Conductivity study of poly($N$-vinylimidazole-$co$-butylmethacrylate) and its fluoroborate salt in solid state

Samadrita Goswami*, Aradhana Dutta
Polymer Research Laboratory, Department of Chemistry, Dibrugarh University, Dibrugarh-786 004, Assam, (INDIA)
E-mail: gsamadrita@yahoo.com
Received: 21st July, 2011 ; Accepted: 21st August, 2011

ABSTRACT

In this paper, the chain flexibility of Poly($N$-vinylimidazole) was tried to increase by lowering its glass transition temperature (T$_g$) and by increasing its amorphous region by copolymerizing with n-butyl methacrylate. The copolymers were prepared in five different feed molar ratios to optimize the required properties such as higher room temperature conductivity and better film forming capacity. The conductivity of copolymers, as well as their fluoroborate salts, have been reported here. The copolymers were prepared by free radical method and the salts were prepared by simple acidification. The copolymers and salts have been characterized by IR, $^1$HNMR, TGA, DSC analysis. Frequency and temperature dependence of a.c. conductivity has been studied to learn about the electrical conduction behavior in the materials.

INTRODUCTION

Polymer electrolytes are the newest area of solid ionics to receive wide attention for application in electrochemical devices such as batteries and electrochemical windows. Two general types of polymer electrolyte have been intensively investigated: polymer salt complexes and polyelectrolytes. A typical polymer electrolyte consists of a coordinating polymer, usually a polyether, in which a salt, e.g. LiClO$_4$ is dissolved. Both anions and cations can be mobile in these types of electrolytes. By contrast, polyelectrolytes contain charged groups, either cations or anions, covalently attached to the polymer, so only the counter ion is mobile$^{[31]}$. Some anionic polyelectrolytes like lithium poly(2-sulphoethyl methacrylate)$^{[21]}$, sodium polystyrene sulphonate$^{[31]}$, poly(dialkyldimethyl ammonium chloride)$^{[41]}$ etc have been investigated in the context of single ion conducting solid ionics. In the last decades conductivity studies of some cationic polyelectrolytes like Poly(2-dimethylaminoethylmethacrylate)-HCl, Poly(2-vinylpyridine)-HX (where, X=F,Cl,Br,NO$_3$,IO$_3$), Poly(4-vinylpyridine)-HX (where, X=Cl,Br,I) salts have also been reported$^{[5-12]}$. Z. Tang et al$^{[13]}$ reported the conductivity study of polymer electrolytes based on the copolymer of $N$-Vynylimidazolium tetrafluoroborate (VyImBF$_4$) and poly (ethyleneglycol) dimethacrylate (PEGDMA). The highest conductivity with a value of 2.9 x 10$^{-6}$ Scm$^{-1}$ was reported for the copolymer prepared from feed molar ratio of VyImBF$_4$:PEGDMA = 80:20, plasticized with 25% ethylene carbonate (EC) and adding 0.70 mol Kg$^{-1}$ of LiClO$_4$ (for the purpose

KEYWORDS

PVIM; BuMA; P(VIM-$co$-BuMA); Polyelectrolytes; Copolymers; AC conductivity.
of getting target ions i.e. Li$^+$ ions)

In this paper we report our attempt to increase the ionic conductivity as well as film forming capacity of Poly(N-vinylimidazole) (PVIM) and its fluoroborate salt PVIM-HBF$_4$\textsuperscript{14} by internal plasticization with butyl methacrylate (BuMA). For this purpose we first prepared the copolymer of N-vinylimidazole and butylmethacrylate (VIM-co-BuMA); the salt was then prepared by simple acidification of the copolymer with HBF$_4$. Both the copolymer and its salt could be cast into thin films. The novelty of our work is that no external salt was used for enhancement of conductivity. Instead the virgin copolymer films were used for measurement of conductivity and conductivity value of $2.7 \times 10^{-5}$ S cm$^{-1}$ could be achieved at 30$^\circ$C. Various experimental techniques such as Infra red (IR), proton nuclear magnetic resonance ($^1$HNMR), Thermogravimetric analysis (TGA), Differential Scanning Calorimetry (DSC) and conductivity studies are employed to characterize the copolymers and the polyelectrolytes.

**EXPERIMENTAL**

**Materials**

$N$-vinylimidazole (Aldrich), n-butylmethacrylate (Fluka), benzene (Merck), methanol (Ranbaxy), acetone (Ranbaxy), were of synthetic grade and purified by distillation under reduced pressure. AIBN (E-Merck) was recrystallised from methanol. Fluoroboric acid, diethyl ether (Ranbaxy) were of analar grade and were used without further purification.

**Preparation of copolymers**

$N$-vinylimidazole (VIM) and butyl methacrylate (BuMA) were copolymerized in five different feed molar ratios (VIM:BuMA::1:1, 1:1.5, 1:2, 1:2.5, 1:3) by free radical method using AIBN as an initiator and benzene as solvent under N$_2$ atmosphere. The reaction was allowed to continue for about 18h at 60$^\circ$C in a thermostatic water bath. After the completion of the reaction, about two third of the solvent was removed by distillation under reduced pressure. The copolymers were precipitated in diethyl ether. The copolymers were then dissolved in methanol (methanol is non solvent for polybutylmethacrylate); the undissolved compounds were filtered off and precipitated with diethyl ether. The precipitate was again dissolved in toluene (toluene is nonsolvent for PVIM), filtered, and reprecipitated with diethyl ether. The entire precipitation procedure was repeated twice to ensure complete removal of unreacted monomers, the homopolymers and initiators. The copolymers so obtained were then dried in a dessicator over fused CaCl$_2$ stored in N$_2$ atmosphere to avoid contact with moisture from air. The copolymers P(VIM-co-BuMA) were solution cast over glass plate and dried in a vacuum oven for overnight. The dried film was used for conductivity measurement.

**Preparation of P(VIM-co-BuMA-HBF$_4$)**

A concentrated solution of each one of the copolymers was prepared in methanol and treated with 10% HBF$_4$ at room temperature and kept for overnight. The P(VIM-co-BuMA-HBF$_4$) salts were then precipitated with acetone. The salts were then dissolved in methanol again and reprecipitated with acetone to get the purified salt. The salts were stored over fused CaCl$_2$ before use. The P(VIM-co-BuMA-HBF$_4$) salts were solution cast over glass plate and dried in a vacuum oven for overnight. The dried film was used for conductivity measurement.

**MEASUREMENTS**

The 400MHz proton NMR spectra were recorded with a VARIAN 400MHz NMR spectrophotometer using CDCl$_3$ as solvent. IR spectra were recorded with a Shimadzu IR Prestige 21 spectrophotometer using thin films of the polymer and polyelectrolyte. TGA were recorded with a Perkin-Elmer Thermal Analyzer with a heating rate of 20$^\circ$C min$^{-1}$. DSC were recorded with a Perkin-Elmer Jade DSC Analyzer with a heating rate of 20$^\circ$C min$^{-1}$. The electrical conductivity of these polymers was evaluated from the complex impedance – admittance plots recorded at different temperatures using a HIOKI LCR HiTESTER 3522 frequency response analyzer. The plots were recorded in the frequency range from 0.001 to 100KHz keeping the signal amplitude of 20mV. The geometry of the cell for the measurement of conductivity was Pt | polymer film | Pt, where platinum plate was used as electrodes. The experiment was carried out under a relative humidity of 55%. The electrical conductivities were subsequently obtained from the relation,
\[ \sigma = \frac{t}{R_b A} \]  
where, \( t \) = thickness of the film, \( A \) = area of the film and \( R_b \) = bulk resistance of the film.

**RESULTS AND DISCUSSION**

For characterization by IR, 1HNMR, TGA, DSC, the copolymer and its salt prepared from 1:2 feed molar ratio of VIM:BuMA were taken since conductivity value was found to be highest for that copolymer (composition VIM:BuMA::0.628:0.372) salt.

**Infrared**

The IR spectra of the copolymer and its fluoroborate salts are shown in figure 1. The peaks at 2958.80 cm\(^{-1}\) (–C–H– asymmetric stretching vibrations), at 2872.01 cm\(^{-1}\) (–C–H– asymmetric stretching vibration), at 1384.89 cm\(^{-1}\) (–C–H– symmetric deformation) are all due to methyl group. The peaks at 750.31 cm\(^{-1}\) skeletal vibration of the –CH\(_2\)– group [for –(–CH\(_2\)–)\(_n\) or more]\(^{16-18}\)

The spectrum of P(VIM-co-BuMA-HBF\(_4\)) (figure 1b) shows a strong peak at 1544.98 cm\(^{-1}\), and this may be due to –N\(^{+}\)-H bending vibration\(^{17,18}\), which confirms the incorporation of fluoro borate ion into the polymer ; this peak is absent in P(VIM-co-BuMA) (figure 1a). The peak at 3149.76 cm\(^{-1}\) is due to C-H (ring) stretching, 2931.80 cm\(^{-1}\) is due to C-H and CH\(_2\) (main chain) stretching, 1633.71 cm\(^{-1}\) is due to C=C (ring) stretching, 1469.76 cm\(^{-1}\) is due to C-C and C=N (ring) stretching; the peaks at 1242.16 cm\(^{-1}\), 1147.65 cm\(^{-1}\), 1062.78 cm\(^{-1}\) are due to C-H (ring) in plane bending, C-N (ring) stretching; the peak at 663.51 cm\(^{-1}\) is due to C-N (ring) stretching\(^{21}\).

Proton nuclear magnetic resonance

Proton NMR spectra of the copolymer and its fluoroborate salts in CDCl\(_3\) are shown in figure 2. The peaks at 2958.80 cm\(^{-1}\) (–C–H– asymmetric stretching vibrations), at 2872.01 cm\(^{-1}\) (–C–H– asymmetric stretching vibration), at 1384.89 cm\(^{-1}\) (–C–H– symmetric deformation) are all due to methyl group. The peaks at 750.31 cm\(^{-1}\) skeletal vibration of the –CH\(_2\)– group [for –(–CH\(_2\)–)\(_n\) or more]. The N-H stretch in P(VIM-co-BuMA-HBF\(_4\)) causes absorption in 3261.63 cm\(^{-1}\)\(^{18,19}\).
The spectrum of P(VIM-co-BuMA) contains the characteristic proton signals from imidazole ring (multiplet with 6.7-7.3 ppm), backbone CH$_2$(1.6-2.3 ppm) group, splitting chain CH group (3.36-3.75 ppm), methyl protons attached to backbone (1.39 ppm), -C(=O)-O-CH$_2$ protons (3.93 ppm) [16-18]. In the spectrum of P(VIM-co-BuMA-HBF$_4$) the signal at 8.1-8.5 ppm indicates the presence of N$^+$-H proton [17-18] confirming the formation of the polyelectrolyte (figure 2b). The spectrum of P(VIM-co-BuMA-HBF$_4$) contains the characteristic proton signals from imidazole ring (multiplet with 6.7-7.3 ppm), backbone CH$_2$(1.6-2.3 ppm) group, splitting chain CH group (3.5-3.75 ppm), methyl protons attached to backbone (1.40 ppm), -C(=O)-O-CH$_2$ protons (3.93 ppm) [16-18]. It is assumed that the reaction proceeds in the following way:

\[
\text{H}_2\text{C}=\text{C}(\text{N})\text{H}_2 + \text{H}_2\text{C}=\text{C}(\text{O})\text{H}_2 \xrightarrow{\text{AIBN} / 60^\circ C} \begin{array}{c}
\text{CH}_3 \\
\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3
\end{array}
\]

Copolymerization of VIM and BuMA

\[
\begin{array}{c}
\text{H}_2\text{C}-\text{CH}_m \\
\text{N}
\end{array} + \text{CH}_2\text{CH}_2\text{CH}_3
\]

Acidification of P(VIM-co-BuMA)

The compositions of the copolymers were derived from $^1$HNMR data [20]. Assuming $m_1$ as the mole fraction of VIM unit and $m_2$ as the mole fraction of BuMA, the composition of VIM in the copolymer was determined by comparing the integral values of aromatic (I$_A$) and aliphatic protons (I$_a$) as shown below:

\[
I_A/I_a = 3m_1/(3m_1 + 14m_2)
\]

The equation is derived from the fact that VIM contains 3 aromatic and 3 aliphatic protons, while BuMA has 14 aliphatic protons. From this and $m_2 = 1-m_1$, we have

\[
m_1 = I_A/(3I_a + 11I_A)
\]

The integral values of VIM ($I_{\text{VIM}}$) and BuMA ($I_{\text{BuMA}}$) are presented in TABLE 1.

<table>
<thead>
<tr>
<th>Composition of VIM in feed</th>
<th>Composition of BuMA in feed</th>
<th>Integral Value $I_{\text{VIM}}$</th>
<th>Integral Value $I_{\text{BuMA}}$</th>
<th>Copolymer composition $m_1$</th>
<th>Copolymer composition $m_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1.00</td>
<td>2.47</td>
<td>0.760</td>
<td>0.240</td>
</tr>
<tr>
<td>1</td>
<td>1.5</td>
<td>1.79</td>
<td>5.07</td>
<td>0.718</td>
<td>0.282</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>1.00</td>
<td>3.76</td>
<td>0.628</td>
<td>0.372</td>
</tr>
<tr>
<td>1</td>
<td>2.5</td>
<td>1.00</td>
<td>6.19</td>
<td>0.473</td>
<td>0.527</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>1.00</td>
<td>6.23</td>
<td>0.471</td>
<td>0.529</td>
</tr>
</tbody>
</table>

From the table it has been observed that with increase in the amount of BuMA in the feed, VIM content in the copolymer decreased.

TGA

TGA thermogram of the copolymer and its fluoroborate salts are shown in Figure 3(a) and 3(b) respectively.

The copolymer showed a single step degradation. However, the salt P(VIM-co-BuMA-HBF$_4$) showed two step decomposition as is evident from figure 3. The first step of decomposition may be due to the loss of
HBF$_4$ molecule and the second step of decomposition may be due to degradation of copolymer backbone.

**DSC**

From the DSC thermogram (Figure 4), glass transition temperatures ($T_g$) were found to be 134.33°C and 152.10°C, for copolymer and its fluoro-borate salt, respectively. The glass transition temperature of the copolymer was lowered in comparison to pure PVIM ($T_g$(PVIM) = 147.663°C). This may be due to incorporation of flexible –O=C-O- group of BuMA, which lowers the value of $T_g$ by increasing the free volume in the copolymer matrices\[21,22\]. Since P(VIM-co-BuMA-HBF$_4$) is a polycation, the electrostatic interaction may increase the $T_g$ as compared to P(VIM-co-BuMA) which contains no charged species\[23\].

**Conductivity**

The conductivity of the copolymers prepared from different feed monomer composition and their polyelec-trolytes is measured by AC impedance spectroscopy. Figure 5 presents the typical impedance plot of fluoro-borate salt having approximately copolymer composition (VIM:BuMA::0.628:0.372) at 30°C. As illustrated in Figure 5, the complex impedance plot is in the form of two regions: an arc and a linear region. The arc at medium-high frequencies is related to the conduction process, and the straight line inclined with respect to the real axis at lower frequencies is due to the effect of blocking electrodes\[13\]. AC conductivities at different temperatures for pure PVIM and the copolymers of five different copolymer compositions are shown in TABLE 2(a) and their HBF$_4$ salts are shown in TABLE 2(b).

![Figure 5: AC impedance spectrum of P(VIM-co-BuMA-HBF$_4$) at 30°C](image)

The measurements for the temperature dependence of conductivity were taken to analyze the mechanism of ionic conduction. In general, the relationship between conductivity of polymer electrolytes and temperature is in accord with either the Vogel–Tamman–Fulcher [VTF; Eq. (4)]\[24\] behaviour or the Arrhenius equation [Eq. (5)]\[25\]:

$$\sigma = AT^{-0.5} \exp \left[-\frac{B}{T-T_0}\right]$$  \hspace{1cm} (4)  

$$\sigma = \sigma_0 \exp \left[-\frac{E_a}{RT}\right]$$ \hspace{1cm} (5)

where $A$ is a pre-exponential factor that is proportional to the number of charge ions, $B$ is the pseudo-activation energy associated with the motion of the polymer, $E_a$ is the activation energy, and $T_0$ is a reference temperature, which has been reported to be 30–50 °C lower than $T_g$ for many polymer electrolytes systems\[26\].

Figure 6 shows the Arrhenius plots of P(VIM-co-BuMA), P(VIM-co-BuMA-HBF$_4$) with different compositions in the temperature range of 30–80°C.

For all the samples, it is clear that the Arrhenius plots of log $\sigma$ versus 1000/T are linear, meaning that the conductivity follows an Arrhenius relationship with
TABLE 2(a): Conductivity data of PVIM and copolymers of different compositions

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Conductivity (S cm⁻¹) values for PVIM</th>
<th>Conductivity(Scm⁻¹) values for copolymers composition VIM:BuMA::</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>σ×10⁶</td>
<td>σ×10⁶</td>
</tr>
<tr>
<td>30</td>
<td>4.11</td>
<td>2.64</td>
</tr>
<tr>
<td>40</td>
<td>13.9</td>
<td>5.86</td>
</tr>
<tr>
<td>50</td>
<td>5.35</td>
<td>0.98</td>
</tr>
<tr>
<td>60</td>
<td>5.55</td>
<td>0.372</td>
</tr>
<tr>
<td>70</td>
<td>4.05</td>
<td>1.43</td>
</tr>
<tr>
<td>80</td>
<td>4.20</td>
<td>1.39</td>
</tr>
<tr>
<td>90</td>
<td>23.4</td>
<td>8.10</td>
</tr>
</tbody>
</table>

TABLE 2(b): Conductivity data of HBF₄ salt of PVIM and copolymers of different compositions

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Conductivity (S cm⁻¹) values for PVIM-HBF₄</th>
<th>Conductivity(Scm⁻¹) values for salt with copolymer composition VIM:BuMA::</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>σ×10⁴</td>
<td>σ×10⁴</td>
</tr>
<tr>
<td>30</td>
<td>3.22</td>
<td>7.37</td>
</tr>
<tr>
<td>40</td>
<td>3.42</td>
<td>13.3</td>
</tr>
<tr>
<td>50</td>
<td>1.74</td>
<td>4.94</td>
</tr>
<tr>
<td>60</td>
<td>2.10</td>
<td>7.00</td>
</tr>
<tr>
<td>70</td>
<td>2.02</td>
<td>6.48</td>
</tr>
<tr>
<td>80</td>
<td>1.32</td>
<td>5.62</td>
</tr>
<tr>
<td>90</td>
<td>10.5</td>
<td>4.93</td>
</tr>
</tbody>
</table>

The curves show that the formation of the salt increases the ionic conductivity. The bulk conductivity of the poly-electrolyte was found to increase with increasing temperature. From the TABLES 2(a), 2(b) and Figure 6, it is observed that there is about 10²-10³ fold increase in the room temperature conductivity of HBF₄ salts than the corresponding copolymers. This can be explained in the following way.

Imidazole molecule in VIM is basic due to the presence of nucleophilic imidazolyl group. In the presence of an acid, the nitrogen lone pair easily forms a new N-H bond with proton of the acid and behaves like a positive ion. This ion then forms stable salt with the negative ion like BF₄⁻. The presence of BuMA as internal plasticizer facilitates the free movement of the ions in the copolymer matrix. In this process the ionic character increases and the salt behaves as fairly good electrolyte.

Also, there was about 10 fold increase in conductivity of the plasticized polyelectrolytes than that of HBF₄ salt of pure PVIM (TABLE 2(a) & 2(b)). This may be due to the fact that copolymerisation of VIM with BuMA lowers Tg, thereby increasing the chain flexibility, which facilitates more ion mobility and hence increases ionic conductivity. The increase in chain flexibility is evident from the lower value of the glass transition temperatures.
of the copolymer (Figure 4(a),(b)) than PVIM. The maximum conductivity was noted for copolymer composition VIM : BuMA :: 0.628:0.372. However, with further increase in the amount of BuMA in the copolymer, the room temperature conductivity of the polyelectrolytes decreased. This may be due to the fact that higher amount of BuMA means VIM content in the copolymer is less. As the VIM unit contains the following ionic moiety:

\[
\text{(H}_2\text{C}_2\text{CH)}_\text{NCH}_\text{H}_\text{2C(H)BF}_\text{4}^{-}
\]

which is responsible for conductivity; the conductivity decreases due to decrease of VIM content.

**CONCLUSION**

The copolymerisation has increased the chain flexibility, as is evident from \( T_g \) values. However, at higher molar ratio of BuMA, the chain flexibility decreases, and therefore, the room temperature conductivity also decreases. This is due to increasing strength of copolymer-copolymer interaction caused by increased polar group of BuMA, thereby decreasing the chain flexibility. Also, decrease in ionic conductivity may be due to less amount of (VIM-HBF\(_4\)) unit in the copolymer, responsible for ionic conductivity. Moreover, the increasing amount of BuMA make the polymer electrolytes more hygroscopic at room temperature, thereby making it difficult to process to cast into thin films. Therefore, polymer host matrix should be copolymerized with optimum amount of BuMA to get good-quality polyelectrolytes having high room temperature conductivity as well as good flexibility. In our study, the copolymer prepared from 1:2 feed molar ratio of VIM:BuMA (copolymer composition (VIM:BuMA::0.628:0.372), evident from Table 1) showed the best results which may find application in electrochemical devices.

**ACKNOWLEDGEMENTS**

Authors are thankful to University Grant Commission (UGC) for the award of fellowship from the scheme Research Fellowship in Sciences for Meritorious Students (RFSSMS), CDRI, Lucknow for recording the NMR spectra of the samples.

**REFERENCES**