Structural, Thermal, Morphological and Electrical Conductivity Analysis of Proton Conducting Tri Block Copolymer P(VdCl-Co-AN-Co-MMA) Based Electrolytes

D. Inbavalli 1,2, S. Selvasekarapandian 3*, C. Sanjeeviraja 3, R. Baskaran 4, Junichi Kawamura 4, Yoshitake Masuda 5

1Research and Development Centre, Bharathiar University, Coimbatore, 641046, India
2Materials Research Centre, Coimbatore, 641045, India
3Department of Physics, Alagappa University, Karaikudi, 630003, India
4Institute of Multi Disciplinary Research for Advanced Materials (IMRAM), Tohoku University, Sendai, Japan
5National Institute of Advanced Industrial Science and Technology (AIST), Nagoya 463 8560, Japan

*E-mail: sekarapandian@rediffmail.com

ABSTRACT: The tri block copolymer electrolytes of Poly(vinylidene chloride-co-acrylonitrile-co-methylmethacrylate) P(VdCl-co-AN-co-MMA) doped with Ammonium thiocyanate (NH₄SCN) of various compositions have been prepared by solution casting technique. The formation of copolymer-salt complexes and the copolymer-proton interaction has been confirmed by fourier transform infra-red spectroscopy. The X-ray diffraction analysis indicated the amorphous nature of the copolymer-salt complexes. The differential scanning calorimetry analysis revealed the increased plasticizer effect with the increase in the salt concentration. The scanning electron microscopy revealed the porous nature of the copolymer electrolytes. The conductivity studies have been carried out using ac impedance spectroscopy and the maximum value of the bulk conductivity for 50 mol% P(VdCl-co-AN-co-MMA):50 mol% NH₄SCN was found to be of the order 2.10 x 10⁻⁴ S cm⁻¹ at 303 K.

Keywords: Tri block copolymer; Ionic conductivity; SEM; NH₄SCN; Electrolytes; Dielectric.

1. Introduction

Proton conducting polymer electrolyte has been receiving considerable attention due to its application in fuel cells [1, 2] for electric vehicles. Polymer electrolyte properties such as thermal, chemical, mechanical stability, as well as water absorption characteristics, are of great importance for constructing fuel cells. The search for new proton-conducting membranes as possible alternatives to Nafion™ is rapidly growing. Fluorinated polymers are particularly appealing because of their chemical and physical affinity with Nafion™ [3].

Although these membranes show good proton conductivities from 0.1 to 0.01 S cm⁻¹ in a humid environment, they have many limitations, such as: 1) dependence on water for conductivity; 2) high methanol permeability; 3) a tendency to disintegrate in the presence of hydroxyl radicals, an intermediate in the cathode reaction; and 4) moderate mechanical and chemical stability [4]. Also most of the perfluorinated membranes have expensive and difficult process. These membrane conductivities are also very sensitive to water management in the electrochemical systems. When they are subjected to temperatures above 100 °C at atmospheric pressure, their conductivity decreases significantly due to their dehydration [5].

Ammonium salts have already been reported as good proton donor to the polymer matrix [6, 7] since one of the proton in the ammonium ion is loosely bound as showed in Scheme 1. In addition to motion of proton ion, the conductivity has also been associated with the segmental motions of the polymer chain [8]. Proton polymeric electrolytes based on complexes of electrodonor polymers with ammonium salts or strong inorganic acids have recently attracted considerable interest from research workers [9].

With the aim of innovating suitable novel copolymer electrolytes for the application in fuel cell, the tri block copolymer electrolyte P(VdCl) doped with NH₄SCN have been prepared by solution casting technique in the mole percentage as showed in Table 1. Its hydrophobic nature and presence of large number of polar groups such as oxygen, nitrogen and chlorine in the copolymer (Figure 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

MMA)

Figure 1: Structure and properties of P(VdCl-co-AN-co-MMA)

Table 1: Compositions of pure copolymer and its complexes

<table>
<thead>
<tr>
<th>Sample Composition</th>
<th>Used Hereafter As</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(VdCl-co-AN-co-MMA) - 70m% P(VdCl.)</td>
<td>P(VdCl.)</td>
</tr>
<tr>
<td>Pure Copolymer</td>
<td></td>
</tr>
<tr>
<td>70m% P(VdCl-co-AN-co-MMA):30m% NH₄SCN</td>
<td>NH₄SCN</td>
</tr>
<tr>
<td>50m% P(VdCl-co-AN-co-MMA):50m% NH₄SCN</td>
<td>NH₄SCN</td>
</tr>
</tbody>
</table>

Molecular weight: 250.1
Polymer weight: 84,000

3. Results and discussion

3.1. X-Ray Diffraction Analysis

To determine the nature of the copolymer and its complexes, XRD studies were performed. Figure 2 (a-c) shows the patterns of P(VdCl.) and P(VdCl.):NH₄SCN complexes of different compositions. For the pure copolymer, the four broad intense peaks have been obtained at angles 2θ = 15.8°, 24.88°, 32.34° and 38.56° which revealed the semicrystalline nature as seen in Figure 2(a). Also it has been observed that the peaks 2θ = 24° and 26° (JCPDS 23-0029) [10] corresponding to pure NH₄SCN were absent in all the complexes of P(VdCl.):NH₄SCN which indicated the complete dissolution of the salt in the copolymer matrix. This has confirmed the existence of definite complexation between the copolymer P(VdCl.) and NH₄SCN.

Figure 2: XRD diffractograms of (a) P(VdCl.), (b) 70m% P(VdCl.):30m% NH₄SCN and (c) 50m% P(VdCl.): 50m% NH₄SCN

3.2. FTIR Analysis

The FTIR spectra of P(VdCl.) and P(VdCl.):NH₄SCN complexes have been shown in Figures 3 (a-c). It was observed that there was a slight shift in the values obtained for pure tri block copolymer (2875-2860) cm⁻¹ for C-H, 1357.14 cm⁻¹ for –CH₂ bending and 1460 cm⁻¹ for –CH₂ bending as seen from Table 2 which might be due to the overlapping of C-H, CH₃ and CH₂ bands of all the three homo polymer. These peak values have been shifted to 2875 cm⁻¹, 1330.96 cm⁻¹ and 1460 cm⁻¹ for 45 mol% NH₄SCN.

Table 2: FTIR Analysis

<table>
<thead>
<tr>
<th>Molecular grouping</th>
<th>Pure</th>
<th>Complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H</td>
<td>2875</td>
<td>2860</td>
</tr>
<tr>
<td>C-H</td>
<td>1357</td>
<td>1330</td>
</tr>
<tr>
<td>C-H</td>
<td>1460</td>
<td>1460</td>
</tr>
</tbody>
</table>
From Table 2, it was seen that the vibrational bands at 685 cm$^{-1}$, 2247.79 cm$^{-1}$ and 1725 cm$^{-1}$ corresponds to C-Cl of P(VdCl..), C≡N of Poly(acrylonitrile) (PAN) and C=O of Poly(methyl methacrylate) (PMMA) of the copolymer respectively [11]. Also the C-Cl bond has been shifted to 675 cm$^{-1}$ for 50 mol% NH$_4$SCN which might be due to the interaction of the proton with the copolymer matrix. The characteristic vibrational bands of NH$_4$SCN [12] were completely absent in the complex which indicated the formation of polymer-salt complexation. This has been in good agreement with XRD results.

Scheme 1: Possible interaction of protons in the copolymer electrolyte

\[ \text{H}^+\text{NH}_4^+\text{SCN} \]

\[ \text{H}^+\text{NH}_4^+\text{SCN} \]

\[ \text{H}^+\text{NH}_4^+\text{SCN} \]

\[ \text{H}^+\text{NH}_4^+\text{SCN} \]

3.3 DSC Analysis

The DSC thermograms of P(VdCl..) and P(VdCl..):NH$_4$SCN copolymer electrolytes have been shown in Figures 4 (a-c). The results were presented in Table 3 which indicated a glass transition temperature ($T_g$) of 144.7 °C for P(VdCl..). Also it was seen that the $T_g$ has been decreased to 141.36 for 70m% P(VdCl..):30m% NH$_4$SCN with the addition of NH$_4$SCN to the copolymer. This was due to the plasticizing effect of increased ion association as the salt has been added. With further addition of NH$_4$SCN, the $T_g$ has been further decreased to 124.20 °C for 50m% P(VdCl..):50m% NH$_4$SCN as shown in Table 3. This decrease in $T_g$ has helped to soften the polymer backbone and thereby increased its segmental motion. The segmental motion provided voids, which enabled the easy flow of ions through the polymer chain network.

3.4 SEM Analysis

Scanning electron micrographs (SEM) of pure P(VdCl..) and P(VdCl..):NH$_4$SCN complexes have been shown in Figures 5(a-c). From Figure 5(a), smooth and non porous morphology has been observed for P(VdCl..). For 70m%P(VdCl..):30m%NH$_4$SCN, the porosity has increased and less number of minute pores has been observed from Figure 5(b). When the concentration of NH$_4$SCN has been increased to 50m%, the size and depth of these pores has been increased and appears like a hole with appreciable size as evident from Figure 5(c) however there was no increase in the number of pores.

3.5 AC Impedance Analysis

The Nyquist plots for P(VdCl..):NH$_4$SCN tri block copolymer electrolyte samples of different compositions at 303 K has been shown in Figures 6 (a-b). The complex impedance plot showed two well defined regions. The semicircle was observed in the high-frequency region due to the bulk effect of the electrolytes i.e. bulk ionic conductivity and the linear region in the low-frequency range which might be attributed to the effect of the
blocking electrodes [12]. A slight degree of decentralization has been observed at impedance semicircles which revealed the Non Debye nature of the material and distribution relaxation time.

The EQ software program developed by Boukamp [13-14] has been used to find the bulk resistance (R_b) of the copolymer electrolytes. The ionic conductivity was calculated using the equation,

\[ \sigma = \frac{1}{R_b A} \]  

where 'l' and 'A' represented the thickness of the copolymer electrolyte film and surface area of the film respectively. It was seen from the Table 4 that at 303 K, the conductivity has increased from 3.94 x 10^{-6} S cm^{-1} for 70m% P(VdCl..):30m%NH_4SCN to 2.10 x 10^{-4} S cm^{-1} for 50m% P(VdCl..):50m%NH_4SCN with the increase in the concentration of NH_4SCN. This improved ionic conductivity was due to the enhancement in the number of carrier ions. At lower salt concentration, the highly conducting phases would have existed in small domains disconnected from each other. When the optimal concentration has reached, the separate domains have grown up and have formed continuously highly conducting phase.

Table 2: Correlation Chart

<table>
<thead>
<tr>
<th>Nature of bond</th>
<th>P(VdCl..)</th>
<th>70m%P(VdCl..):30m%NH_4SCN</th>
<th>50m% P(VdCl..):50m%NH_4SCN</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H Stretch</td>
<td>2875-2860 cm^{-1}</td>
<td>2880 cm^{-1}</td>
<td>2875 cm^{-1}</td>
</tr>
<tr>
<td>-CH_3(bend)</td>
<td>1357.14 cm^{-1}</td>
<td>1350 cm^{-1}</td>
<td>1330.96 cm^{-1}</td>
</tr>
<tr>
<td>-CH_2(bend)</td>
<td>1460 cm^{-1}</td>
<td>1450 cm^{-1}</td>
<td>1460 cm^{-1}</td>
</tr>
<tr>
<td>C-Cl</td>
<td>685 cm^{-1}</td>
<td>680 cm^{-1}</td>
<td>675 cm^{-1}</td>
</tr>
<tr>
<td>C≡N</td>
<td>2247.79 cm^{-1}</td>
<td>2200 cm^{-1}</td>
<td>2248 cm^{-1}</td>
</tr>
<tr>
<td>C=O</td>
<td>1725 cm^{-1}</td>
<td>1750 cm^{-1}</td>
<td>1760 cm^{-1}</td>
</tr>
</tbody>
</table>

![Figure 4: DSC thermograms of (a) P(VdCl..), (b) 70m% P(VdCl..):30m% NH_4SCN and (c) 50m% P(VdCl..):50m% NH_4SCN](image-url)
Table 3: $T_g$ obtained from DSC Analysis

<table>
<thead>
<tr>
<th>Sample composition</th>
<th>$T_g$ (in °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(VdCl..)</td>
<td>144.70</td>
</tr>
<tr>
<td>70m% P(VdCl..):30m% NH$_4$SCN</td>
<td>141.36</td>
</tr>
<tr>
<td>50m% P(VdCl..):50m% NH$_4$SCN</td>
<td>124.20</td>
</tr>
</tbody>
</table>

Figure 5: SEM micrograph of (a) P(VdCl..), (b) 70m% P(VdCl..):30m% NH$_4$SCN and (c) 50m% P(VdCl..):50m% NH$_4$SCN

Figure 6: Nyquist Plots of (a) 70m% P(VdCl..):30m% NH$_4$SCN and (b) 50m% P(VdCl..):50m% NH$_4$SCN at 303 K
Table 4: Calculated $\sigma$ (S cm$^{-1}$) from Nyquist Plot

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>$\Sigma$ From Nyquist Plot (S cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70m% P(VdCl..): 30m% NH$_4$SCN</td>
<td>3.94 x 10$^{-6}$</td>
</tr>
<tr>
<td>50m% P(VdCl..): 50m% NH$_4$SCN</td>
<td>2.10 x 10$^{-4}$</td>
</tr>
</tbody>
</table>

3.6 Conductance Spectra Analysis

The logarithmic plots of the conductivity as a function of angular frequency for P(VdCl: NH$_4$SCN complexes at room temperature have been shown in Figure 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. The ionic conductivity was high enough to produce the buildup of charges at the electrodes at low frequency which has reduced the effective field and enhanced the conductivity.

The extrapolation of the d.c. plateau region on the log $f$ axis has given the d.c. conductivity. The d.c. conductivity values obtained from the conductance spectra have been found to be in good agreement with the bulk conductivity values obtained from Nyquist plot as showed in Table 5.

Table 5: Calculated $\sigma_{dc}$ (S cm$^{-1}$) from Conductance Spectra for the copolymer complexes

<table>
<thead>
<tr>
<th>Sample composition</th>
<th>$\Sigma_{dc}$ from conductance spectra (S cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70m% P(VdCl..):30m% NH$_4$SCN</td>
<td>7.69 x 10$^{-7}$</td>
</tr>
<tr>
<td>50m% P(VdCl..):50m% NH$_4$SCN</td>
<td>1.30 x 10$^{-4}$</td>
</tr>
</tbody>
</table>

3.7 Modulus Spectra Analysis

The Figure 8(a) and Figure 8(b) showed the variation of $M'$ against log $f$ and the variation of $M''$ against log $f$ for different concentrations of NH$_4$SCN. At low frequencies $M''$ approached to zero and indicated that the electrode polarization phenomena has made a negligible contribution and increased at high frequency due to bulk effect of the copolymer electrolyte [15]. The broad nature of the peak revealed the non-Debye nature of the ionic conductor represented by a single parallel RC element as confirmed in the impedance spectra.

Figure 7: Conductance Spectra of (a) 70m% P(VdCl..):30m% NH$_4$SCN & (c) 50m% P(VdCl..):50m% NH$_4$SCN

Figure 8(a): Variation of log $f$ with $M'$ at 303K

Figure 8(b): Variation of log $f$ with $M''$ at 303K
3.8 Dielectric Spectra

The complex permittivity ($\varepsilon'$) or dielectric constant of a system has been defined by:

$$\varepsilon^* = \varepsilon' - j \varepsilon'' = \varepsilon' - j (\varepsilon''/\varepsilon')$$  (2)

where $\varepsilon'$, $\varepsilon''$, $\sigma$ and $\varepsilon_0$ represented the real part of dielectric constant of the material, imaginary part of dielectric constant of the material, conductivity, angular frequency and permittivity of free space respectively. The Figures 9(a) and 9(b) showed $\varepsilon'$ Vs log $f$ and $\varepsilon''$ Vs log $f$ plots respectively for P(VdCl..):NH$_4$SCN copolymer complexes. It was seen from the Figures 9(a) and 9(b) that for both the P(VdCl..):NH$_4$SCN system, the dielectric permittivity has risen sharply towards low frequency which was due to the electrode polarization effects [16].

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 has decreased with increasing frequency. Hence $\varepsilon'$ has decreased with increasing frequency.

From Figures 9(b), it has been observed that the dielectric loss ($\varepsilon''$) became very large (~8x10$^4$) at lower frequencies which was due to free charge motion within the material [17]. 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 $\varepsilon''$. This phenomenon has lead to the so called “conductivity relaxation” [18].

3.9 Loss Tangent Spectra

The dielectric relaxation parameter of the copolymer complexes (P(VdCl..):NH$_4$SCN has been obtained from the plot of $\tan \delta$ as a function of frequency. The dielectric loss tangent ($\tan \delta$) has been defined by the equation;

$$\tan \delta = \varepsilon''/\varepsilon'$$  (3)

The variation of $\tan \delta$ with frequency has been presented in Figure 10 for all the copolymer complexes P(VdCl..):NH$_4$SCN at 303 K. It has been observed from Figure 10 that for all the copolymer complexes $\tan \delta$ increases with increasing frequency, reaches a maximum and then decreases with further increase of frequency. For the maximum dielectric loss, the loss tangent peak has been described by the relation $\omega \tau = 1$ where $\tau$ and $\omega$ represented relaxation time and angular frequency of the applied electric field [19] respectively. The relaxation parameters for all the copolymer complexes at 303 K have been calculated and tabulated in Table 6.

From Table 6, it was seen that the relaxation time ($\tau$) has decreased from 4.98 x 10$^{-4}$ s for 70m% P(VdCl..):30m% NH$_4$SCN to 4.89 x 10$^{-5}$ s for 50m% P(VdCl..):50m% NH$_4$SCN. This decrease in relaxation time $\tau$ has enhanced the ionic conductivity. From Table 6, it was noted that the relaxation time was lowest for 50m% P(VdCl..):50m% NH$_4$SCN and hence exhibited highest ionic conductivity which was in good agreement with the results of Nyquist plots.

Figure 9(a): Dielectric spectra of (a) 70m% P(VdCl..):30m% NH$_4$SCN and (b) 50m% P(VdCl..):50m% NH$_4$SCN at 303 K

Figure 9(b): Dielectric Spectra of (a) 70m% P(VdCl..):30m% NH$_4$SCN and (b) 50m% P(VdCl..):50m% NH$_4$SCN at 303 K
Table 6: Calculated dielectric relaxation parameters for the copolymer complexes

<table>
<thead>
<tr>
<th>Sample Composition</th>
<th>Relaxation Frequency</th>
<th>Frequency Unit</th>
<th>Relaxation Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>70m% P(VdCl..):30m% NH₃SCN</td>
<td>3.30</td>
<td>10⁴ (Hz)</td>
<td>4.98 x 10⁻⁴ S</td>
</tr>
<tr>
<td>50m% P(VdCl..):50m% NH₃SCN</td>
<td>4.31</td>
<td>10⁴ (Hz)</td>
<td>4.89 x 10⁻⁵ S</td>
</tr>
</tbody>
</table>

Figure 10: Loss tangent spectra of (a) 70m% P(VdCl..):30m% NH₃SCN and (b) 50m% P(VdCl..):50m% NH₃SCN at 303 K

4.0 Conclusion
The copolymer electrolytes of P(VdCl..):NH₃SCN complexes of various compositions have been prepared by solution casting method. XRD studies revealed the increase in amorphous nature of P(VdCl..):NH₃SCN thereby producing greater ionic diffusivity. The SEM micrographs have revealed the porosity and formation of pores for P(VdCl..):NH₃SCN complexes. The conductivity was found to exhibit increasing trend with increasing concentration of NH₃SCN. In P(VdCl..):NH₃SCN system, the maximum conductivity observed was 2.10 x 10⁻⁴ S cm⁻¹ for 50m% P(VdCl..):50m% NH₃SCN. The low frequency dispersion of dielectric constant for both P(VdCl..):NH₃SCN complexes revealed the space charge effects that have arisen from the electrodes. From the loss tangent spectra, it was found that the relaxation time (τ) was lowest for 50m% P(VdCl..):50m%NH₃SCN and hence exhibited highest ionic conductivity.

References

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