary between  $7.6 \times 10^{-7}$  and  $4.1 \times 10^{-4}$  S cm<sup>-1</sup> at 303 K depending on the concentration of DMF (10–20 wt %) in the polymer electrolytes. The temperature dependence of conductivity of the polymer electrolyte complexes appears to obey the VTF behavior. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1945–1954, 2008

**Key words:** gel polymer electrolytes; ionic conductivity; PVAc; VTF behavior; DSC; TG/DTA; <sup>1</sup>H NMR

## INTRODUCTION

Extensive commercial interest in new portable and renewable energy sources has been the driving force for the development of rechargeable lithium-based polymer-batteries.<sup>1</sup> Conventional poly(ethylene oxide) (PEO) based polymer electrolytes are the most commonly studied, and exhibited conductivities ranging from  $10^{-8}$  to  $10^{-5}$  S cm<sup>-1</sup> at room temperature, which excludes practical application at ambient temperature.<sup>2</sup> To achieve high conductivity, many researchers add plasticizers with solid polymer electrolytes and achieve conductivity enhancement.<sup>3–5</sup>

In most of the plasticized systems such as P(VCAC),<sup>6</sup> P(VdF-HFP),<sup>7</sup> and PMMA,<sup>8</sup> both high conductivity ( $\sim 10^{-3}$  S cm<sup>-1</sup>) and relatively good electrochemical properties have been achieved. The plasticizer substantially reduces the brittleness of many polymers because the addition of even small quantities of the plasticizer markedly reduces the glass transition temperature,  $T_g$  of the polymer. It is

well established<sup>9–11</sup> that ion conduction takes place predominantly in the amorphous region, and that high segmental mobility of the polymers corresponding to low glass transition temperature ( $T_g$ ) ensures high mobility of the dissociated ions. The increasing volume fraction of the amorphous domains and the decreasing  $T_g$  appear to be the main path for obtaining better ionic conductivity. The effect of the addition of plasticizers such as EC, PC, and DMF etc. to polymer electrolytes and its effect on conductivity have been investigated by many workers.<sup>12,13</sup>

In the present study, the plasticized polymer electrolytes composed of the PVAc : DMF : LiClO<sub>4</sub> have been studied. The effect of the plasticizer (DMF) concentration on the conductivity has been discussed on the basis of conductance and impedance spectroscopy analysis at various temperatures. The results have been compared with the PVAc-LiClO<sub>4</sub> solid polymer electrolyte systems. <sup>1</sup>H NMR measurements have been carried out to confirm the existence of DMF in the polymer electrolyte matrix. Structural characteristics of these electrolytes have been studied by XRD and SEM analysis. Glass transition temperature ( $T_g$ ) has been obtained from the DSC analysis and thermal stability of these gel electrolytes have been discussed using TG/DTA.

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TABLE I  
<sup>1</sup>H NMR Results of PVAc : LiClO<sub>4</sub> : DMF (wt %) Gel Polymer Electrolyte

Sample	Presence of proton					
	CH <sub>3</sub> (PVAc) (ppm)	CH <sub>3</sub> (DMF) (ppm)	CH <sub>2</sub> (ppm)	New peak (ppm)	CH (PVAc) (ppm)	CH (DMF) (ppm)
D-Acetone	2.2789			3.06361		
THF			1.4172, 3.2597			
DMF		2.537, 2.706				7.779
PVAc	2.0277 (End chain), 2.192			3.047 (D-Acetone)	5.106	
80PVAc : 20DMF	1.983, 2.1414	2.944, 3.116		3.7859	5.056	8.123
90PVAc : 10LiClO <sub>4</sub>	1.88, 2.066			3.72	4.979	
80PVAc : 10LiClO <sub>4</sub> : 10DMF	1.96, 2.16	2.97, 3.13		3.46, 3.79	5.05	8.131
75PVAc : 10LiClO <sub>4</sub> : 15DMF	1.95, 2.12	2.95, 3.12		3.49, 3.77	5.03	8.139
70PVAc : 10LiClO <sub>4</sub> : 20DMF	1.94, 2.11	2.94, 3.1		3.51, 3.75	5.01	8.123

### EXPERIMENTAL ANALYSIS

PVAc (Himedia) and LiClO<sub>4</sub> (Himedia) are dried under vacuum at 100 and 120°C for 12 and 10 h, respectively. *N,N*-Dimethylformamide (DMF) (E-Merck) and THF (S.d.fine. chem.) are used as plasticizer and solvent, respectively. The gel samples of PVAc-DMF-LiClO<sub>4</sub> at different weight ratios have been prepared by solution cast technique. The appropriate weight ratios of PVAc and LiClO<sub>4</sub> (Table I), are dissolved in THF (tetrahydrofuran) followed by the addition of plasticizer (DMF). The solution is then stirred continuously until the mixture took a homogeneous viscous liquid appearance. The viscous solution is dispersed on a Petri dish and dried for 48 h at 45°C in a vacuum oven. The films are further dried for 5 h in vacuum at 60°C to remove any trace of tetrahydrofuran. Gel-like and solvent-free polymer electrolyte films with thickness of 1–2 mm are obtained. The polymer electrolytes of various weight ratios such as 80 : 10 : 10; 75 : 15 : 10 and 70 : 20 : 10 (PVAc : DMF: LiClO<sub>4</sub>) have been prepared. The (PVAc : DMF : LiClO<sub>4</sub>) complex formation has already been confirmed by FTIR spectral analysis in earlier report.<sup>14</sup>

The resulting transparent films are characterized by structural, thermal, and electrical analyses. The gel polymer electrolytes and their constituents are dissolved in Acetone-*d*<sub>6</sub> (99.9%, Wako pure chem. Ltd.) solvent for <sup>1</sup>H NMR measurements. <sup>1</sup>H NMR measurements for PVAc : DMF : LiClO<sub>4</sub> gel polymer electrolytes and their constituents have been carried out at 303 K by using Bruker Avance 400 spectrometer at a Larmor frequency of 400 MHz, 9.4 Tesla under static probe condition with reference to the compound tetramethylsilane (TMS) (99.9+%, NMR grade, Sigma Aldrich). The proton peaks have been deconvoluted by using 1D WIN NMR (Bruker) software. The Cu-K<sub>α</sub> line has been used for XRD measurements by the usual θ–2θ scan. SEM micrographs of dried and platinum coated (~ 30 nm) membrane

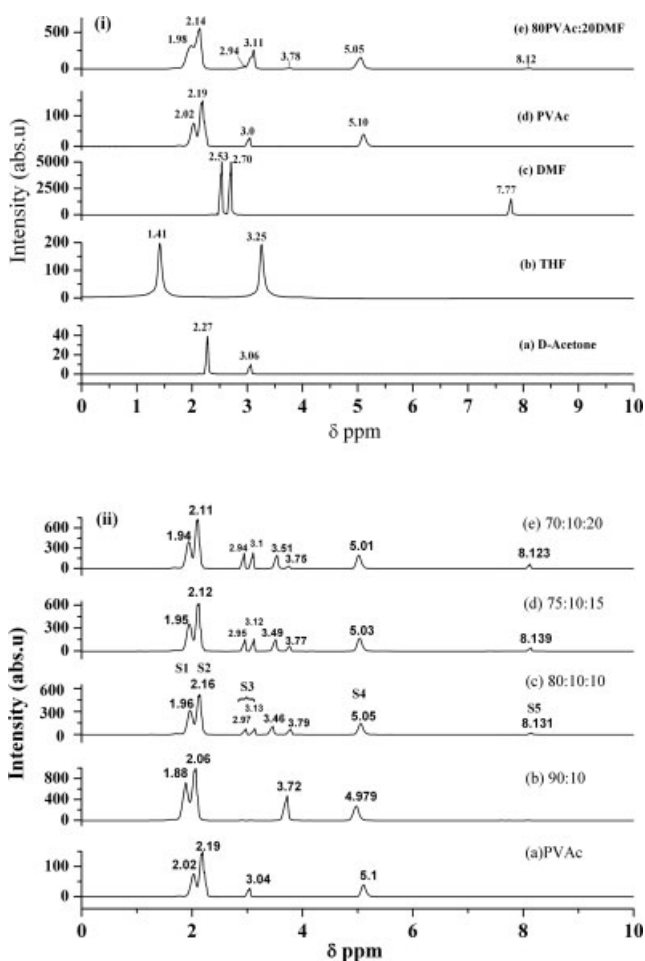
samples are taken with a Philips XL-30 instrument. The glass transition temperature, *T*<sub>g</sub> of different samples are obtained from DSC measurements performed using a MAS-5800, model DSC-200 differential scanning calorimeter. Thermal stability (TG/DTA) of the electrolytes is studied using STA-1500 thermal analyzer with a resolution of 0.01 mg. The sample is taken in a ceramic crucible and heated from room temperature to 560/400°C.

The electrical conductivity studies are carried out on the polymer electrolyte films with aluminium blocking electrodes by using a computer controlled HIOKI model 3532 LCZ meter of frequency range of 42 Hz–5 MHz and in the temperature range of 303–373 K. Before taking the electrical studies, the samples are heated to 373 K to remove the solvent traces.

### RESULTS AND DISCUSSION

#### <sup>1</sup>H NMR analysis

<sup>1</sup>H NMR measurements have been carried out to confirm the existence of DMF, in the gel polymer electrolytes. Figure 1(i,ii) shows the <sup>1</sup>H NMR spectrum for various compositions of PVAc : LiClO<sub>4</sub> : DMF gel polymer electrolytes with their constituents THF, DMF, PVAc, and D-Acetone solvent. The peak positions and attributions for all the raw materials and the gel polymer electrolytes have been extracted from the <sup>1</sup>H NMR spectra and tabulated in Table I. In Figure 1(ib), the solvent THF shows two sharp peaks at 1.41 and 3.25 ppm which are corresponding to proton in CH<sub>2</sub> of THF. <sup>1</sup>H NMR spectrum of plasticizer DMF shows [Fig. 1(i,c)] two methyl proton peaks at 2.53, 2.706 ppm and a proton (CH) peak at 7.77 ppm. <sup>1</sup>H NMR spectrum of PVAc shows [Fig. 1(i,d)] two methyl proton peaks at 2.0277 and 2.192 ppm which are corresponding to end chain of CH<sub>3</sub> and CH<sub>3</sub> in each monomer unit, respectively. When the PVAc matrix is plasticized with DMF, the methyl



**Figure 1** (i-ii) <sup>1</sup>H-NMR spectra for various ratios of PVAc : LiClO<sub>4</sub> : DMF gel polymer electrolytes and its constituents.

proton peaks of PVAc have been found to be broadened as shown in Figure 1(i,e) and two peaks at 2.94 and 3.116 ppm corresponding to methyl proton of DMF have appeared. Also, a new peak at 3.78 ppm with very less intensity has appeared which might be due to the interaction of PVAc with DMF plasticizer.

In Figure 1(ii,b) the 90PVAc : 10LiClO<sub>4</sub> polymer electrolyte matrix, a new peak at 3.72 ppm have been observed. The cause for appearance of new peak and peak shift observed in the PVAc : LiClO<sub>4</sub> matrix may be due to the Li<sup>+</sup> interaction with carbonyl oxygen and C(O)—O—C ester oxygen, which disturbs the delocalization of electrons in the ester oxygens, and hence an inductive withdrawal of electron density from the ester linkage through the C=O.<sup>15,16</sup> In Figure 1(ii,c) the plasticized PVAc : LiClO<sub>4</sub> : DMF matrix, a pair of less intense peaks at 2.97 and 3.13 ppm corresponding to methyl proton of DMF have been found. Intensity of the methyl proton peaks of DMF has been found to increase when the ratio of DMF increases from 10 to 20 wt %

in the PVAc : LiClO<sub>4</sub> polymer matrix. It is interesting to note that the new proton peak observed at 3.72 ppm in the 90PVAc : 10LiClO<sub>4</sub> matrix has been found to be shifted from 3.79 to 3.75 ppm in the DMF plasticized PVAc : LiClO<sub>4</sub> polymer electrolyte matrix, [Fig. 1(ii,c-e)] and also the intensity of the peak is decreased when the DMF content is increased. In the 10 wt % DMF plasticized system a new peak at 3.46 ppm has been observed and the intensity has been found to increase when the DMF content is increased. The cause for the appearance of new peak at 3.46–3.51 ppm in the gel polymer electrolytes, and the intensity increase might be because of the increase in number of lithium ion interaction with DMF plasticizer. The decrease in the intensity of the peak appeared at 3.79–3.75 in the gel polymer electrolytes may be because of the decrease in number of Li<sup>+</sup> ion interaction with PVAc since the DMF concentration is high. However, the exact reason for the new proton peaks corresponding to the location of proton in the gel polymer electrolytes could not be understood. The existence of DMF in the PVAc : LiClO<sub>4</sub> : DMF polymer electrolyte matrix, and the interaction of DMF with PVAc have been confirmed from the <sup>1</sup>H NMR results. The <sup>1</sup>H NMR results of all the PVAc : LiClO<sub>4</sub> : DMF gel polymer electrolytes show the absence of THF peaks in the spectra which indicates the complete evaporation of the solvent THF from the gel polymer matrix.

To confirm the increase of DMF ratio in the PVAc : LiClO<sub>4</sub> : DMF polymer electrolyte matrix, the <sup>1</sup>H NMR data has been Lorentzian fit by using 1D WIN NMR software and the integral ratio of proton peaks have been compared. The ratio of integral values of two methyl proton peaks of DMF and methyl proton peaks of PVAc have been calculated and the results have been compared as shown in Table II. The tail and head of end chain in PVAc has two methyl groups as per the structural hypothesis shown in the scheme 1 and also the two methyl group of DMF has six protons. In Table II, “n<sub>1</sub>” and “n<sub>2</sub>” are constants related with number of monomer units in PVAc which can be obtained by calculating the ratio of end chain methyl proton (peak S<sub>1</sub>) and CH<sub>3</sub> or CH protons in each monomer unit (peak S<sub>2</sub> or S<sub>4</sub>). The ratio of methyl protons of PVAc monomer units and DMF methyl protons can be obtained by using the “n<sub>1</sub>” value. The results of integral ratios, (Table II) of PVAc and DMF methyl protons, indicate increase of DMF ratio with respect to PVAc in the PVAc : LiClO<sub>4</sub> : DMF matrix when the DMF content increases.

### XRD analysis

X-ray diffraction measurements were conducted to examine the nature of the crystallinity of the

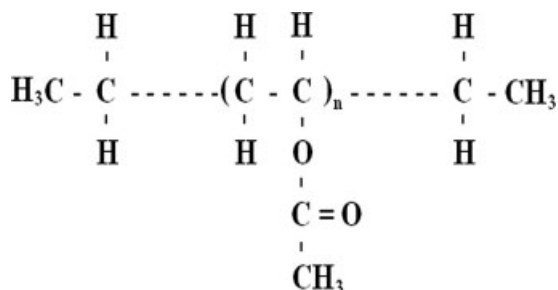
TABLE II  
Ratio of Proton in PVAc and DMF

Sample	Presence of $^1\text{H}$				
	$\int S_3/\int S_1$	$n_1$	$n_1 \times \int S_3/\int S_2$	$n_2$	$n_2 \times \int S_5/\int S_4$
A: 80 : 10 : 10	0.174	2.69	0.174	2.36	0.152
B: 75 : 10 : 15	0.25	2.612	0.25	2.36	0.281
C: 70 : 10 : 20	0.382	2.802	0.382	2.69	0.403

Where  $S_1$ : End group Methyl  $^1\text{H}$ ;  $S_2$ : Methyl  $^1\text{H}$  of monomer units in PVAc;  $S_3$ : Pair of Methyl  $^1\text{H}$  in DMF;  $S_4$ :  $^1\text{H}$  in CH unit of PVAc monomer units;  $S_5$ :  $^1\text{H}$  in CH unit of DMF.

polymer electrolyte films with respect to pure PVAc, DMF, and  $\text{LiClO}_4$  and to investigate the occurrence of complexation. X ray diffraction patterns of  $\text{LiClO}_4$ , PVAc (pure), and PVAc : DMF :  $\text{LiClO}_4$  complexes of different compositions are depicted in Figure 2. The XRD pattern, Figure 1(a) of  $\text{LiClO}_4$  shows intense peaks at angles  $2\theta = 18.36^\circ, 21.14^\circ, 23.2^\circ, 27.5^\circ, 32.99^\circ$  and  $36.58^\circ$  which reveals the crystalline nature of the ionic salt [PCPDF:30-0751]. Figure 2(b) shows two broad peaks at angles  $2\theta = 15.07^\circ$  and  $22.7^\circ$  which reveals the amorphous nature of the PVAc polymer.

In Figure 2(c) of 90PVAc : 10 $\text{LiClO}_4$ , the incorporation of  $\text{LiClO}_4$  into the polymer matrix causes a decrease in the intensity of the PVAc peaks mentioned earlier. As DMF is added with the PVAc :  $\text{LiClO}_4$  matrix at different concentrations, the intensity of the PVAc peak is greatly reduced [Fig. 2(d,e)]. This implies that the  $\text{LiClO}_4$  and plasticizer have disrupted the regions of PVAc and increased the amorphous nature.<sup>17</sup> It has been observed from the XRD pattern for all the compositions of PVAc : DMF :  $\text{LiClO}_4$ , that there are no peaks corresponding to pure  $\text{LiClO}_4$  appearing in the complex which indicates the complete dissolution of salt in the amorphous region of network polymers and inhibited the crystallization of PVAc-DMF- $\text{LiClO}_4$  complexes. This behavior demonstrates that complexation among the polymer, plasticizer, and salt takes place in the amorphous region.<sup>18</sup> The amorphous nature produces greater ionic diffusivity leading to the



Scheme 1 Structure of poly(vinylacetate).

high ionic conductivity, which can be obtained in amorphous polymers that have a fully flexible backbone.<sup>19</sup>

### SEM analysis

Scanning electron microscopy (SEM) images of the cross section of the pure PVAc and PVAc-DMF- $\text{LiClO}_4$  at various compositions [Fig. 3(a-e)] reveal the amorphous phase. Figure 3(a,b) shows smooth morphology of PVAc, but with 10 wt %  $\text{LiClO}_4$ , an irregular wavelike uneven appearance, owing to the polymer-salt complex formation. A comparison of the surface morphology of 90PVAc : 10 $\text{LiClO}_4$  with the plasticized polymer electrolytes shows a marked change in the surface properties and texture of the plasticized polymeric films. In Figure 3(c), foam-like rough morphology has been observed on addition of 10 wt % DMF with the 80PVAc : 10 $\text{LiClO}_4$  polymer matrix. SEM image of 75PVAc : 10 $\text{LiClO}_4$  : 15DMF [Fig. 3(d)] shows a sponge-like rough morphology with fine pores on the surface. When the DMF concentration is 20 wt % [Fig. 3(e)], gel-like uneven

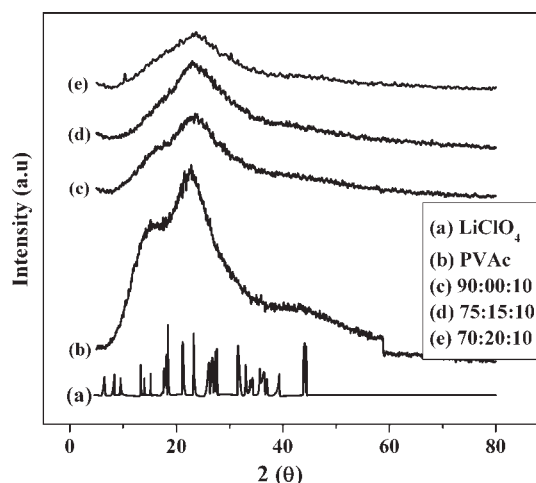
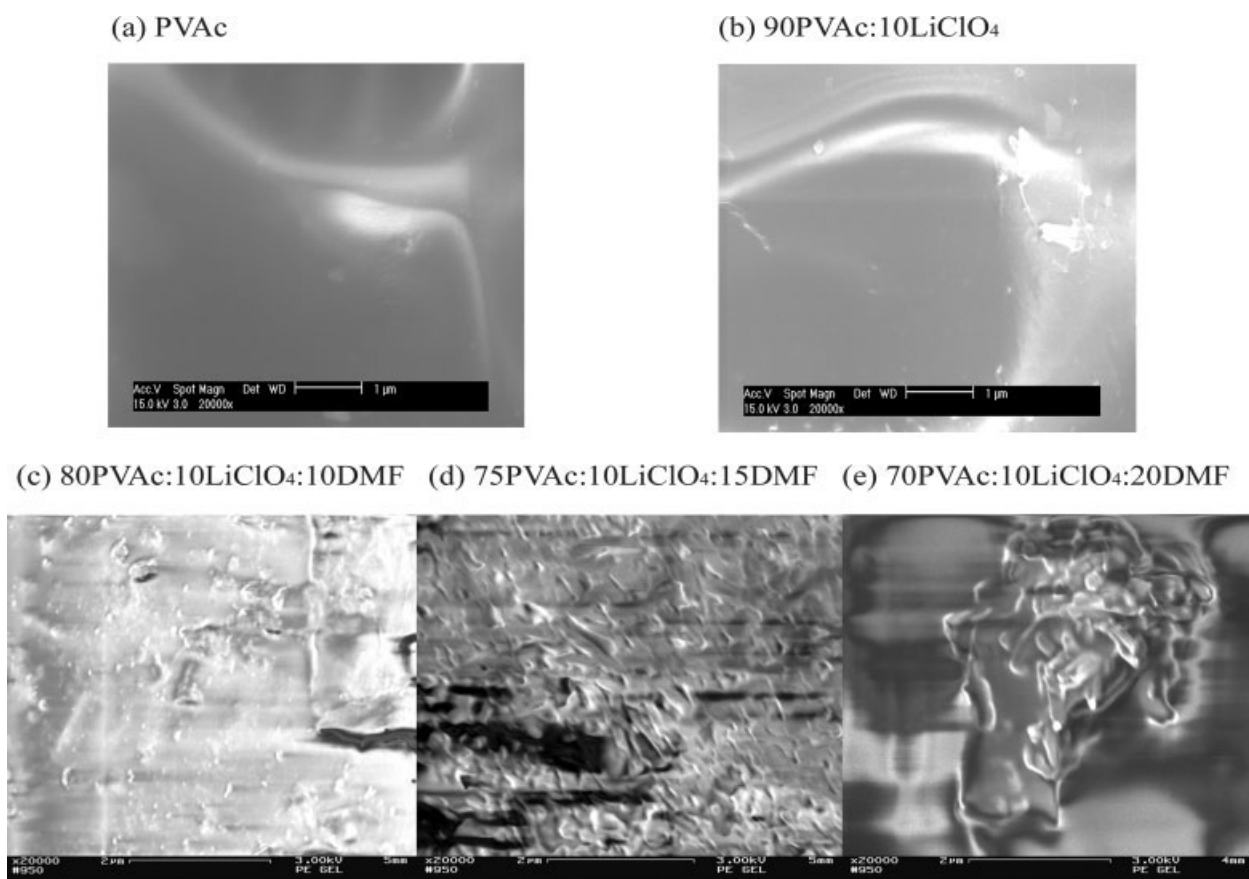


Figure 2 XRD plot for (a)  $\text{LiClO}_4$ ; (b) pure PVAc; (c) 90 : 00 : 10; (d) 75 : 15 : 10; and (e) 70 : 20 : 10 (PVAc : DMF :  $\text{LiClO}_4$ ) gel polymer electrolytes.





**Figure 3** SEM micrographs for (a) Pure PVAc; (b) 90 wt %PVAc : 10 wt %LiClO<sub>4</sub>; (c) 80 : 10 : 10; (d) 75 : 15 : 10; and (e) 70 : 20 : 10 (PVAc : DMF : LiClO<sub>4</sub>) electrolytes.

surface with many micropores spread over the surface. Tao Wang et al. has reported that the pore fraction of the gel polymer membranes increases with the increase of plasticizer content.<sup>20</sup> Such changes may be attributed to the fact that plasticization causes an increase in the amorphous nature of the host polymer, (i.e., polyvinylacetate) and subsequent enhancement in the overall amorphous fraction in the material. The viscid nature of the gel electrolytes is because of the plasticization of the rigid polymer matrix, which causes a decrease in glass transition temperatures of the gel polymer electrolytes as dis-

cussed in DSC analysis. This observation appears to be in good agreement with the XRD results (Fig. 2).

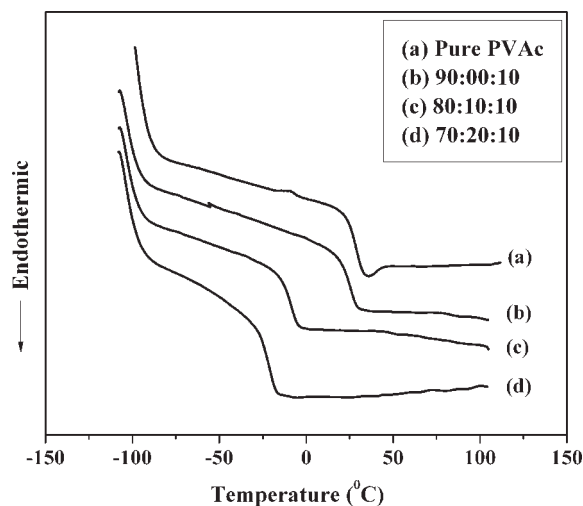
### DSC thermograms

DSC study has been used to elucidate the effect of LiClO<sub>4</sub> and DMF on the thermal transitions of the poly(vinyl acetate) chain, and the results are shown in Table III. The DSC curves for pure PVAc and PVAc : DMF : LiClO<sub>4</sub> plasticized polymer electrolytes are shown in Figure 4(a–d). The good miscibility between PVAc and DMF has been confirmed by

**TABLE III**  
Conductivity Parameters of PVAc : DMF : LiClO<sub>4</sub> Gel Polymer Electrolytes

PVAc : DMF : LiClO <sub>4</sub> compositions (wt %)	dc conductivity (S cm <sup>-1</sup> )			Glass transition temperature <sup>a</sup> (T <sub>g</sub> K)
	303 (K)	333 (K)	373 (K)	
90 : 00 : 10	7.6 × 10 <sup>-7</sup>	8.1 × 10 <sup>-6</sup>	1.3 × 10 <sup>-4</sup>	297
80 : 10 : 10	6.9 × 10 <sup>-6</sup>	1.2 × 10 <sup>-4</sup>	3.5 × 10 <sup>-3</sup>	282
75 : 15 : 10	4.5 × 10 <sup>-5</sup>	6.2 × 10 <sup>-4</sup>	1.4 × 10 <sup>-2</sup>	262
70 : 20 : 10	4.1 × 10 <sup>-4</sup>	3.1 × 10 <sup>-3</sup>	1.6 × 10 <sup>-2</sup>	251

<sup>a</sup> T<sub>g</sub> for pure PVAc = 303 K.



**Figure 4** DSC plots for (a) pure PVAc; (b) 90 PVAc : 10 LiClO<sub>4</sub>; (c) 80 : 10 : 10; and (d) 70 : 20 : 10 (PVAc: DMF: LiClO<sub>4</sub>) gel polymer electrolytes.

single glass transition behavior of the PVAc : DMF : LiClO<sub>4</sub> matrix as shown in Figure 4(c–d). The second heating scan is also performed immediately after the samples have been cooled to room temperature following the first heating.

The  $T_g$  of PVAc which is calculated from Figure 4(a) is 30°C. The DSC results (Table III) indicate a decrease in the  $T_g$  of the 90PVAc-10LiClO<sub>4</sub> polymer electrolyte complex. This could be accounted by the availability of ester oxygens, and the plasticizing effect of ion association as the salt is added. The incorporated salt gets dissociated and is attached with ester group in network polymer which acts as ionic crosslinks. The presence of charge neutral contact ion pairs act as main plasticizers, which do not form transient crosslinks. Similar results have also been previously reported by M. M. Silva et al. and G. Chiodelli et al., for the poly(trimethylenecarbonate) with LiBF<sub>4</sub> and PEO-LiBF<sub>4</sub> polymer electrolytes respectively.<sup>21,22</sup>

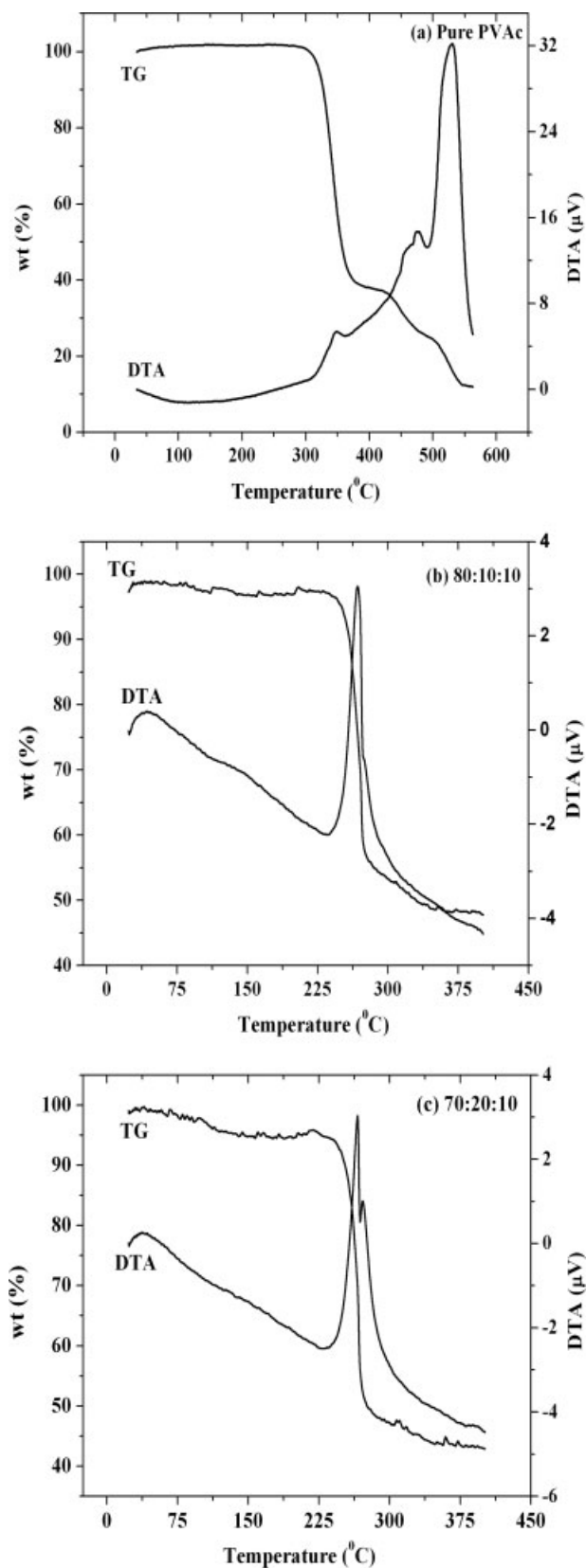
The plasticized samples have lower values of  $T_g$  than the plasticizer free sample because of a reduction in the cohesive forces of attraction between polymer chains.<sup>23</sup> Plasticizer molecules penetrate into the polymer matrix and establish attractive forces between plasticizer molecules and the chain segments. These attractive forces reduce the cohesive forces between the polymer chains and increase the segmental mobility, thus enhancing conductivity.<sup>23</sup> The conductivity of a polymer electrolyte, therefore, increases due to the addition of plasticizer. The effect of the addition of plasticizers to polymer electrolytes and the enhancement of conductivity has been studied by many researchers.<sup>12,24</sup> The plasticization effect is related to weakening of the dipole-dipole interactions because of the presence of the plasticizer molecules between the PVAc chains.<sup>25</sup>

### TG/DTA analysis

To ascertain the thermal stability of the polymer electrolytes, the prepared films were subjected to TG-DTA analysis. The thermogravimetric curve for pure PVAc film has been shown in Figure 5(a). The film appears to be quite dry since its weight is almost constant up to 307°C. At elevated temperatures (307–367°C), however, initiation of weight loss due to the mixture of chain end cleaving and chain scission processes is followed by dissociation of the polymer chain. It is known that the probability of cleaving a particular bond during thermal degradation depends not only upon its inherent strength, but also on the stability of the products formed. McNeill et al.<sup>26,27</sup> and Zulfiqar et al.<sup>28</sup> reported that in pure PVAc, decomposition occurred in two stages and it was thermally stable up to 250°C. No effort has been made to confirm the decomposition products, as it is well known that PVAc degrades in two stages, around 347 and 530°C, corresponding to deacetylation and disintegration of the polyolefinic backbone, respectively.<sup>28</sup> It is observed from DTA curves that the two decompositions of PVAc are also accompanied with the exothermic peaks in the range 307–367°C and multiplets of exotherms in the range 421–560°C simultaneous with the weight losses. The DTA traces for the PVAc show an exotherm at 347°C due to the evolution of acetic acid, and an exotherm (530°C) on account of decomposition of the polyene to volatile products.

The TG and DTA curve of PVAc : DMF : LiClO<sub>4</sub> gel polymer electrolytes at various concentrations are shown in Figure 5(b,c) and the results are shown in Table IV. In the PVAc : DMF : LiClO<sub>4</sub> gel polymer electrolytes, the mass loss starts at temperature above 61°C as shown in Table IV for 10–20 wt % DMF concentrations. This mass loss might be due to the evaporation of DMF plasticizer from the gel polymer electrolyte matrix and continues till 154°C since the boiling point of DMF is 153°C. The second weight loss begins at temperature above 237 and 231°C for 10 and 20 wt % DMF plasticized systems, respectively, that reveal the degradation of polymer electrolytes.

The presence of additive (plasticizer) in the solid polymer electrolyte has a variable dissociation effect on the thermal events observed in the region III as shown in Table IV. The nature of this thermal feature has been confirmed by thermogravimetric analysis, degenerative deacetylation, and destabilization, due to the effect of the guest salt, plasticizer on the host polymer. The addition of plasticizers appears to cause a slight decrease in the thermal stability and the onset of decomposition which are in good agreement with the DSC results. Zukowska et al. investigated conductivity values for PVdF-DMF-H<sub>3</sub>PO<sub>4</sub>



**Figure 5** TG/DTA plot for (a) pure PVAc; (b) 80 : 10 : 10 and (c) 70 : 20 : 10 (PVAc : DMF : LiClO<sub>4</sub>) gel polymer electrolytes.

proton conducting polymer electrolytes up to 80°C, and from the DSC results they also reported that the gel polymer electrolytes were stable up to 100°C.<sup>29</sup> Ward et al studied conductivity measurements for PVdF-DMF-LiT gel electrolytes up to 85°C.<sup>30</sup>

The <sup>1</sup>H NMR results indicate the existence of DMF in the PVAc : DMF : LiClO<sub>4</sub> polymer electrolyte matrix at 30°C. However, TG results reveal that evaporation of DMF has been started at 61°C, and the rate of evaporation increases when the temperature increases above 100°C as shown in Table IV. Thermal analysis clearly indicates that these DMF plasticized PVAc : LiClO<sub>4</sub> polymer electrolytes can be used in lithium-polymer batteries with in the operating temperature range 30–50°C.

### Conductance spectra analysis

The logarithmic plots of the conductivity as a function of frequency for PVAc : DMF : LiClO<sub>4</sub> samples of different compositions at 303 K is shown in Figure 6. The spectra can be divided into a low frequency dispersion region, an almost frequency independent plateau region in the intermediate frequencies, and a high frequency dispersion region (Fig. 6). The plateau characterizes the conduction, which is caused mainly by the hopping motion of the mobile ions and extrapolations determine the dc value of conductivity and are tabulated in Table III. The high frequency behavior is attributed to the relaxation of the mobile ion hopping which is due to the Coulomb interactions of the charge carriers and the disorder within the structure.<sup>31</sup> This non-Debye characteristic which cannot be expressed by a single relaxation equation, has been accounted for by Jonscher's universal power law,

$$\sigma(\omega) = \sigma(0) + A\omega^s, \quad 0 < s < 1, \quad (1)$$

where  $\sigma(0)$  is the dc limit of conductivity and  $A$  and  $s$  are temperature dependent constants.<sup>32</sup> The observed values of ' $s$ ' are in the  $1.36 > s > 1.23$  range for 80 : 10 : 10 and 70 : 20 : 10 (PVAc : DMF : LiClO<sub>4</sub>) polymer electrolytes at ambient temperature. This large value of ' $s$ ' suggests that existence of more than one type of migration mechanism in the plasticized polymer matrix<sup>33</sup> may be because of the existence of interactions among polymer, salt, and plasticizer.<sup>14</sup>

The low-frequency dispersion region increase with temperature (Fig. 7). This low-frequency dispersion may be because of the interfacial impedance or space charge polarization.<sup>32</sup> As the frequency decreases, more and more charge accumulation occurs at the electrode and electrolyte interface, which leads to a decrease in the number of mobile ions and eventually to a drop in conductivity at low

TABLE IV  
TGA Results of PVAc : DMF : LiClO<sub>4</sub> Gel Polymer Electrolyte Complexes

Compositions of PVAc : DMF : LiClO <sub>4</sub> gel electrolytes (wt %)	Weight loss (%)			
	Region-I (30–100°C)	Region-II (100–230°C)	Region-III (230–390°C)	Region-IV (>390°C)
Pure PVAc	Constant	Const. (100–307°C)	62% (307–393°C)	26.2% (393–560°C)
80 : 10 : 10	Const. (30–61°C); 1.17% (61–100 °C)	1% (100–154°C); Const. (154–237°C)	48.2% (237–349°C)	–
70 : 20 : 10	Const. (30–61°C) 1.45%; (61–100 °C)	2.3% (100–154°C); Const. (154–231°C)	51.2% (231–373°C)	–

frequency. In the high frequency region, the mobility of charge carriers is high and hence the conductivity increases with frequency. The high frequency dispersion region almost disappears at higher temperatures within the frequency range measured, since the jump frequency of the charge carriers increases with temperature.<sup>34</sup>

### Impedance analysis

The typical impedance plots ( $Z'$  vs.  $Z''$ ) for all the polymer electrolytes at 303 K are shown in Figure 8. The low frequency intercept on the  $Z'$  axis gives the bulk electrical resistance ( $R_b$ ) value. The bulk resistance decreases with the addition of DMF in the polymer electrolyte. It is noted that the semicircle observed at high frequency region gradually fades away as the content of DMF increases, and completely disappears in the polymer electrolytes with 20 wt % DMF. This result suggests that only the resistive component of polymer electrolyte prevails.

The ionic conductivity ( $\sigma$ ) has been calculated using the equation  $\sigma = L/R_b A$ , where ' $L$ ' is the thickness of the polymer electrolyte film and ' $A$ ' the surface area of the film. From the impedance results

(Table III), conductivity of solid polymer complex (90PVAc : 10LiClO<sub>4</sub>)  $7.6 \times 10^{-7} \text{ S cm}^{-1}$  increases to  $6.9 \times 10^{-6} \text{ S cm}^{-1}$  at ambient temperature with the addition of 10 wt % of DMF with 80PVAc : 10LiClO<sub>4</sub>. The conductivity value increases to  $4.1 \times 10^{-4} \text{ S cm}^{-1}$  at 303 K when the DMF concentration increases to 20 wt % in 70PVAc : 10LiClO<sub>4</sub>. The incorporation of plasticizer DMF leads to more vacancy sites and interactions with the Li<sup>+</sup> ion and the polymer as discussed in <sup>1</sup>H NMR analysis. The interaction among the polymer chain, DMF and Li<sup>+</sup>---ClO<sub>4</sub><sup>-</sup> has been analysed in the earlier report from FTIR results.<sup>14</sup> Concerning the ionic conductivity, the incorporation of DMF plasticizer in to a polymer matrix leads to two effects: (i) enhancement of amorphous phase and hence, of the ionic conductivity and (ii) decrease in  $T_g$  which increases the segmental motion of the polymer chain and hence the conductivity, as discussed in the XRD, SEM, and DSC analyses.

### Temperature dependence of conductivity

Figure 9(a) shows the temperature dependence of the ionic conductivity for polymeric gel membranes

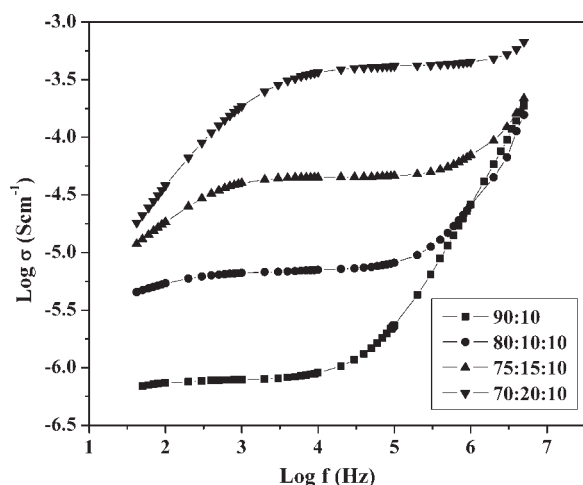


Figure 6 Conductance spectra for all the compositions of PVAc : DMF : LiClO<sub>4</sub> polymer electrolytes at 303 K.

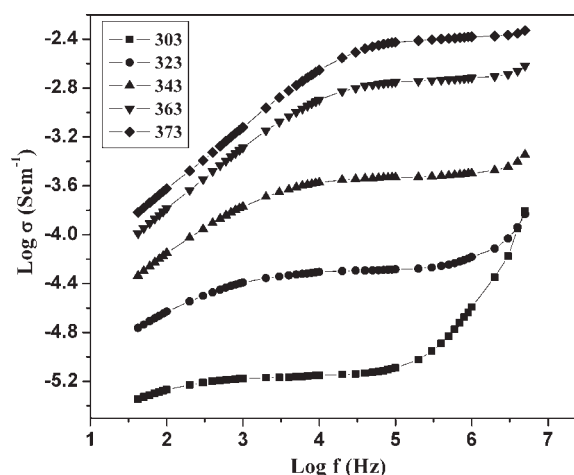


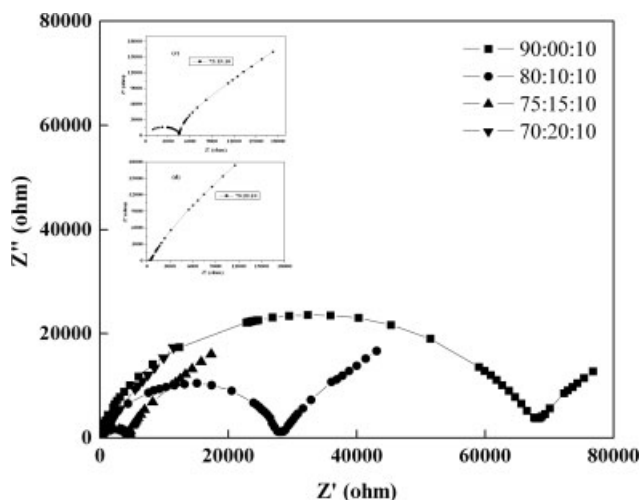
Figure 7 Conductance spectra for 80 : 10 : 10 PVAc : DMF : LiClO<sub>4</sub> polymer electrolyte at various temperatures.



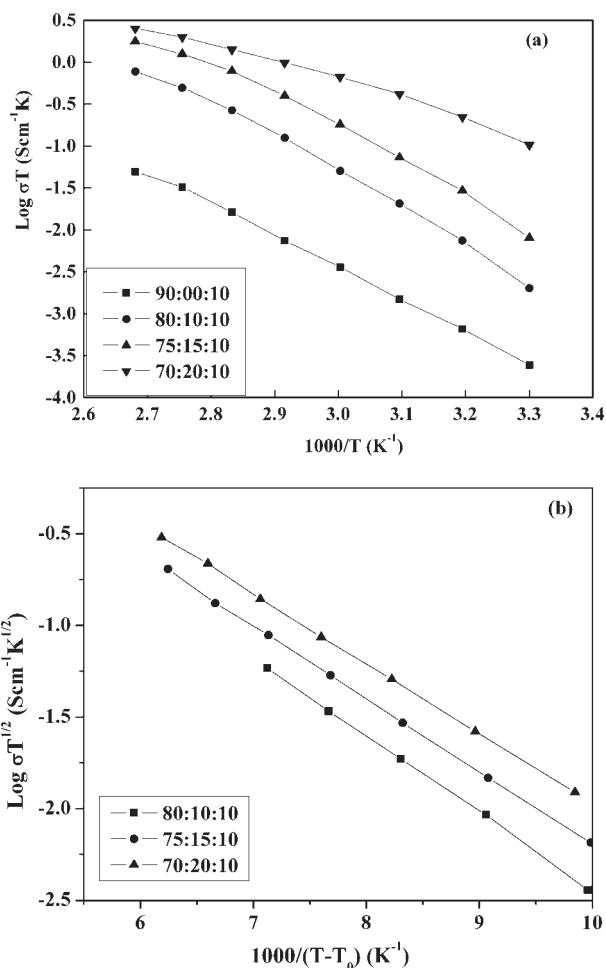
with different DMF concentrations. It can be seen that 90PVAc : 10LiClO<sub>4</sub> solid polymer electrolyte sample has been fitted well with Arrhenius relation. However, when the solid polymer electrolyte (PVAc : LiClO<sub>4</sub>) is plasticized with DMF, it is interesting to note that a slight curvature has been obtained as shown in Arrhenius plot. The linear and nonlinear temperature dependence conductivity of polymer electrolytes has been analysed by Ratner in detail.<sup>35</sup> According to Ratner, the gel polymer electrolytes are following VTF behaviour at temperatures greater than  $T_g$  and the solid polymer electrolyte 90PVAc : 10LiClO<sub>4</sub> seems to follow Arrhenius behavior in the temperature range studied [Fig. 9(a)]. The Vogel-Tamman-Fulcher (VTF) like behavior of conductivity implies the coupling of the charge carriers with the segmental motion of the polymer chains. The data are therefore, examined in view of the VTF equation;

$$\sigma = A_0 T^{-1/2} \exp[-B/K(T - T_0)] \quad (2)$$

where is the  $B$  the activation energy and  $T_0$  the equilibrium glass transition temperatures, which is close to the experimental  $T_g$ . The VTF equation was developed to deal with the viscosity of supercooled liquids. By replotting the data shown in Figure 9(a) as  $\log \sigma T^{1/2}$  versus  $1/(T - T_0)$ , assuming  $T_0 = T_g - 50$  K, a linear plot is obtained as shown in Figure 9(b). The maximum conductivity of  $1.6 \times 10^{-2}$  S cm<sup>-1</sup> (Table III) has been obtained at 373 K for the 70 : 20 : 10 (PVAc : DMF : LiClO<sub>4</sub>) polymer electrolyte. This conductivity enhancement in the plasticized polymer electrolytes might be due to the increase in charge carrier concentration of Li<sup>+</sup> ions with increasing the DMF concentration. Even though



**Figure 8** Impedance spectra for all the compositions of PVAc : DMF : LiClO<sub>4</sub> gel polymer electrolytes at 303 K (inner plot: Enlarged spectra for 15 and 20 wt % DMF plasticized systems).



**Figure 9** (a) Temperature dependence of ionic conductivity and (b) VTF plots of ionic conductivity for PVAc-DMF-LiClO<sub>4</sub> gel polymer electrolytes of various compositions.

high conductivity results is obtained for 70 : 20 : 10 (PVAc : DMF : LiClO<sub>4</sub>), its thermal stability is poor due to the gelatinous nature as evidenced from SEM and TG-DTA results. In the 15 and 20 wt % DMF plasticized systems, there is no reasonable increase in conductivity at 373 K even though there is a one order of conductivity enhancement at the ambient temperature which might be due to the partial DMF evaporation as discussed in TG-DTA analysis.

## CONCLUSION

Plasticized polymer electrolytes (PVAc : DMF : LiClO<sub>4</sub>) of various compositions (polymer- and plasticizer-salt) have been studied. The effect of plasticization on the change in the structural, electrical, and thermal stability properties has been investigated. <sup>1</sup>H NMR results reveal the existence of DMF in the gel polymer matrix and also the appearance of new peaks indicates the Li<sup>+</sup> ion interaction with polymer and plasticizer. XRD and SEM morphology analysis

reveals the amorphous nature of the gel polymer electrolytes. TG/DTA results indicate the thermal stability of the electrolyte, is ascertained as 30–60°C. DSC results show the decrease of  $T_g$  with the increase of DMF concentrations which reveals the increase of segmental mobility. The parameter 's' measured from the conductance spectra, reveals the existence of more than one migration mechanism of  $\text{Li}^+$  in the gel polymer electrolytes. A substantial enhancement in the electrical conductivity (about three orders of magnitude at room temperature) has been found on plasticization. A maximum ionic conductivity of  $4.1 \times 10^{-4} \text{ S cm}^{-1}$  at 303 K has been observed for 20 wt % of DMF plasticizer. The ionic conduction behavior of the PVAc : DMF :  $\text{LiClO}_4$  is of the VTF type in sharp contrast to the Arrhenius behaviour displayed by unplasticized solid polymer electrolyte. The substantial improvement in the electrical properties and having thermal stability in the operating temperature in these gel polymer electrolytes, they are found to be possible application in energy-storage devices in the range up to 60°C.

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