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

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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}H NMR, TGA, DSC analysis. Frequency and temperature dependence of a.c. conductivity has been studied to learn about the electrical conduction behavior in the materials. © 2011 Trade Science Inc. - INDIA

KEYWORDS

PVIM;
BuMA;
P(VIM-*co*-BuMA);
Polyelectrolytes;
Copolymers;
AC conductivity.

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[1]. Some anionic polyelectrolytes like lithium poly(2-sulphoethyl methacrylate)[2], sodium polystyrene sulphonate[3], poly(dialkyl dimethyl ammonium chloride)[4] 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*-Vinylimidazolium tetrafluoroborate ($VyImBF_4$) and poly (ethyleneglycol) dimethacrylate (PEGDMA). The highest conductivity with a value of 2.9×10^{-6} Scm^{-1} was reported for the copolymer prepared from feed molar ratio of VyIm BF_4:PEGDMA = 80:20, plasticized with 25% ethylene carbonate (EC) and adding 0.70 mol Kg^{-1} of $LiClO_4$ (for the purpose

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 fluroborate salt PVIM-HBF_4 [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 novelity 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 2.7×10^{-5} S cm^{-1} could be achieved at 30^0C. 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 60^0C 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 20^0 C min^{-1}. DSC were recorded with a Perkin-Elmer Jade DSC Analyzer with a heating rate of 20^0 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[15] of 55%. The electrical conductivities were subsequently obtained from the relation,

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$\sigma = t/R_b.A$ (1)

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 ^{1}HNMR, 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.

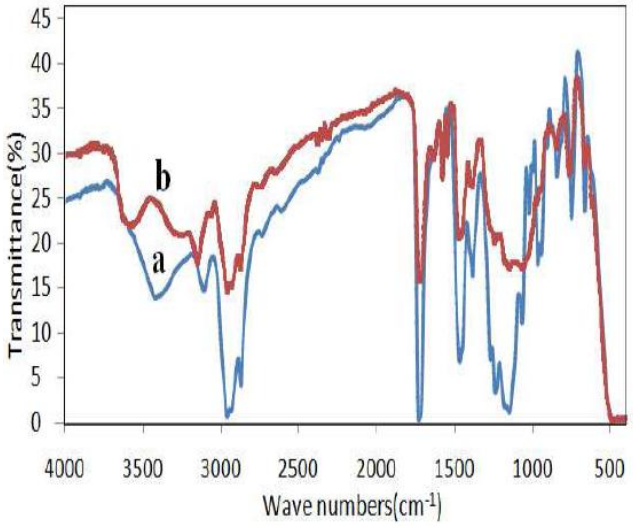


Figure 1 : IR spectra of (a) P(VIM-*co*-BuMA) (b) P(VIM-*co*-BuMA-HBF$_4$)

In P(VIM-*co*-BuMA) the peak at 663.51 cm^{-1} is due to C-N(ring)stretching, which is a characteristic imidazole ring band in VIM unit[16]. The peaks at 1732.08 and 1176.58 cm^{-1} are due to -C=O- and -O-(C=O)-, respectively, and this indicates the incorporation of butyl methacrylate unit into the copolymer matrices[17]. The peak at 3109.25 cm^{-1} is due to C-H(ring)stretching, 2933.73cm^{-1} is due to C-H and CH_2(main chain) stretching, The peak at 1568.13 cm^{-1} is due to C=C(ring) stretching . The peak at 1467.83 cm^{-1} is due to C-C and C=N(ring)stretching. The peaks at 1271.09.59cm^{-1}, 1238.30cm^{-1}, 1066.64cm^{-1} are due to C-H (ring) in plane bending, C-N(ring)stretching ; the peak at 945.12 cm^{-1} is due to ring stretching and in plane bending [25]. 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–)$_4$ 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 fluroborate 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, 2931.80cm^{-1} is due to C-H and CH_2(main chain) stretching, 1633.71cm^{-1} is due to C=C(ring) stretching, 1469.76cm^{-1} is due to C-C and C=N(ring) stretching; the peaks at 1242.16cm^{-1}, 1147.65cm^{-1}, 1062.78 cm^{-1} are due to C-H (ring)in plane bending, C-N(ring)stretching ; the peak at 663.51cm^{-1} is due to C-N(ring)stretching[25]. The peaks at 2958.80 cm^{-1} (–C–H– asymmetric stretching vibrations), at 2873.94 cm^{-1}(–C–H– asymmetric stretching vibration), at 1,382.96 cm^{-1} (–C–H– symmetric deformation) are all due to methyl group. The peaks at 761.88 cm^{-1} skeletal vibration of the –CH_2– group [for –(–CH_2–)$_4$ or more]. The N-H stretch in P(VIM-*co*-BuMA-HBF$_4$) causes absorption in 3261.63 cm^{-1}[18,19]

Proton nuclear magnetic resonance

Proton NMR spectra of the copolymer and its fluoroborate salts in $CDCl_3$ are shown in figure 2.

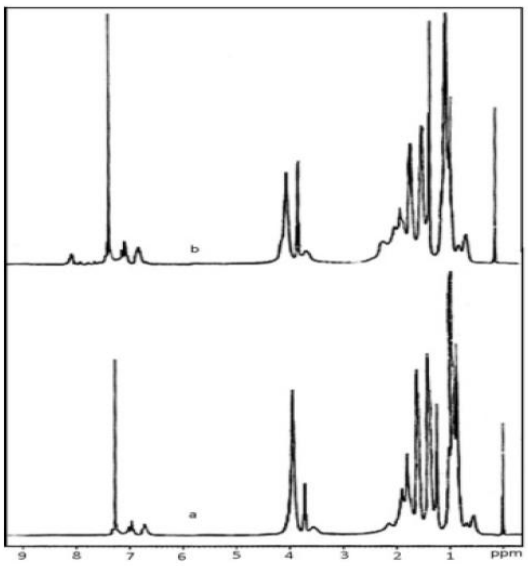
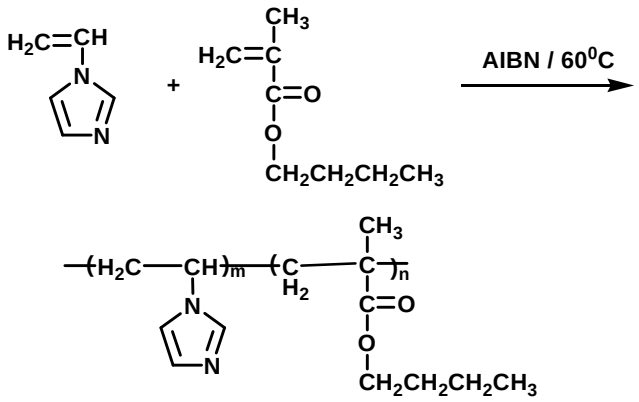


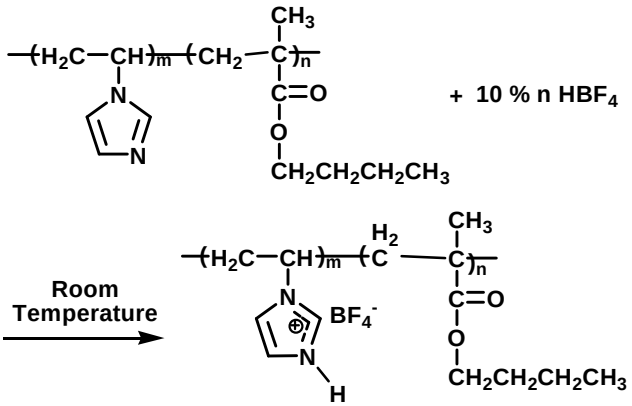
Figure 2 : ^{1}H NMR spectra of (a) P(VIM-*co*-BuMA) (b) P(VIM-*co*-BuMA-HBF$_4$)

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(1.6-2.3ppm)group, splitting chain CH group (3.36-3.75ppm), methyl protons attached to backbone(1.391 ppm),-C(=O)-O-CH_2 protons (3.934 ppm)[16-18]. In the spectrum of P(VIM-*co*-BuMA-HBF_4) the signal at 8.1-8.5ppm 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(1.6-2.3ppm)group, splitting chain CH group (3.5-3.75ppm),methyl protons attached to backbone(1.40 ppm),-C(=O)-O-CH_2 protons (3.937 ppm)[16-18].

It is assumed that the reaction proceeds in the following way:



Copolymerization of VIM and BuMA



Acidification of P(VIM-*co*-BuMA)

Copolymer composition

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:

$$I_A / I_a = 3m_1 / (3m_1+14m_2) \quad (2)$$

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

$$m_1 = I_A / (3I_a+11I_A) \quad (3)$$

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

TABLE 1 : Integral values of VIM (I_{VIM}) and BuMA (I_{BuMA})

Composition of VIM in feed	Composition of BuMA in feed	Integral Value I_{VIM}	Integral value I_{BuMA}	Copolymer composition m_1	Copolymer composion m_2
1	1	1.00	2.47	0.760	0.240
1	1.5	1.79	5.07	0.718	0.282
1	2	1.00	3.76	0.628	0.372
1	2.5	1.00	6.19	0.473	0.527
1	3	1.00	6.23	0.471	0.529

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.

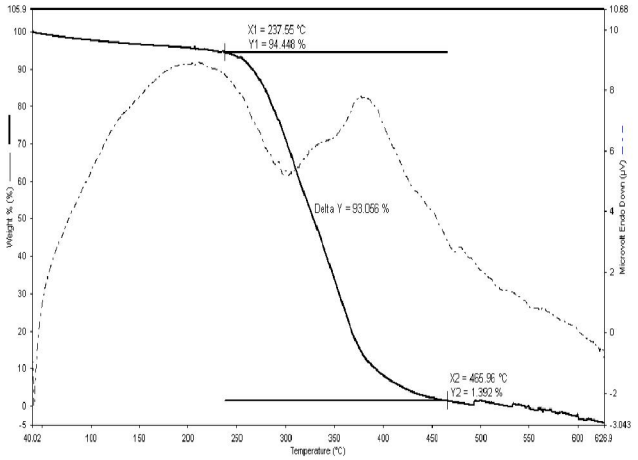


Figure 3(a) : TGA curve of P(VIM-*co*-BuMA)

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

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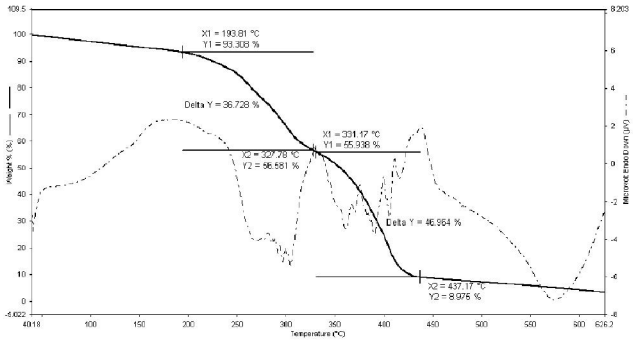

Figure 3(b) : TGA curve of P(VIM-*co*-BuMA-HBF$_4$)

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 be134.33^{0}C and 152.10 ^{0}C, for copolymer and its fluroborate salt, respectively. The glass transition temperature of the copolymer was lowered in comparison to pure PVIM ($Tg_{(PVIM)}$=147.663^0 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].

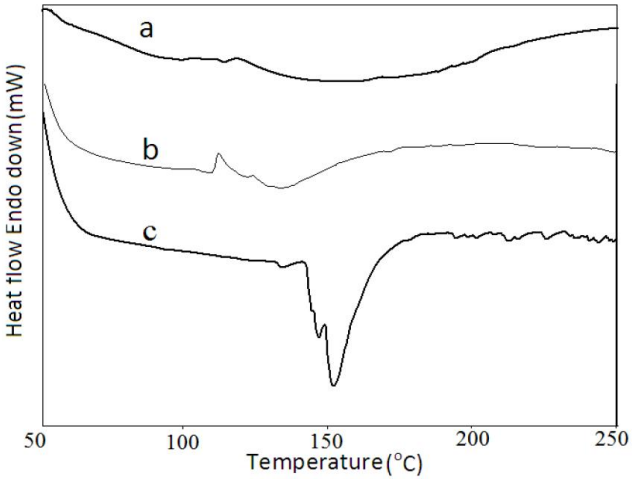

Figure 4 : DSC curves of (a) PVIM (b) P(VIM-*co*-BuMA) (c) P(VIM-*co*-BuMA-HBF$_4$)

Conductivity

The conductivity of the copolymers prepared from different feed monomer composition and their polyelectrolytes is measured by AC impedance spectroscopy. Figure 5 presents the typical impedance plot of fluroborate salt having approximately copolymer composition (VIM:BuMA::0.628:0.372) at 30^{0}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).

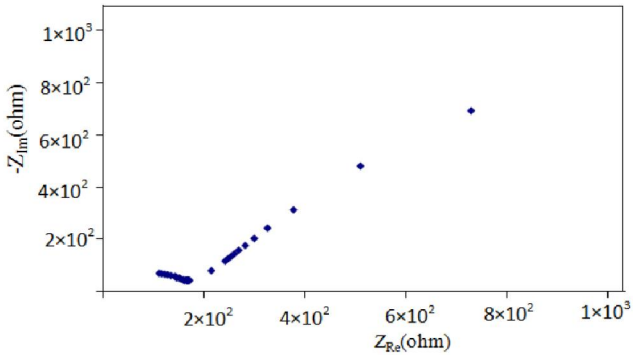

Figure 5 : AC impedance spectrum of P(VIM-*co*-BuMA-HBF$_4$) at 30^{0}C

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]:

$$\sigma = AT^{-0.5}\exp[-B/(T-T_0)] \quad (4)$$

$$\sigma = \sigma_0 \exp(-E_a/RT) \quad (5)$$

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^{0}C.

For all the samples, it is clear that the Arrhenius plots of log σ 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

Temperature (^{0}C)	Conductivity (S cm^{-1}) values for PVIM $\sigma\times10^{-9}$	Conductivity(Scm^{-1}) values for copolymers composition VIM:BuMA::				
		0.760: 0.240	0.718: 0.282	0.628: 0.372	0.473: 0.527	0.471: 0.529
		$\sigma\times10^{-8}$	$\sigma\times10^{-8}$	$\sigma\times10^{-7}$	$\sigma\times10^{-8}$	$\sigma\times10^{-8}$
30	4.11	2.64	5.86	0 .98	5.33	5.00
40	13.9	4.59	6.02	1.43	6.39	5.85
50	5.53	5.51	6.12	1.94	7.01	6.34
60	5.55	5.53	7.13	2.27	7.90	6.95
70	4.05	8.52	8.80	2.89	8.10	7.12
80	4.20	4.59	9.30	4.57	8.50	7.94
90	23.4	16.9	20.07	6.54	9.00	8.21

TABLE 2(b) : Conductivity data of HBF_4 salt of PVIM and copolymers of different compositions

Temperature (^{0}C)	Conductivity (Scm^{-1}) values for PVIM-HBF_4 $\sigma\times10^{-6}$	Conductivity(Scm^{-1}) values for salt with copolymer composition VIM:BuMA::				
		0.760: 0.240	0.718: 0.282	0.628: 0.372	0.473: 0.527	0.471: 0.529
		$\sigma\times10^{-6}$	$\sigma\times10^{-6}$	$\sigma\times10^{-5}$	$\sigma\times10^{-6}$	$\sigma\times10^{-6}$
30	3.22	3.28	7.37	2.76	5.24	4.93
40	3.42	6.36	13.3	4.13	6.48	5.62
50	1.74	7.73	18.2	4.94	7.00	6.40
60	2.10	9.07	22.1	5.79	7.60	7.55
70	2.02	18.0	41.3	7.38	8.59	8.55
80	1.32	26.1	55.4	8.59	9.10	8.92
90	10.5	27.6	61.4	13.30	12.2	19.8

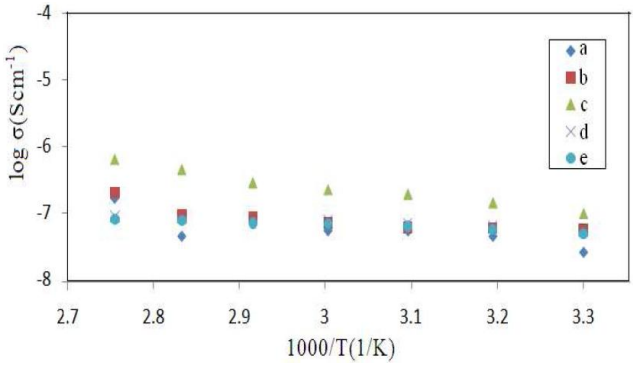

Figure 6(a) : Plot of *log σ* vs. *1/T* of P(VIM-*co*-BuMA)

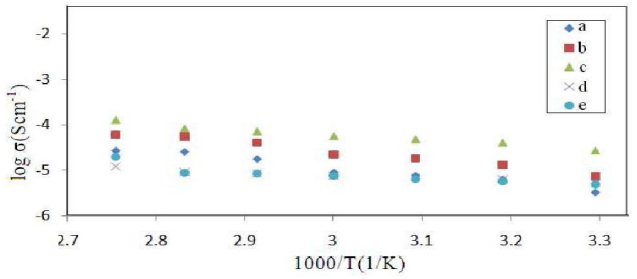

Figure 6(b) : Plot of *log σ* vs. *1/T* of P(VIM-*co*-BuMA-HBF_4)

temperature in the temperature range measured. These curves show that the formation of the salt increases the ionic conductivity. The bulk conductivity of the polyelectrolyte was found to increase with increasing temperature. From the TABLES 2(a), 2(b) and Figure 6, it is observed that there is about 10^2-10^3 fold increase in the room temperature conductivity of HBF_4 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 BF_4^-. 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 HBF_4 salt of pure PVIM (TABLE 2(a) & 2(b))[14]. 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

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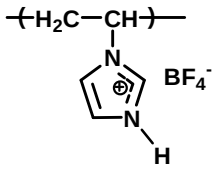
of the copolymer (Figure 4(a),(b)) than PVIM. The maximum conductivity was noted for copolymer composition VIM : BuMA :: 0.628:0.372. However, with further increase in the amount of BuMA in the copolymer, the room temperature conductivity of the polyelectrolytes decreased. This may be due to the fact that higher amount of BuMA means VIM content in the copolymer is less. As the VIM unit contains the following ionic moiety:



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.

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