

Conductivity study of solid polyelectrolytes based on hydroiodide salt of poly(4-vinyl pyridine-co-butylmethacrylate), poly(4-vinyl pyridine-co-butylacrylate)

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Abstract. The chain flexibility of poly(4-vinylpyridine) was tried to increase by lowering its glass transition temperature (T_g) and by increasing its amorphous region by copolymerizing with butyl methacrylate and butylacrylate which act as internal plasticizer. 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 and conduction behaviour of the copolymers, as well as their hydroiodide salts have been reported. There was about 10^3 – 10^4 -fold increase in room temperature conductivity of these plasticized polyelectrolytes.

Keywords. Ion conducting polymer; polyelectrolyte; conductivity; copolymer; P-4VP; transport number.

1. Introduction

Ion conducting polymers have shown great potential for many applications such as batteries, fuel cells, supercapacitors, hybrid power sources, sensors, electrochromic display devices, etc. The matrix flexibility ensures proper electrode–electrolyte contact in different electrochemical devices (Sorensen and Jacobson 1982; MacCallum and Vincent 1987, 1989; Ratner and Shriver 1988; Grey 1991). After Wright (1975) reported that poly(ethylene oxide) (PEO) with alkaline metal salts exhibited significant ionic conductivity, Armand *et al* (1979) recognized the potential of these materials in lithium batteries. 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 (Bruce 1995). Unfortunately, solid-state polymer electrolytes have inherent problem of low ionic conductivity at ambient temperature that acts as a barrier to their utility when compared with the easily conventional liquid/hybrid electrolytes (Pradhan *et al* 2008). Most of the research on ion conducting polymers has addressed this problem. This may be due to poor segmental motion of the polymer host. The strategy being used is modification of the polymer, to reduce crystallinity of the starting host macromolecule. As a rule, pendant PEO segments, copolymers or crosslinking networks, introduce disorder which leads to amorphous materials (Armand 1990). Further, it is generally agreed that, to maximize the segmental motion and thereby ionic

conductivity of polyelectrolytes, the polymer host should be flexible, as well as amorphous materials with low T_g . A variety of such polymers have been developed (Druger *et al* 1983; Blonsky *et al* 1984; Ratner and Shriver 1988; Allock *et al* 1996; Hutchison *et al* 1996). This can be achieved either by internal or external plasticization (Gowariker *et al* 1996). Recently, some single ion-conducting polymers have been developed. This can be classified as an acid base reactive (Elliot *et al* 2003) polyacids or acid-like molecules and base centres of the polymers (Moulic and Dutta 2002; Chetia *et al* 2004a, b; Borah and Dutta 2007, 2008; Chetri *et al* 2007; Goswami and Dutta 2011). Unlike PEO complexes with alkali metals or other salts, in these conducting polymers, no external salt is used; instead, virgin polymer and polyelectrolytes (inherently conducting polymers) are used for measurement of conductivity.

The virgin polymer P-4VP, showed both ionic and electronic conduction. It was suggested that in case of P-4VP, the polymeric backbone might have acquired some polar character due to the presence of lone pair of electrons on pendant groups, as a result of which some methine protons might have been released under the influence of an external electric field showing ionic conduction. It was evidenced by the fact that conductivity measurement made on the solid charge transfer (CT) complex formed between P-4VP and iodine showed no ionic conduction because of the loss of polar character of the polymeric backbone due to the involvement of lone pair of electrons on nitrogen atom in CT complex formation. Again in P-4VP, the nitrogen lone pair easily forms a new N–H bond with proton of the acid (HX, where X = Cl, Br, I, BF_4 , ClO_4 , etc) and quaternary pyridinium ion behaves like a positive ion which then forms stable salts with negative ions like I^- . In this process, ionic character increases resulting in good polyelectrolytes.

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The conductivity study of poly(4-vinylpyridine) (P-4VP) and its HI salt (P-4VP-HI) has already been reported (Chetia *et al* 2004a, b). In this paper, we report our attempt to increase the ionic conductivity, as well as thermal stability of P-4VP and P-4VP-HI by internal plasticization with butylmethacrylate (BuMA) and butylacrylate (BuA). The plasticization effect of both the plasticizers on conductivity of P-4VP is also studied. Various experimental techniques such as IR, ^1H NMR, TGA, DSC, frequency and temperature dependence of conductivity measurements are employed to characterize copolymers and polyelectrolytes.

2. Experimental

2.1 Preparation of copolymers

The 4-Vinyl pyridine and butylmethacrylate were copolymerized in five different feed molar ratios (1:0.5, 1:1, 1:1.5, 1:2 and 1:2.5) by using AIBN as initiator and tetrahydrofuran (THF) as solvent in nitrogen atmosphere. The reaction was allowed to continue for about 18 h at around 60 °C in a thermostatic water bath. After the completion of reaction, about two-thirds of the solvent was removed by distillation under reduced pressure. The copolymers were precipitated in diethyl ether. The copolymers, poly(4-vinyl pyridine-co-butylmethacrylate) and P(4VP-co-BuMA), 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 non-solvent for P-4VP), filtered and reprecipitated with diethyl ether. The entire precipitation procedure was repeated twice to ensure complete removal of unreacted monomers, homopolymers and initiator. The copolymers were then dried in a desiccator over fused CaCl_2 stored in N_2 atmosphere to avoid contact with moisture from air.

4-Vinyl pyridine and butylacrylate were copolymerized and the copolymers, poly(4-vinyl pyridine-co-butylacrylate) P(4VP-co-BuA), were purified in the same way. The copolymers were solution cast over glass plate and dried in a vacuum oven for overnight. The dried film was used for conductivity measurement.

2.2 Preparation of hydroiodide salt of poly(4-vinyl pyridine-co-butylmethacrylate) P(4-VP-co-BuMA)-HI and poly(4-vinyl pyridine-co-butylacrylate) P(4-VP-co-BuA)-HI

A concentrated solution of each one of the copolymers was prepared in methanol and treated with 10% HI at room temperature and kept overnight. P(4-VP-co-BuMA)-HI and P(4-VP-co-BuMA)-HI salts were then precipitated with acetone. The salts were then dissolved in methanol again and reprecipitated with acetone to get purified salts. The salts were stored in N_2 atmosphere to avoid contact with moisture from air. The salts were solution cast over glass plate

and dried in a vacuum oven for overnight. The dried film was used for conductivity measurement.

3. Measurements

The 400 MHz proton NMR spectra were recorded with a VARIAN 400 MHz NMR spectrophotometer using CDCl_3 as solvent. IR spectra were recorded with a Shimadzu IR Prestige 21 spectrophotometer using thin films of polymer and polyelectrolyte. TGA were recorded with a Perkin-Elmer Thermal Analyser with a heating rate of 20 °C min^{-1} . DSC were recorded with a Perkin-Elmer Jade DSC Analyser with a heating rate of 20 °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 analyser. The plots were recorded in the frequency range from 0.001 to 100 kHz keeping a signal amplitude of 20 mV. The geometry of the cell for the measurement of conductivity was:



where platinum plate was used as electrodes. The experiment was carried out under a relative humidity (Foot *et al* 1988) of 57%. The electrical conductivities were subsequently obtained from the relation:

$$\sigma = t/R_b \cdot A \quad (1)$$

where t is the thickness of the film, A the area of film and R_b the bulk resistance.

The total ionic transport number, t_{ion} , was evaluated by the standard Wagner polarization technique (Hasmi and Chandra 1995). The cells, SS|P(4-VP-co-BuMA)|SS, SS|P(4-VP-co-BuMA)-HI|SS, SS|P(4-VP-co-BuA)|SS and SS|P(4-VP-co-BuA)-HI|SS, were polarized by a step potential (about 1.5 V) and the resulting potentiostatic current was monitored as a function of time. The stainless steel acts as a blocking electrode for the above cell.

4. Results and discussion

4.1 IR, ^1H NMR, DSC and TGA

The IR spectra of the copolymers, as well as their salts, exhibited peaks at 1,635 and 1,604 cm^{-1} , which are due to $-\text{C}=\text{C}-$ stretching and $-\text{C}=\text{N}-$ stretching vibrations, respectively of 4VP unit. This indicates the presence of 4-VP unit in the copolymer matrices. The peaks at 1,726 and 1,191 cm^{-1} are due to $-\text{C}=\text{O}-$ and $-\text{O}-(\text{C}=\text{O})-$, respectively and this indicates the incorporation of butylmethacrylate or butylacrylate unit into copolymer matrices and also into their salts. The salts of copolymers show a strong peak at about 1,503 cm^{-1} (figures 1a and b), which is absent in the spectra of all the copolymers (Borah and Dutta 2007, 2008) and this may be due to $-\text{N}^+\text{H}-$ bending vibration (Silverstein and Webster 1998), which indicates the incorporation of HI molecule into

the copolymer chain and thus confirmed the formation of hydroiodide salt. $^1\text{H NMR}$ signals observed at $\delta 7.822\text{--}7.920$ for the salts which is due to $-\text{N}^+\text{H}$ protons, confirmed the formation of HI salts.

From DSC thermogram, glass transition temperatures (T_g) were found to be 83 and 158 °C, for copolymer P(4-VP-co-BuMA) having $\sim 1:2$ feed molar ratio of 4-VP:BuMA and its hydroiodide salt, respectively; the T_g were found to

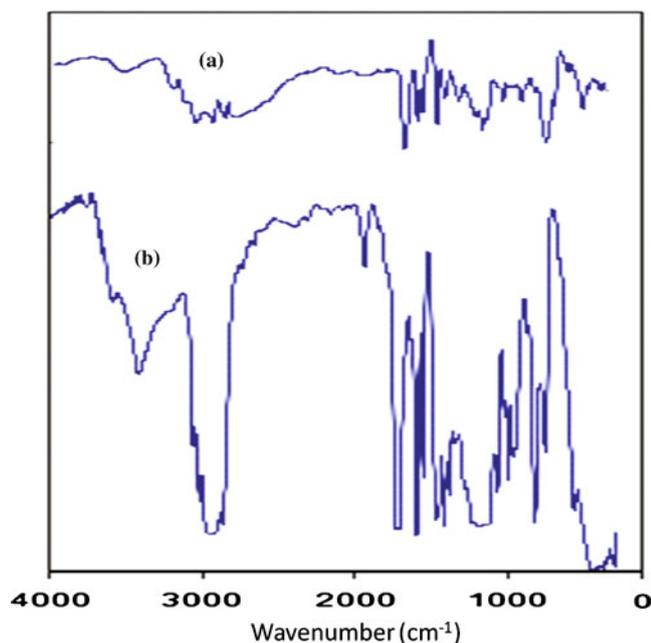


Figure 1. IR spectra of (a) HI salt of copolymer of 4-VP and BuA (feed molar ratio 1:2), P(4-VP-co-BuA)-HI and (b) HI salt of copolymer of 4-VP and BuMA (feed molar ratio 1:2), P(4-VP-co-BuMA)-HI.

be 65 and 69.12 °C, for copolymer P(4VP-co-BuA) having $\sim 1:2$ feed molar ratio of 4VP:BuA and its hydroiodide salt, respectively. The glass transition temperature of the copolymer was lowered in comparison to pure P-4VP (Foot *et al* 1988). This may be due to incorporation of flexible $-\text{O}=\text{C}-\text{O}-$ group of BuMA or BuA, which lowers the value of T_g by increasing the free volume in the copolymer matrices (Xu *et al* 2001; Walton and Lorimer 2003). Since P(4-VP-co-BuMA)-HI or P(4-VP-co-BuA)-HI is a polycation, the electrostatic interaction may increase T_g as compared to their copolymer which contains no charged species (Hirao *et al* 2000) (figure 2). From TGA, it is found that the copolymers have single-step degradation. However, HI salts showed a two-step decomposition. The first step of decomposition may be due to the loss of HI molecule and the second step may be due to the degradation of copolymer backbone.

It is assumed that the reactions follow schemes 1 and 2.

4.2 Conductivity

The conductivity of the copolymer and polyelectrolyte is measured by a.c. impedance spectroscopy. In general, the relationship between conductivity of polymer electrolytes and temperature is in accordance with either Vogel–Tamman–Fulcher (VTF; (4)) (Le Nest *et al* 1987) behaviour or Arrhenius equation (3) (Wright 1975):

$$\sigma = AT^{-0.5} \exp[-B/(T - T_0)] \quad (2)$$

$$\sigma = \sigma_0 \exp(-E_a/RT) \quad (3)$$

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

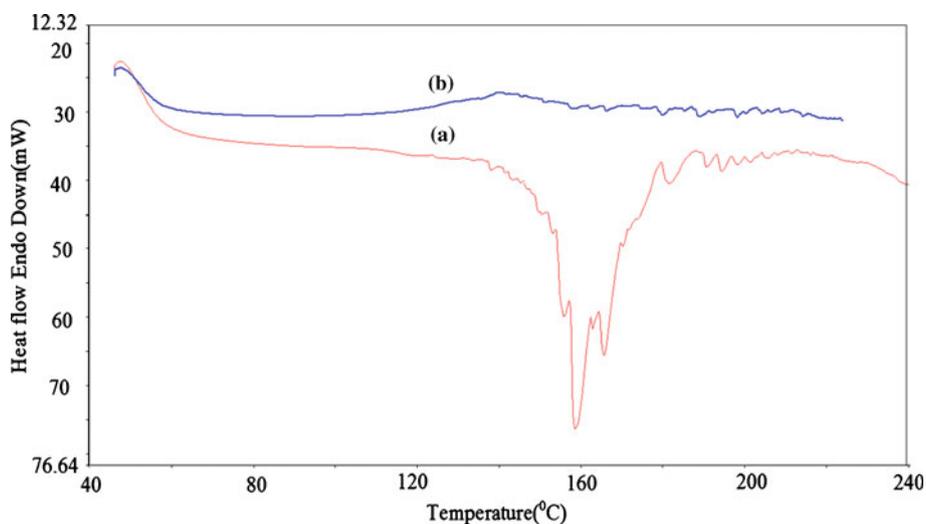
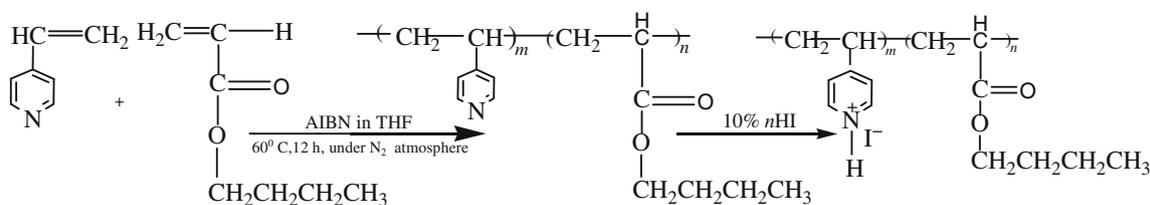
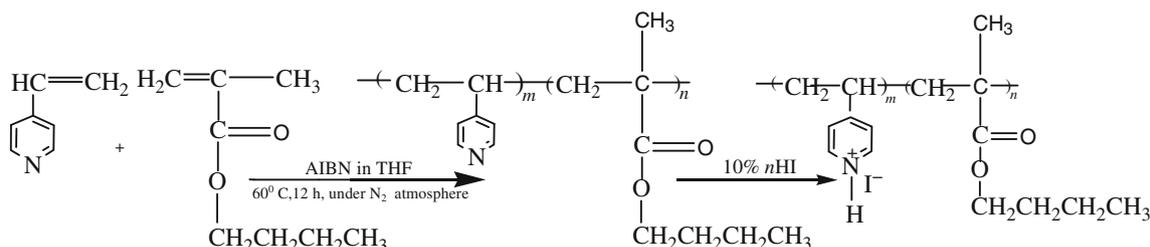


Figure 2. DSC curve of (a) HI salt of copolymer of 4-VP and BuMA (feed molar ratio 1:2), P(4-VP-co-BuMA)-HI and (b) HI salt of copolymer of 4-VP and BuA (feed molar ratio 1:2), P(4-VP-co-BuA)-HI.



Scheme 1. Copolymerization and acidification of 4-VP and BuA.



Scheme 2. Copolymerization and acidification of 4-VP and BuMA.

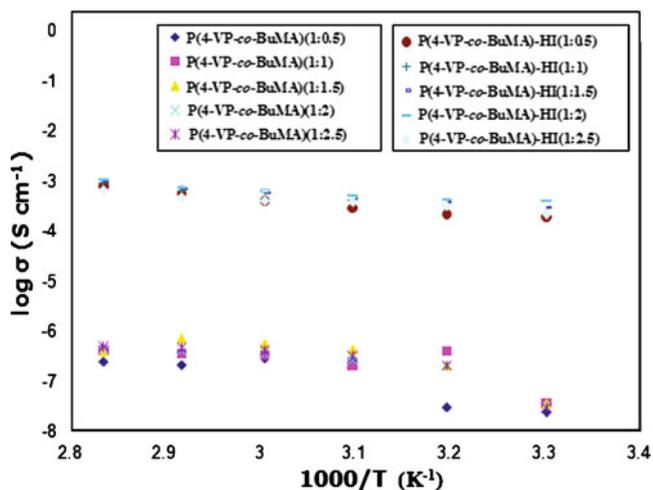


Figure 3. Plot of $\log \sigma$ vs $1/T$ of copolymer of 4-VP and BuMA [P(4-VP-co-BuMA)] at different feed molar ratios and their corresponding HI salts.

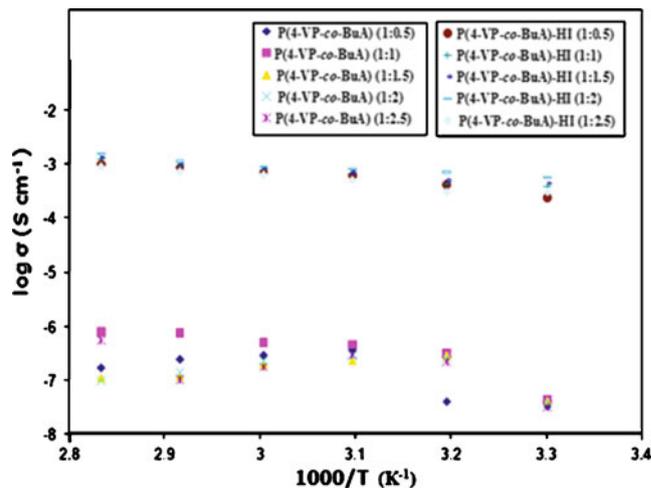


Figure 4. Plot of $\log \sigma$ vs $1/T$ of copolymer of 4-VP and BuA [P(4-VP-co-BuA)] at different feed molar ratios and their corresponding HI salts.

electrolytes systems (Adam and Gibbs 1965). Figures 3 and 4 show $\log \sigma$ vs $1000/T$ plot of P(4-VP-co-BuMA), P(4-VP-co-BuMA)-HI, P(4-VP-co-BuA) and P(4-VP-co-BuA)-HI, respectively with different compositions in the temperature range of 30–80 °C. For all samples, it is clear that the plots of $\log \sigma$ vs $1000/T$ are linear, meaning that the conductivity follows Arrhenius relationship with temperature in the temperature range measured. These curves show that the formation of salt increases the ionic conductivity. Activation energy obtained from Arrhenius dependency of $\log \sigma$ on $1000/T$ of the copolymers prepared from 1:2 feed molar ratio and their HI salts, viz. P(4-VP-co-BuMA), P(4-VP-co-BuMA)-HI, P(4-VP-co-BuA) and P(4-VP-co-BuA)-HI are 0.819, 0.411, 0.914 and 2.04 eV, respectively. The lower value of

activation energies may be due to the mobility of I^- ions attached to cationic polyelectrolytes for P(4-VP-co-BuMA)-HI and P(4-VP-co-BuA)-HI, while in the case of copolymers, it may be due to the mobility of methane proton. It has been observed that there was about 10^3 – 10^4 -fold increase in room temperature conductivity of HI salts than the corresponding copolymers. Also, there was about 10^1 – 10^2 -fold increase in conductivity of the plasticized polyelectrolytes than that of HI salts of pure P-4VP (Chetia *et al* 2004a, b). This can be explained as follows.

Pyridine molecule in 4-VP is more basic than an unsubstituted pyridine molecule due to the presence of nucleophilic pyridinyl group. However, in P-4VP, the nitrogen lone pair easily forms a new N–H bond with proton of the acid and quaternary pyridinium ion behaves like a positive

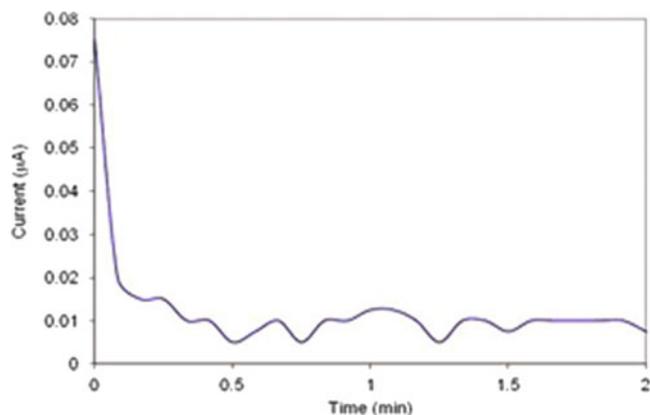
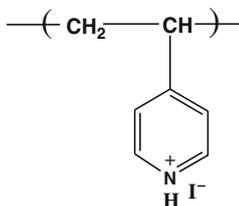


Figure 5. Plot of current vs time of HI salt of copolymer of 4-VP and BuA (feed molar ratio 1:2), P(4-VP-co-BuA).

ion. This ion then forms stable salt with negative ions like I^- . The presence of BuMA or BuA as internal plasticizer facilitates the free movement of ions in the copolymer matrix. In this process, ionic character increases and the salts behave fairly as good electrolyte. Also, it was observed that the room temperature conductivity increased after the internal plasticization with BuMA or BuA in comparison to pure P-4VP and its HI salts (Chetia *et al* 2004a, b). This may be due to the fact that copolymerization of 4-VP with BuMA or BuA lower T_g , thereby increasing chain flexibility, which facilitates more ionic mobility, thereby increasing ionic conductivity. However, with further increase in the amount of BuMA or BuA in the copolymer, the room temperature conductivity of the polyelectrolytes decreased. This may be due to the fact that higher amount of BuMA or BuA means 4-VP content in the copolymer is less. As 4-VP unit contains the following ionic moiety:



which is responsible for conductivity; the conductivity decreases due to decrease of 4-VP content.

4.3 Transport number

The t_{ion} was evaluated using the formula:

$$t_{\text{ion}} = (i_T - i_e) / i_T,$$

where i_T and i_e are total and residual current, respectively.

It has been observed that the major mechanism for conduction was ionic. The percentage of ionic conduction as evaluated by Wagner polarization technique was found to be $\geq 72\%$ in the case of poly(4-vinyl pyridine-co-butylacrylate) copolymer (having $\sim 1:2$ feed molar ratio of 4VP:BuA),

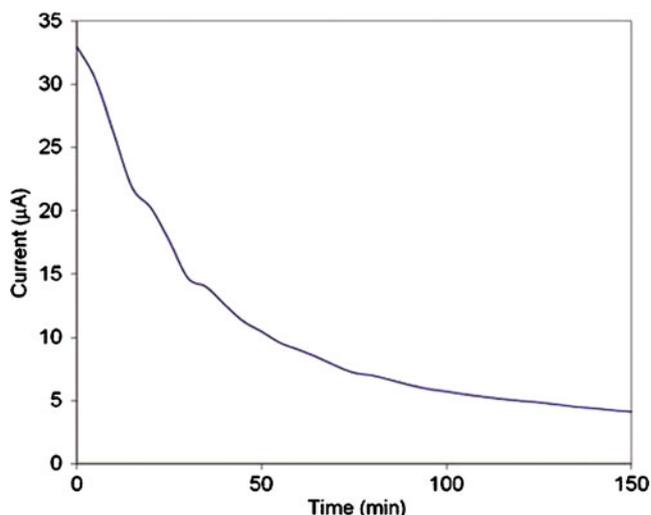


Figure 6. Plot of current vs time of HI salt of copolymer of 4-VP and BuMA (feed molar ratio 1:2), P(4-VP-co-BuMA).

96-67% (figure 5) in the case of hydroiodide salt, $\geq 72\%$ in the case of poly(4-vinyl pyridine-co-butylmethacrylate) copolymer (having $\sim 1:2$ feed molar ratio of 4VP:BuMA) and 88% in the case of hydroiodide salt (figure 6). These data confirmed that the conduction mechanism is predominantly ionic. The variation of electrical conductivity with time has been taken as a measure of ionic conduction. These plots indicate fast exponential type decrease in electrical conductivity initially, saturating later to almost constant values, which could be separated as electronic and ionic part by extrapolating the linear part to zero time for electronic and point-wise subtraction for ionic conduction. It is evident that mobile ions are present in the compounds.

5. Conclusions

The copolymerization has increased the amorphous phase of P-4VP, as is evident from T_g values. However, at higher molar ratio of BuMA or BuA, 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 or BuA, thereby decreasing the chain flexibility and hence the conductivity. Also, increasing amount of BuMA or BuA 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 or BuA (in our case, 1:2 feed molar ratio of 4VP:BuMA or 4VP:BuA) to get good quality polyelectrolytes having high room temperature conductivity as well as good thermostability. Even though polybutylacrylate has lower T_g (-54°C) than polybutylmethacrylate (T_g , 20°C) (Brandrup *et al* 1975), no noticeable change in conductivity has been observed in the salts of two copolymers. In both cases, HI salt of copolymer

prepared from 1:2 feed molar ratio of 4VP:BuMA or 4VP:BuA showed maximum room temperature conductivity.

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