

Investigations on Pyridinium Salts as a Solid-State Ionics

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ABSTRACT: The object of this work is to prepare polymer poly(2vinylpyridine), P-2VP, and its salts like P-2VP-HI, P-2VP-HIO₃, and P-2VP-HIO₄. The formation of P-2VP salts was confirmed by IR and ¹H NMR techniques. Conductivities of these were determined in solid state at various temperatures from 30 to 90°C. Observations indicated that the addition of I⁻ or IO₃⁻ or IO₄⁻ ions affect the ionic conductivity of P-2VP. Molecular mass determination and analytical results indicated that 94, 92.5, and 95% of the

pyridine molecules in the P-2VP chain were hydroiodated, iodated, and periodated, respectively, with the corresponding acids of iodine. The total ionic transport number and activation energy of the polymers were also determined. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1444–1447, 2009

Key words: ionics; poly-2vinylpyridine; poly-2vinylpyridinium salt; conductivity; polymer electrolyte

INTRODUCTION

Solid polymer electrolytes are gaining importance as ionics in solid-state electrochemistry because of their potential uses in high energy density batteries.^{1,2} The main advantages of polymer electrolytes are their mechanical properties, ease of fabrication of thin films of desired sizes, and their ability to form proper electrode–electrolyte contact. The first solvent-free polymer electrolyte reported is the poly(ethylene oxide) (PEO)-based complex with alkali metal salts.³ Some of the important classes of polymer electrolytes are PEO, polypropylene oxide, polyvinyl alcohol doped with alkali-metal salts or metal salts or acids.^{4,5}

Another high-conductivity polymer electrolyte is MEEP-(LiX)_n, formed between poly[bis-(methoxy ethoxy ethoxide) phosphazene], MEEP, and certain Li salts.⁶ However, such MEEP-(LiX)_n polymer electrolytes have poor mechanical properties and hence cannot be used as good materials for thin film electrolytes in solid-state Li batteries. To overcome this problem, Saibaba and coworkers synthesized and studied the conductivity of lithium salt complexes of mixed MEEP : PEO polymer electrolytes⁷ with considerable success. The aim of this work is to synthesize and study the conductivity of some salts of poly(2vinylpyridine) (P-2VP) with acids of iodine. The beauty of this system is that unlike most of the

well-known polymer electrolytes based on PEO, complexed with alkali metal salts,^{8–10} no external salt is necessary to impart ionic character.

EXPERIMENTAL

Materials

2VP (Acros Organics, NJ) was purified by distillation under vacuum. Acetone (Ranbaxy, New Delhi, India), hydroiodic acid (Acros Organics), iodic acid (Acros Organic), and periodic acid (Acros Organic) were used without further purification. Benzene (Ranbaxy) was purified as reported in the literature.¹¹

METHODS

IR spectra of the polymers were recorded with a BRUKER VECTOR 22 spectrophotometer. Concentrations of the ions were determined using oxygen flask method.¹² The 300 MHz proton NMR spectra were recorded with a BRUKER DPX-300 NMR spectrometer using CDCl₃ and D₂O as solvents. Molecular mass was determined by GPC method with a GPC-150C instrument using THF as the solvent for P-2VP and water for the salts. Intrinsic viscosity [η] was determined by UBBELOHDE viscometer.

The bulk electrical conductivity of the polymeric compounds was evaluated from the complex impedance–admittance plots recorded at different temperatures using a HIOKI 3532-50, frequency response analyzer. The plots were recorded in the frequency range from 40 Hz to 100 kHz keeping a signal amplitude of 20 mV. The geometry of the cell for the measurement of conductivity was SS|polymer

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film|SS (SS, Stainless Steel plate). The experiment was carried out under a relative humidity of 58%.¹³

The total ionic transport number, t_{ion} was evaluated by the standard Wagner polarization technique.¹⁴ The SS|P-2VP|SS, SS|P-2VP-HI|SS, SS|P-2VP-HIO₃|SS, or SS|P-2VP-HIO₄|SS cell was polarized by a step potential (about 1.0 V), and the resulting potentiostatic current in each case was monitored as a function of time. The stainless steel acts as blocking electrode for the above cell. 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.

RESULTS AND DISCUSSION

Preparation of P-2VP

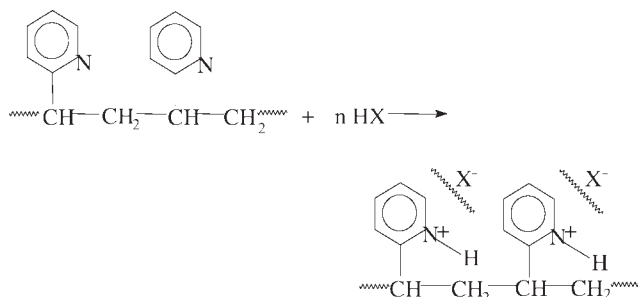
The distilled monomer 2VP was polymerized thermally in vacuum at 60°C for 24 h. The polymer P-2VP formed was dissolved in benzene and then precipitated in water. Reprecipitation was done to remove the last traces of 2VP. The product obtained was then dried in an oven at 60°C for 12 h and stored in P₂O₅.

Preparation of P-2VP-HI and other salts

A concentrated solution of P-2VP in benzene was treated with 10% hydroiodic acid at room temperature and was kept overnight. P-2VP-HI was then precipitated by acetone. Next, the precipitated P-2VP-HI was dissolved in distilled water and double precipitation was done to obtain the purified salt. Finally, it was stored in P₂O₅ before use.

The salts of iodic acid (P-2VP-HIO₃) and periodic acid were prepared similarly replacing HI with HIO₃ and HIO₄, respectively.

The following reaction may take place between P-2VP and HX for the production of P-2VP-HX (here, X = I or IO₃ or IO₄).



IR spectra of P-2VP-HI, P-2VP-HIO₃, and that of P-2VP-HIO₄ (Fig. 1) indicate that the peaks at 1535,

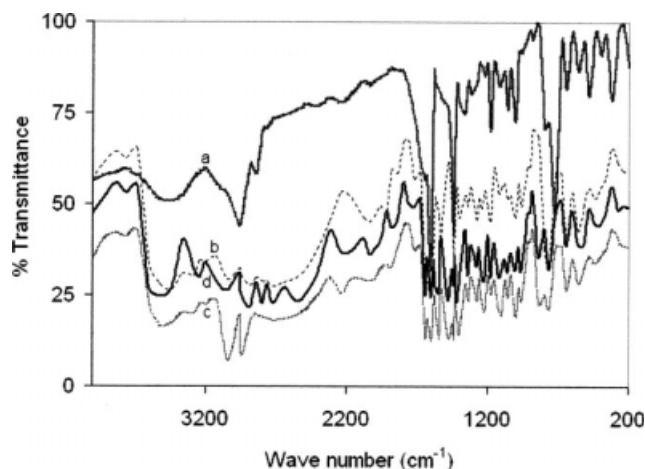


Figure 1 IR spectrum of (a) P-2VP-HI, (b) P-2VP-HIO₃, (c) P-2VP-HIO₃, and (d) P-2VP-HIO₄.

1546, and 1550 cm^{-1} are due to the incorporation of I^- , IO_3^- , and IO_4^- ions,¹⁵ respectively, into the pyridine molecules of the P-2VP chains [Fig. 1(a)]. The percentages of I^- , IO_3^- , and that of IO_4^- estimated by oxygen flask method are 55.22% (theoretically: 54.48%), 60.4% (theoretically: 62.27%), and 62.65% (theoretically: 64.30%), respectively, indicating the formation of the corresponding salts.

Proton NMR data indicates that the two signals observed at 1.75 and 2.6 ppm are due to $-\text{CH}_2-$ and $-\text{CH}-$ proton, respectively. The signals ranging from 6.7 to 7.4 are due to the protons of pyridine molecule of P-2VP. The addition of HI, HIO₃, or HIO₄ molecules was confirmed by the appearance of the signals near 8–9 ppm.¹⁶

From GPC data (Table I), it is ascertained that 94, 92.5, and 95% of the pyridine molecules present in P-2VP are hydroiodated, iodated, and periodated, respectively. The percentage of I^- , IO_3^- , and IO_4^- are computed from GPC data on the basis of the differences in the molecular mass of the polymer electrolyte and that of the polymer, P-2VP.

The ion transport number as evaluated by the Wagner polarization technique was found to be 0.739 for P-2VP. The ion transport number computed for P-2VP-HI, P-2VP-HIO₃, and that of P-2VP-HIO₄ were 0.926, 0.785, and 0.838, respectively. The plot of time versus current is shown in Figure 2. The variation of electrical conductivity with time has been

TABLE I
GPC Data of the Polymers

Compound	$M_n \times 10^{-5}$ (g/mol)	$M_w \times 10^{-5}$ (g/mol)	$[\eta]$ (dL/g)	$DP_n \times 10^{-3}$
P-2VP	1.836	5.280	0.733	1.748
P-2VP-HI	3.926	11.005	1.798	1.643
P-2VP-HIO ₃	4.697	13.512	1.876	1.672
P-2VP-HIO ₄	5.025	14.449	1.986	1.693

taken as a measure of ion transport number. These graphs indicate a fast exponential type decrease in the electrical conductivity initially, saturating later to almost constant values. The electronic and ionic part could be separated by extrapolating the linear part to zero time for electronic conduction, and the point wise subtraction gave the ionic conduction. It is evident that mobile ions are present in the material.¹⁷ The mobile ions responsible for ion transfer are mainly the poly(2vinylpyridinium) ions after acquiring the H^+ ions from the respective acid groups.¹⁸ The transport number varies because of the presence of these acidic groups.

The reason for the conduction of P-2VP may be summarized as follows. The polymeric backbone of P-2VP might have acquired some polar character because of 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.

Conductivity data for P-2VP, P-2VP-HI, P-2VP-HIO₃, and P-2VP-HIO₄ with respect to temperature showed that the P-2VP-HIO₃ and P-2VP-HIO₄ salts need higher activation energy. The mechanism of conduction for the polymeric material is a mixture of ionic and electronic conduction. The activation energy computed from the Arrhenius plot (Fig. 3) of $\text{Log}(\sigma T)$ versus $1/T$ of the compounds P-2VP, P-2VP-HI, P-2VP-HIO₃, and P-2VP-HIO₄ are 0.292, 0.069, 0.854, and 0.879 eV, respectively. Activation energy was computed from the straight line drawn by the two end points of the curve. Out of these four materials, P-2VP-HI shows least amount of activation energy indicating the ease of ion formation. Therefore, it is obvious that P-2VP-HI shows good polymer electrolyte quality. There was about 5.0×10^6 -fold increase of conductivity in the case of P-

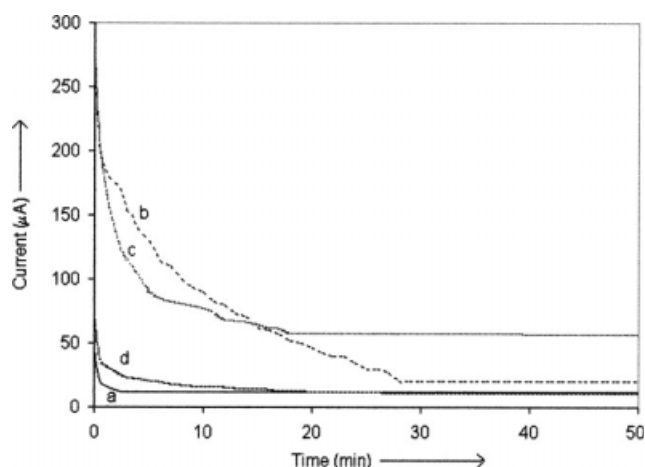


Figure 2 Time versus current plots of (a) P-2VP-HI, (b) P-2VP-HIO₃, (c) P-2VP-HIO₃, and (d) P-2VP-HIO₄.

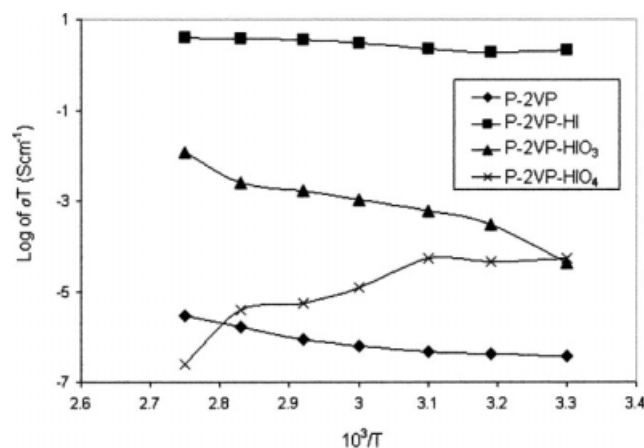


Figure 3 $\text{Log}(\sigma T)$ versus $1/T$ curves.

2VP-HI and about 1.0×10^2 -fold for P-2VP-HIO₃ from that of P-2VP. These can be explained in the following way.

Because of the presence of the nucleophilic pyridinyl group, P-2VP is more basic than an unsubstituted pyridine molecule. In P-2VP, the polymeric character predominates. In the presence of an acid, the nitrogen lone pair residing in each 2VP unit easily forms a new N—H bond with the proton of the acid and behaves like a positive ion. This ion then forms a stable salt with the negative ions like I^- and IO_3^- . So ionic character increases in the P-2VP salts and they behave fairly as good electrolytes. The ionic conduction for P-2VP-HIO₃ is less than that of P-2VP-HI and this may be due to the bulky nature of iodate ion restricting its mobility.¹⁹

The ionic conductivity of P-2VP-HIO₄ is very poor and the conductivity decreases with the rise in temperature, which is just the reverse to that of P-2VP-HI and P-2VP-HIO₃. This is because of the degradation of the polymer, P-2VP-HIO₄, with the increase in temperature, and at 90°C it is completely degraded.

CONCLUSION

From this study it is apparent that P-2VP shows mixed ionic and electronic conduction. Formation of the salts increases the ionic conduction of both P-2VP-HI and P-2VP-HIO₃, and P-2VP-HI shows marked increase in conductivity. P-2VP-HI behaves as an intrinsic conducting polymer, and therefore it is a potential candidate for use in solid-state batteries.

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