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Electrochemical preparation and study of transport properties of polypyrrole doped with unsaturated organic sulfonates

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Electrochemical synthesis of polypyrrole films containing vinyl sulphonate and styrene sulphonate dopants were carried out in a three-electrode one-compartment cell employing galvanostatic conditions at constant charge density. Various parameters like current density, dopant concentration, pH and temperature during synthesis were varied for both the dopant anions. Room temperature conductivity for each sample was measured and their surface morphologies were analysed from the scanning electron microscope pictures. Dependence of conductivity and surface morphology on different synthetic conditions were discussed and probable reasons for the dependence were indicated. For each of the dopant anions, resistivities were measured down to 25 K for samples synthesized at 0°C and room temperature. From the resistivity data, charge transport behaviour in these films were analysed in the light of Mott's variable range hopping model. Ageing effects of conductivity for films containing both the dopant anions were studied by storing them in ambient atmosphere and measuring their conductivities from time to time. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Electrically conducting films of polypyrrole (PPy) can be easily prepared electrochemically. Electrochemical polymerization is generally achieved both in organic and in aqueous solutions. Owing to its low cost, nowadays aqueous solution is most often employed by many workers to synthesize polypyrrole films. The variety of processing parameters, e.g. type of counter ion and solvent type, their concentration, synthesis temperature, electrochemical voltage and current density, have a great impact on the properties of the resulting films[1–7]. A number of techniques for laboratory scale synthesis of PPy film have been employed, of which the most important are the potentiostatic and galvanostatic methods. In the potentiostatic method a predetermined optimum voltage is applied during synthesis, whereas in the latter a fixed oxidation current is supplied with no control over the resulting potential of the system. Both the methods have certain advantages and disadvantages. In our present investigation we employed the galvanostatic method for the synthesis of PPy films.

Conducting films of PPy can be modified by introducing substituents into the cationic PPy or by varying the accompanying anion. The electrochemical route for the preparation of these films is particularly convenient for making these modifications, since the variations are made in the selection of the monomer or the electrolyte. This eliminates the need for subsequent chemical treatment of the films. As expected, the electrochemical and conducting properties of the films are changed by these chemical modifications.

Extensive reports on the electrochemical synthesis of PPy films using various types of dopant anions, including inorganic and organic counter ions, have been found in the literature[8–13]. Among the organic dopants, aliphatic and aromatic sulfonates in particular are of special interest to researchers because they confer upon the polymer a good mixture of electrical and mechanical properties and also stability.

In the present contribution we have prepared PPy films using unsaturated organic sulfonate dopant anions, i.e. vinyl sulfonate doped PPy (PPy-v) and styrene sulfonate doped PPy (PPy-st), with variation of the different parameters mentioned earlier and have compared their conductivities, surface morphologies and stability in ambient conditions. We have also studied the behaviour of conductivity of these films at low temperatures and shown how their charge transport behaviour varies with the dopant anions by fitting conductivity data in the standard Mott's model.

EXPERIMENTAL

Materials

The monomer pyrrole was procured from SRL (India), distilled prior to use and stored in a sealed tube in an argon atmosphere. The supporting electrolytes, sodium vinyl sulfonate and sodium styrene sulfonate were obtained from Fluka and Aldrich Chemicals, respectively. All the chemicals used were of AR grade.

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Electrochemical preparation of PPy films

The PPy films for our studies were prepared by electrodeposition of monomer pyrrole taken in aqueous solution, using vinyl and styrene sulfonate as dopant anions. A three-electrode one-compartment cell was used for the preparation of the films, comprising a specially designed platinum working electrode (1 × 1 cm^2, fitted on a glass substrate such that only one surface of it is exposed in the electrolyte solution where film deposition occurs), a platinum counter electrode and a reference calomel electrode. PPy was synthesized using galvanostatic conditions (at a constant current density). A large number of samples of PPy film were prepared by variation of different parameters during synthesis, viz. pH of the solution, current density, dopant concentration and temperature of the solution (at least four samples were prepared with each identical experimental condition). The pH of the solution adjusted by dilute HCl and dilute NH_4OH solution (in both cases introduced anion or cation concentration can be neglected in comparison with the electrolyte concentration). The pyrrole concentration was always kept at 0.2 M and the total charge density also remained constant (10.8 C cm^{-2}). The polymerization time was adjusted according to the current density used. After the electrolysis was over the platinum electrode containing the film was removed from the cell compartment, washed with water and dried under vacuum overnight. Dried films were removed from the electrode surface by scratching. Thickness of the films (measured using a Dial gauge) was found to be in the range 50–60 μm when styrene sulfonate was used as dopant anion and 30–40 μm for vinyl sulfonate dopants.

Conductivity measurements

Room temperature conductivity of the PPy film was measured using a standard four-probe technique, electrical contacts being made by conducting silver paints. The conductivity data presented here are the average values of the measured conductivity for four samples prepared in identical experimental conditions; the value which deviated more than 5% from the average was rejected. Resistivity measurements of the films in the temperature range 25–300 K were performed using an Oxford model 22 closed cycle helium refrigerator attached to a Lakeshore cryotonics (model DTC 500 A) temperature controller. Details of low temperature measurements were described in our earlier report[14].

Other measurements

The X-ray diffraction (XRD) pattern and Fourier transform i.r. (*FT*i.r.) spectra of the films were taken from a Philips X-ray diffractometer and Nicolet *FT*i.r. spectrometer, respectively. Surface morphologies of the prepared films were studied by taking scanning electron microscope (SEM) photographs of different samples from a Hitachi Model S415A SEM.

Variation of conductivity in air with time was examined for both PPy-st and PPy-v samples by keeping them in air and measuring the conductivity time to time.

RESULTS AND DISCUSSION

Effect of structure of dopants

Electrical properties like conductivity in these polymers depends on factors like charge transfer between chains, between different conjugated segments on the same chain and in doped materials between the dopant anion and the polymer segment[15]. In addition to these effects, which may act at a molecular level, the actual values measured are likely to be dominated by grain boundaries and other morphological effects. From the results it is observed that, in general, the conductivity values for PPy-st are much higher than those for PPy-v. Reasons for such differences in conductivity values can be explained as follows.

The counter ion is indispensable for charge compensation of conducting PPys; at the same time the size, shape and structure of the counter ion are expected to influence the electrical conductivity[9]. Recently, Yamashiro *et al.*[16] have shown from detailed calculations that interchain charge transfer occurs via dopants in the case of K-doped polyacetylene. They indicated that direct interchain transfers are possible if C π atomic orbitals in different chains have an overlap without penetration into dopant cores. We have prepared the PPy samples using vinyl sulfonate and styrene sulfonate as dopant ions. Similar interchain charge transfer is possible in our system, evidently owing to the presence of the benzene ring (*Figure 1*) in styrene sulfonate ions—better overlap of molecular orbitals (MOs) of the dopant ion with π atomic orbitals (AOs) of the C atom of the polymer chain are possible compared to the vinyl sulfonate dopant ions. In other words, presence of the benzene ring will facilitate interchain tunnelling or hopping in PPy-st samples, which would result in a higher conductivity in PPy-st samples compared to that in PPy-v samples. Already there exist a large number of reports in the literature comparing conductivity values of PPy containing aromatic sulfonate anion such as *p*-toluene sulfonates, aromatic carboxylates, etc., and inorganic anions such as Cl^-, ClO_4^-, SO_4^{2-}, etc., and it was found that conductivity was always higher in the case of aromatic dopants[17].

If the surface morphologies of the films containing styrene and vinyl sulfonate as dopants are compared from the SEM pictures, it is observed that the growth

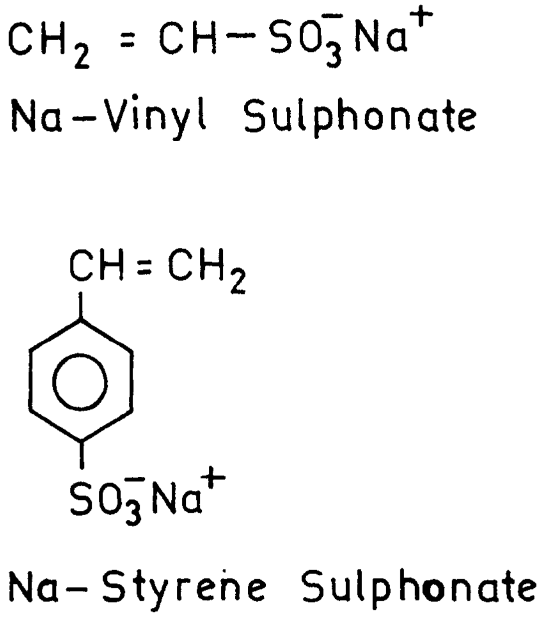

Figure 1 Structure of dopant anions

Table 1 Variation of conductivity with pH

PPy-styrene sulfonate		PPy-vinyl sulfonate	
pH	Conductivity (S cm^{-1})	pH	Conductivity (S cm^{-1})
4.08	69.4	3.10	12.5
6.61	71.1	4.12	13.0
9.1	69.1	7.53	7.8
10.48	65.2	10.2	7.6
		10.63	6.2

Estimated error range 2–5%

patterns in the two samples are different. In some cases of PPy-st a nodular-like structure was observed. No such growth was visible in the case of PPy-v, instead a compact cauliflower-like structure was found.

Effect of pH

PPy films were prepared with both the dopant anions at different solution pH; all other parameters remained fixed (dopant concentration 0.2 M, current density 3 mA cm^{-2}). Conductivity data are listed in *Table 1*.

From the above results it follows that, in the case of PPy-st films, conductivity values are more or less independent of solution pH, whereas in the case of PPy-v the samples synthesized at lower pH have considerably higher conductivity than those synthesized at neutral or alkaline pH. This observation was also reported by Murthy *et al.*[18] using tetraethylammonium fluoroborate as the dopant anion. Decrease in conductivity at higher electrolyte pH for PPy-v may be attributed to the existence of hydroxyl groups, which reduces polymer conjugation length by reacting with the generated oligomer radical during electropolymerization[19], and possibly due to dopant displacement from within the polymer in favour of the OH^- ions. In the case of PPy-st, increasing concentrations of OH^- ions at higher pH are insufficient to change the conductivity values, which are much higher than those of PPy-v.

The SEM picture for PPy-v film (*Figure 2a*) shows that, at pH 10, synthesized film has a coarse globular surface containing small spherical bubbles, whereas the picture at lower pH (*Figure 2b*) indicates a similar, but more regular, surface. In the case of PPy-st a typical SEM picture taken of a sample synthesized at pH > 10 (*Figure 2c*) shows a similar globular growth pattern as in *Figure 2a*, but for samples synthesized at pH $\sim$ 4, a characteristic nodular shaped growth is observed (*Figure 2d*). SEM pictures taken for samples synthesized at different pH suggest that the surface morphology of the synthesized PPy films are strongly dependent on solution pH for both the dopant anions.

Dependence of conductivity on current density

In *Figure 3* the normalized conductivity (normalized against the conductivity of the sample synthesized at 1 mA cm^{-2}) of PPy films prepared using both the dopant

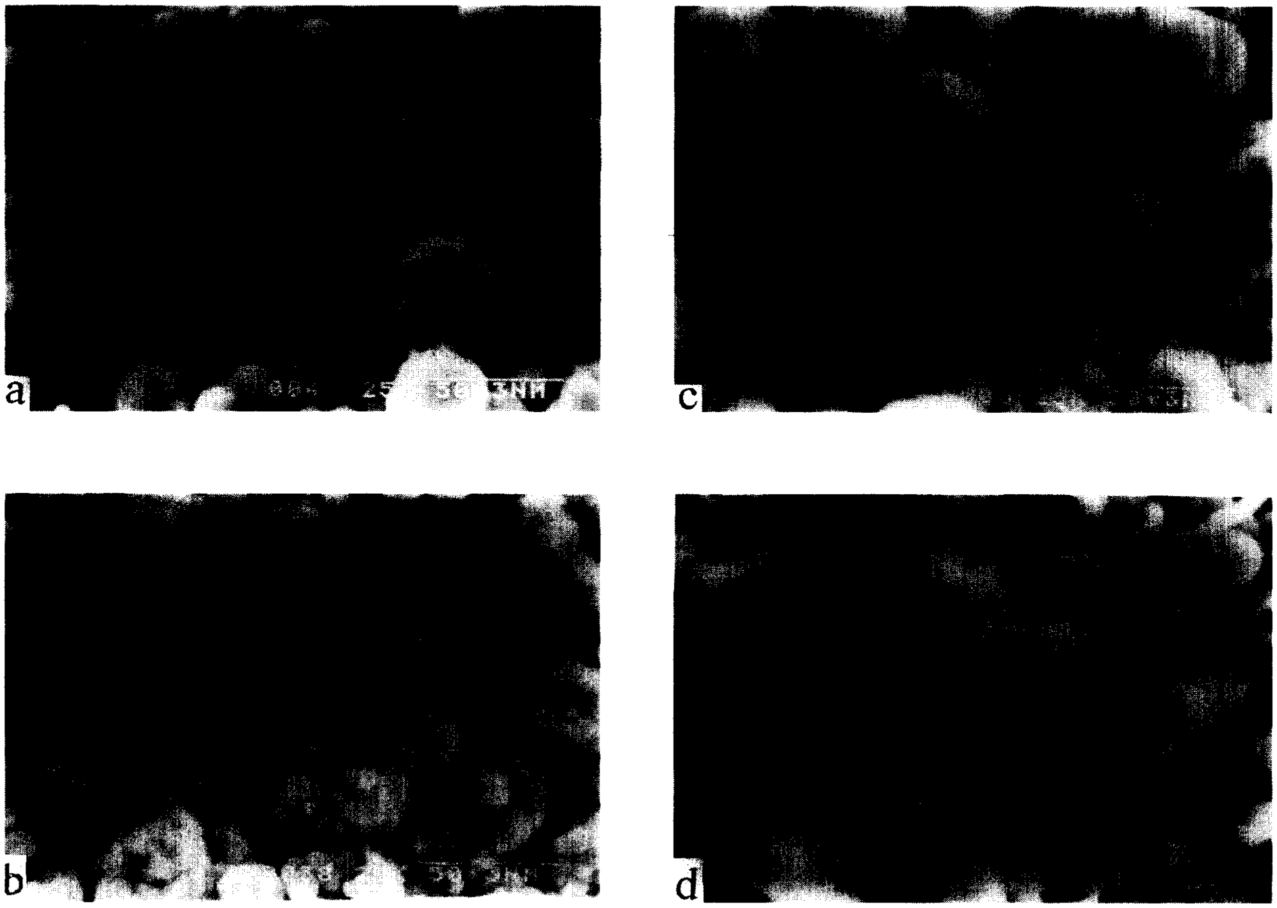

Figure 2 SEM pictures of PPy-v at (a) pH 10.2 and (b) pH 3.1 and PPy-st at (c) pH 10.48 and (d) pH 4.08 (synthesis parameters: dopant concentration 0.2 M; current density 3 mA cm^{-2}; temperature 22°C)

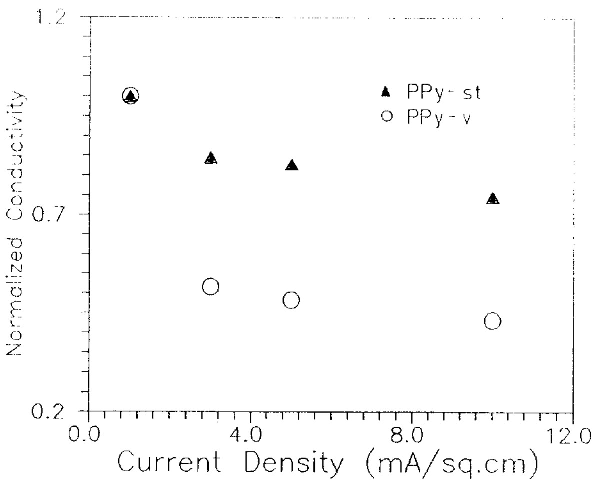

Figure 3 Variation of normalized conductivity with current density for PPy films (synthesis parameters: pH 6.6 for PPy-st and pH 7.5 for PPy-v; dopant concentration 0.2 M)

Figure 4 SEM picture of PPy-st at (a) 1 mA cm^{-2} and (b) 10 mA cm^{-2} (synthesis parameters: pH 6.6; dopant concentration 0.2 M; temperature: 22°C)

anions are plotted against current density during synthesis. It is evident from the figure that for both the dopant anions there is an initial decrease in conductivity when the current density is increased from 1 to 3 mA cm^{-2}. For PPy-v samples the effect is more pronounced. The conductivity remained practically independent of current density at higher values for both the dopant anions.

Our results on the dependence of conductivity of samples on current density during synthesis is consistent with the data obtained by West *et al.*[2] on the influence of current density on the structure of PPy. According to them PPys synthesized at lower current density can accommodate more dopant anion per polymer unit, which results in higher conductivity.

For the PPy-st films a predominant growth of nodular structure is observed at the lowest current density (1 mA cm^{-2}), as shown in *Figure 4a*, and this growth diminishes with increasing current density. At 10 mA cm^{-2} this nodular structure appears to be totally absent and a more regular growth pattern is observed (*Figure 4b*). The occurrence of similar growth patterns during PPy synthesis at low growth rate were observed by Hahn *et al.*[20].

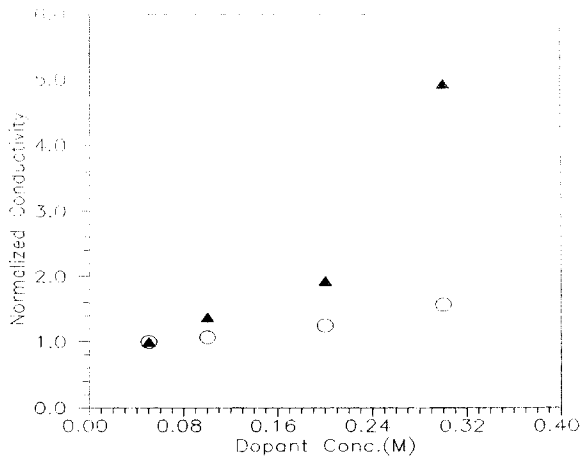

Figure 5 Variation of normalized conductivity with dopant concentration for PPy films (synthesis parameters: pH 6.6 for PPy-st; 7.5 for PPy-v; temperature 22°C; current density 3 mA cm^{-2})

Effect of dopant concentration

In *Figure 5* the normalized conductivity (normalized against the conductivity of the sample synthesized at 0.05 M) for both the films are plotted against the dopant concentration and we observe an increase in conductivity of the PPy films with increase in dopant anion concentration from 0.05 to 0.3 M, in the case of both PPy-v and PPy-st. For vinyl sulfonate the effect is more pronounced. Our observation on the dependence of conductivity on anion concentrations is consistent with the findings of the Lei *et al.*[5].

We have taken XRD patterns of PPy films synthesized at various dopant concentrations for both the dopant anions. We observed that all the films were amorphous in nature. The width of the half height of the peak found in the range 15–35° changed with dopant anion concentration for both the dopant anions shown in *Figure 6*. It showed narrowing of peak width with increase in dopant concentration. The results are consistent with those obtained by Tsutsumi *et al.* for poly(*N*-vinyl pyrrolidone)[21].

SEM pictures of the films for both the dopant anions for various dopant concentrations showed no significant change.

Effect of synthesis temperature

We have synthesized PPy films at three different temperatures (40, 22 and 0°C), using both the dopant anions. The conductivity of the samples synthesized at various temperatures are listed in *Table 2*, keeping all other parameters constant. It is evident from the values that, for both the dopant anions, samples synthesized at

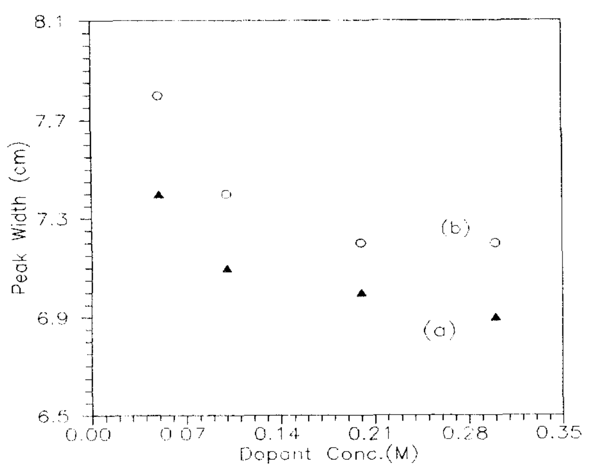

Figure 6 Variation of peak width with dopant concentration for PPy films (synthesis parameters same as in *Figure 5*)

Table 2 Variation of conductivity with temperature

Temperature (°C)	PPy-styrene sulfonate conductivity (S cm^{-1})	PPy-vinyl sulfonate conductivity (S cm^{-1})
0	125.1	25.3
22	71.1	7.8
40	44.4	1.4

Estimated error range 2–5%

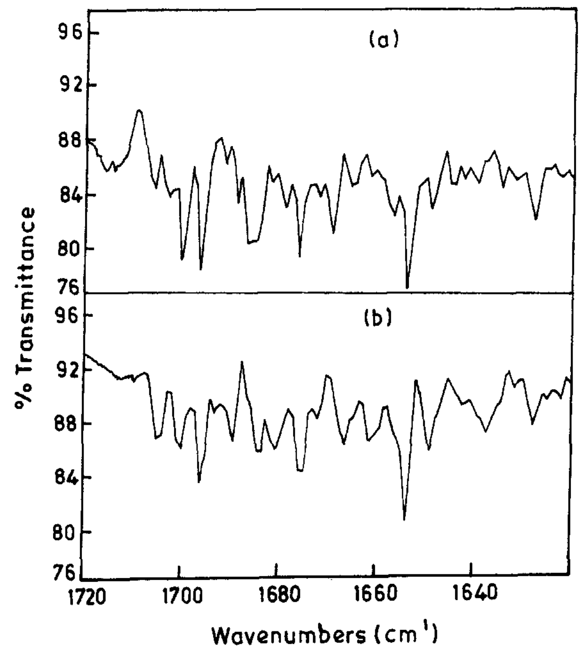

Figure 7 *FT*i.r. spectra of PPy-v at (a) room temperature and at (b) 0°C (synthesis parameters: pH 7.5; current density 3 mA cm^{-2}, dopant concentration 0.2 M)

0°C have the highest conductivity and this decreases as the synthesis temperature increases. Similar results were obtained in the case of PPy synthesized chemically[3] and electrochemically[22,23]. Reasons for the higher conductivity at low synthesis temperature were explained by earlier workers as due to fewer structural defects, which leads to a longer conjugation length in the polymers prepared at lower temperature. These defects may result from unwanted side reactions which occur in competition with the desired reaction, α–α coupling of oxidized monomer units to produce a defect-free polymer chain. The conductivity order of the samples prepared at different temperatures is 0°C > 22°C > 40°C.

To confirm the existence of carbonyl defects arising due to over-oxidation of PPy or as the product of the chain termination by nucleophilic attack by water on the pyrrole rings we have studied the *FT*i.r. spectra for PPy-v synthesized at room temperature and at 0°C. *Figure 7a* shows weak absorption in the region 1705–1710 cm^{-1} at room temperature, and this band is completely absent in the spectra of samples synthesized at 0°C (*Figure 7b*). Similar behaviour was also observed in the case of PPy-st. The results suggest that carbonyl defects are incorporated into the polymer for both the dopant anions at room temperature, as shown by Liang *et al.*[3] in chemically prepared ClO_4^- doped PPy samples.

SEM pictures for PPy-st film prepared at 0°C and room temperature show that samples synthesized at 0°C (*Figure 8a*) have uniform fine globular surface morphology whereas samples synthesized at room temperature have rough, nodule shaped growth (*Figure 8b*). The SEM picture for PPy-v film also shows uniform growth for 0°C synthesized samples, but, in the case of a sample prepared at room temperature, clustering on the surface is observed (*Figures 8c* and *d*). However, unlike the PPy-st films, nodular growth is totally absent here.

Ageing effect in ambient conditions

In order to observe how the conductivity of the PPy samples change with time we kept samples of PPy films containing both the dopant ions in ambient conditions (in normal atmosphere) for several days and measured their conductivity after certain time intervals. In *Figure 9* the percentage of initial conductivity is plotted against time for both the PPy samples. In the case of PPy-v, conductivity decreased steadily with time and after 35 days only 52% of the initial conductivity was retained; on the other hand, for PPy-st, conductivity was fairly stable, changed very slowly and after 35 days about 88% of the initial conductivity was retained.

Effect of dopant ions and synthesis temperature on the transport properties of PPy films

During doping with different ions, electrons are either removed from the chain or donated to the chain. Electrons interact very strongly with the dopant ions in the polymer crystal through an electrostatic interaction. Due to the two-fold coordination of the polymer chain, the polymer lattice itself gets distorted around the injected charge, giving rise to the formation of polarons in the bound localized states. The *in situ* optical absorption and spin concentration measurements[24–27] show that the ground state excitations in doped polypyrrole are caused by polarons and bipolarons. The e.s.r. and magnetic susceptibility measurements[25–27] show an increase in the spin concentration during the initial stages of doping, while at the higher doping levels there is a decrease in spin concentration. These results indicate the formation of polarons and bipolarons. The concentration of polarons and bipolarons increase in highly doped PPy. The activation energy required for hopping of the bipolaron is greater than that for polarons, but the bipolarons get split into single polarons by the thermal energy at higher temperatures, resulting in bipolaron hopping[28–30]. The

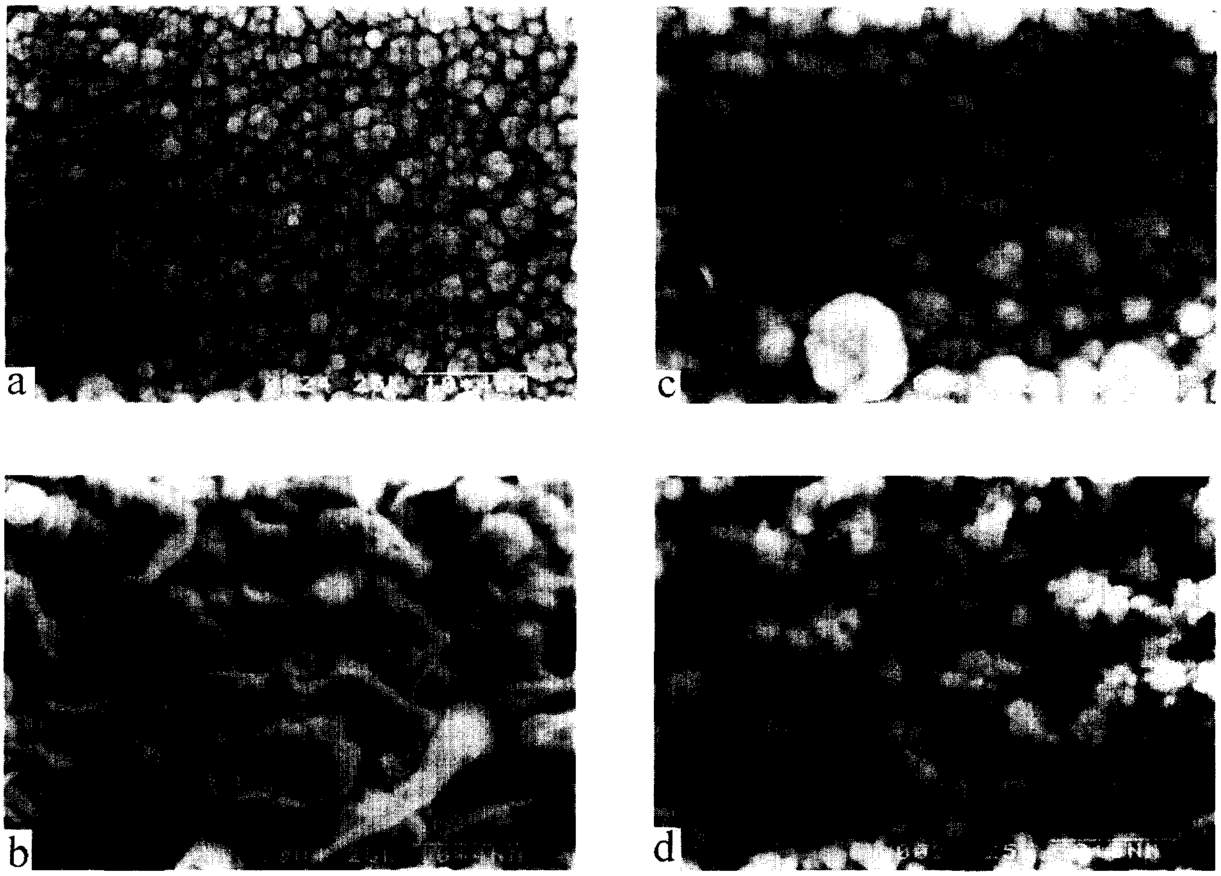

Figure 8 SEM picture of PPy-st synthesised at (a) 0°C and (b) 22°C and PPy-v at (c) 0°C and at (d) 22°C (synthesis parameters: pH 6.6 and 7.5 for PPy-st and PPy-v, respectively; other parameters same as in *Figure 7*)

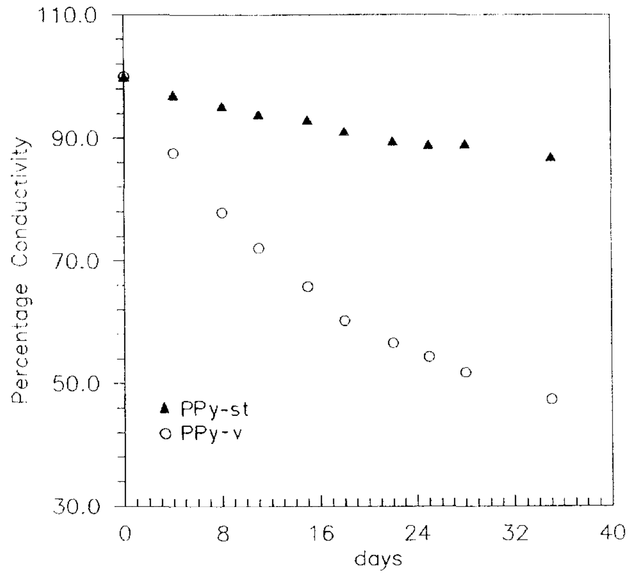

Figure 9 Variation of percentage conductivity with time for PPy films (synthesis parameters: pH 6.6 and 7.5 for PPy-st and PPy-v, respectively; temperature 22°C; dopant concentration 0.2 M; current density 3 mA cm^{-2})

dimensionality of the system, electron–phonon coupling strength and the extent of the disorder in the system help to reduce the size of the polaron. Thus, in conducting PPy the size of the polarons is assumed to be the intermediate ones and their behaviour follows the physics of small polarons.

The temperature dependence of conductivity due to polaron hopping in such a system can be described by Mott's variable range hopping (VRH) model[31–34] where the conductivity σ can be expressed as

$$\sigma = \sigma_0 \exp[-(T_0/T)^{1/n}] \tag{1}$$

where the exponent n is 4 for three-dimensional transport, and T_0 is the characteristic temperature.

$$T_0 = \lambda\alpha^3/kN(\epsilon_F) \tag{2}$$

and

$$\sigma_0 = e^2R^2\nu_0 N(\epsilon_F) \tag{3}$$

where ν_0 is the phonon frequency, k is the Boltzmann constant, α is the decay length of localized states and $N(\epsilon_F)$ is the density of states at the Fermi level[35,36]. Here, λ is a dimensionless constant ($\sim$18.1)[35,37–39]. The hopping distance R may be represented as

$$R = [9/8\pi\alpha kTN(\epsilon_F)]^{1/4} \tag{4}$$

As discussed earlier, owing to the presence of the benzene ring in styrene sulfonate better overlap between the polymer and dopant MOs is possible, which leads to better conductivity in PPy-st samples compared to PPy-v samples, which is evident from our conductivity data. For both the dopant ions the PPy films synthesized at 0°C exhibit higher conductivity than does the sample prepared at higher temperature due to structural defects in samples synthesized at 0°C (see i.r. spectra in *Figure*

Table 3 Variable range hopping parameters in PPy-v and PPy-st films

Sample	Synthesis temperature (°C)	σ_0 (S cm^{-1})	Characteristic temperature T_0 (K)	Density of states $N(\epsilon_F)$ (α^{-1} = 10 Å) (eV^{-1} cm^{-3})	Hopping distance R_{300} (α^{-1} = 10 Å) (Å)
PPy-v	0	909	17217	1.22×10^{22}	18.36
	22	694	32566	6.45×10^{21}	21.53
PPy-st	0	1575	10492	2.002×10^{22}	16.22
	22	629	6831	3.075×10^{22}	14.6

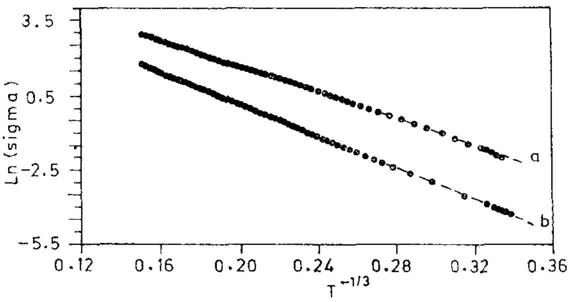

Figure 10 Plot of $\ln\sigma$ as a function of $T^{-1/3}$. Dotted lines are theoretically fitted curves: (a) PPy-v at 0°C and (b) PPy-v at 22°C (synthesis parameters for PPy-v samples same as in *Figure 7*)

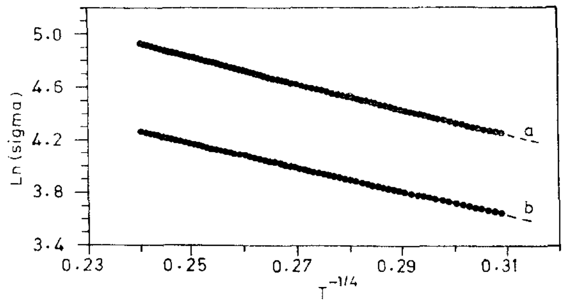

Figure 11 Variation in $\ln\sigma$ as a function of $T^{-1/4}$ for PPy-st synthesized at (a) 0°C and (b) 22°C. The dotted lines are theoretically fitted curves (synthesis parameters for PPy-st same as in *Figure 8*)

7). During fitting the conductivity data for PPy-v (prepared both at 0°C and at room temperature) it was found that the data were better fitted by the $T^{-1/3}$ than $T^{-1/4}$ form. A typical plot of the conductivity of PPy-v as a function of temperature is shown in *Figure 10*. During doping, the dopant ions reside adjacent to the chains, and the potential of the dopant ions pins or traps the charge carriers. The deep trapped states are bound localized ones. For the participation in the conduction process the deep trapped states have to be ionized first before hopping among localized states. The ionization energy is dependent on the conjugation length and the pinning potential of the dopant ions. The ionization energy of the carrier decreases as the conjugation length increases because the increase in conjugation length enhances the screening of the counter ion potential. If in the ionization process the trapped sites are large in number the theory predicts that $T^{-1/2}$ will be the dominating factor which here is identified as $T^{-1/3}$ because of the comparability of $T^{-1/2}$ and $T^{-1/4}$ factors[28,40,41]. Such behaviour was also observed by others[42]. For conducting polymers having short conjugation lengths, Baughman and Shacklette[41] predicted theoretically that the conductivity should be proportional to $\exp[-(T_0/T)^{1/3}]$ where T_0 is inversely proportional to the conjugation length. They derived the expression for nearest neighbour hopping with a distribution of activation energies arising from a distribution of conjugation lengths.

Table 3 represents the different parameters obtained by fitting our conductivity data with Mott's VRH theory. Here, we have calculated the parameters assuming that the localization length α^{-1} of localized electrons is about four pyrrole rings, i.e. $\alpha^{-1} = 10$ Å[43]. From *Table 3* it is found that a PPy-v sample prepared at 0°C has higher density of states, smaller hopping distance and characteristic temperature T_0 and larger σ_0 value than those parameters of the sample synthesized at room temperature. The significance of the lower T_0 value for the sample prepared at lower temperature is that the sample has a higher density of states $N(\epsilon_F)$ and a larger conjugation length (α^{-1}). *Table 3* shows that PPy film prepared at 0°C possesses a larger σ_0 value than that prepared at room temperature, suggesting a higher hopping attempt frequency in the case of PPy film prepared at 0°C. The temperature dependence of conductivity of the samples synthesized under the same conditions may vary according to the nature of the dopant ions and doping levels, due to the variation in ionization energy. The conductivity data for the PPy-st can be better fitted by the $T^{-1/4}$ form than the $T^{-1/3}$ one because, in this case, hopping between localized states becomes predominant. In *Figure 11* we plotted $\ln\sigma$ vs. $T^{-1/4}$ curves together with the theoretical curves. From *Table 3* it is observed that the σ_0 value is larger for PPy-st prepared at 0°C than that of PPy-st prepared at room temperature. The density of states of the two PPy-st samples are nearly equal. This may be due to the arbitrary choice of the localization length $\alpha^{-1} = 10$ Å for the samples. The value of T_0 depends largely on the localization length and the density of states at the Fermi level. The variation in these two parameters may induce change in the value of T_0. The hopping frequency ν_0 is found to be $\sim 10^{13}$ s^{-1}.

CONCLUSIONS

We have studied the influence of various parameters during electrochemical synthesis of PPy doped with vinyl sulfonate and styrene sulfonate anions. It was found that room temperature conductivity for PPy-st was always much higher compared to PPy-v. This is due to the presence of the benzene ring, which facilitates interchain tunnelling or hopping in PPy-st samples. The pH of the solution during synthesis had practically no influence on the conductivity of PPy-st; in the case of PPy-v, samples synthesized at higher pH had lower conductivity. For both PPy-v and PPy-st, conductivity decreased with increasing current density and decreasing dopant concentration. In general, samples synthesized at 0°C have much higher conductivity than those synthesized at higher temperature; the highest conductivity of $125\,\mathrm{S\,cm^{-1}}$ was recorded in PPy-st synthesized at 0°C. Surface morphologies of PPy-v and PPy-st, as revealed from SEM pictures, are dependent on synthetic conditions. PPy-st has better stability in ambient conditions as reflected from its conductivity value after 35 days. Low temperature resistivity measurements on PPy-v and PPy-st synthesized at different temperature, and subsequent fitting of the data in Mott's VRH model, revealed that in both cases the hopping conduction mechanism operates.

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REFERENCES

1 Yamamura, M., Hagiwara, T. and Iwata, K. M. *Synth. Met.* 1988, **26**, 209

2 West, K., Jacobsen, T. and Zachau-Christiansen, B. *Synth. Met.* 1993, **55–57**, 1412

3 Liang, W., Lei, J. and Martin, R. C. *Synth. Met.* 1992, **52**, 227

4 Maddison, D. S. and Unsworth, J. *Synth. Met.* 1989, **30**, 47

5 Lei, J., Cai, Z. and Martin, R. C. *Synth. Met.* 1992, **46**, 53

6 Kupila, E. L. and Kankare, J. *Synth. Met.* 1993, **55–57**, 1402

7 Kiani, M. S. and Mitchell, G. R. *Synth. Met.* 1992, **48**, 203

8 Diaz, F. A., Kanazawa, K. K. and Gardini, G. P. *J. Chem. Soc., Chem. Commun.* 1979, 635

9 Saunders, B. R., Murray, K. S. and Flemming, R. J. *Synth. Met.* 1992, **47**, 167

10 Visy, C., Lukkari, J., Pajunen, T. and Kankare, J. *Synth. Met.* 1989, **33**, 289

11 Zotti, G., Schiavon, G. and Comisso, N. *Synth. Met.* 1991, **40**, 309

12 Kassim, A., Davis, F. J. and Mitchell, G. R. *Synth. Met.* 1994, **62**, 41

13 Kuwabata, S., Nakamura, J. and Yoneyama, H. *J. Electrochem. Soc.* 1990, **137**, 1788

14 Bhattacharya, A., De, A., Bhattacharyya, S. N. and Das, S. *J. Phys.: Condens. Matter* 1994, **6**, 10499

15 Evans, G. P. in 'Advances in Electrochemical Science and Engineering' (Eds H. Gerischer and C. W. Tobias), Vol. 1, VCH, Weinheim, New York, 1990

16 Yamashiro, A., Ikawa, A. and Fukutome, H. *Synth. Met.* 1994, **65**, 233

17 Warren, F. L. and Anderson, P. *J. Electrochem. Soc.* 1987, **134**, 101

18 Murthy, N. S. A., Pal, S. and Reddy, K. S. *J. Mater. Sci. Lett.* 1984, **3**, 745

19 Unsworth, J., Innis, P. C., Lunn, B. A., Jin, Z. and Norton, G. P. *Synth. Met.* 1992, **53**, 59

20 Hahn, S. J., Stanchina, W. E., Gajda, W. J. and Vogelhut, P. J. *Electron. Mater.* 1986, **15**, 145

21 Tsutsumi, H., Hamamoto, S. and Matsuda, Y. *J. Polym. Sci., Part A: Polym. Chem.* 1993, **31**, 2883

22 Sato, K., Yamamura, M., Hagiwara, T., Murata, K. and Tokumoto, M. *Synth. Met.* 1991, **40**, 35

23 Reghu, M., Yoon, C. O., Moses D. and Heeger, A. J. *Synth. Met.* 1994, **64**, 53

24 Ford, W. K., Duke, C. B. and Salocneck, W. R. *J. Chem. Phys.* 1982, **77**, 5030

25 Genoud, F., Gugliemi, M., Mechtschein, M., Genies, E. and Salmon, M. *Phys. Rev. Lett.* 1985, **55**, 118

26 Zotti, G. and Schiavon, G. *Synth. Met.* 1989, **30**, 151

27 Mechtstein, M., Devreas, F., Genoud, F., Vieil, E., Pernaut, J. M. and Genies, E. *Synth. Met.* 1986, **15**, 59

28 Reghu, M., Subramanyam, S. V. and Chatterjee, S. *Phys. Rev. B* 1991, **43**, 4236

29 Bryskin, V. V. and Voloshin, V. S. *Fiz. Tverd Tela (Leningrad)* 1984, **26**, 2357 (*Sov. Phys. Solid State* 1984, **26**, 1429)

30 Bryskin, V. V. and Gottsev, A. V. *Fiz. Tverd Tela (Leningrad)* 1988, **30**, 1476 (*Sov. Phys. Solid State* 1988, **30**, 851)

31 Mott, N. F. *Adv. Phys.* 1967, **16**, 49

32 Mott, N. F. *Phil. Mag.* 1969, **19**, 835

33 Mott, N. F. and Davis, E. A. 'Electronic Processes in Noncrystalline Materials', Clarendon Press, Oxford, UK, 1979, pp. 32–34

34 Chien, J. C. W. 'Polyacetylene', Academic Press, Orlando, 1984, p. 485

35 Paul, D. K. and Mitra, S. S. *Phys. Rev. Lett.* 1973, **31**, 1000

36 Nair, K. and Mitra, S. S. *J. Non-Cryst. Solids* 1977, **24**, 1

37 Ambegaokar, V., Halperin, B. J. and Langer, J. S. *Phys. Rev. B* 1971, **4**, 2612

38 Fritzsche, H. in 'Amorphous Semiconductors' (Ed. J. Tauc), Plenum Press, New York, 1974, p. 233

39 Brodsky, M. H. and Gambino, R. J. in Proc. 4th Int. Conf. on Amorphous and Liquid Semiconductors, Ann Arbor, MI, 1971 (Eds M. H. Cohen and Lukovscky), North Holland Amsterdam, 1972, p. 742

40 Reghu, M. and Subramanyam, S. V. *Phys. Lett. A* 1990, **145**, 371

41 Baughman, R. H. and Shacklette, L. W. *Phys. Rev. B* 1989, **39**, 5872

42 Roy, R., Sen, S. K., Digar, M. and Bhattacharyya, S. N. *J. Phys.: Condens. Matter* 1991, **3**, 7849

43 Bredas, J. L., Scott, J. C., Yakushi, K. and Street, G. B. *Phys. Rev. B* 1984, **30**, 1023