Mechanism of Electrical Conduction in Doped Poly-2-Vinylpyridine

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Summary: Poly-2-vinylpyridine (P2VP) and its composites with uniformly distributed dopant have been synthesized and characterized through analytical measurements such as glass transition temperature Tg, molecular mass and screening etc. The d.c. conductivity of these samples was studied as a function of temperature. The conductivity of P2VP is seen to increase by many orders of magnitude on addition of dopant. Energy of activation, charge carrier concentration and carrier mobility is determined and conduction mechanism proposed.

Introduction

Although high conductivities have been found in organic polymers containing conjugated double bond in the backbone, they degrade due to oxidation by air resulting into their crystalline to amorphous structural phase transition and decrease in conductivity [1-3]. p and n doping of these polymers enhance their stability, as well as, their conductivity [4,5]. Charge transfer heterocyclic molecular complexes exhibit high conductivity due to strong interchain coupling. The conjugated double bond and charge transfer characteristics are mainly responsible for conductivity in these structures. The conduction phenomenon in such complexes is electronic and involves narrow bands formed from overlapping π-orbitals.

Several polymer metal complexes e.g., 2-amino-3-hydroxy pyridine with Mn, Co, Ni were prepared and their electrical conductivity was shown to increase as compared to the polymer [6-8]. However, they were environmentally unstable due to lack of stable polymer backbone. The present work attempts to explore the possibility of designing a polymer backbone which will be embedded, so as to say, in an electron cloud not only of the delocalized π-electrons of carbon-carbon multiple bond, but also the non-bonding electrons of heteroatom such as nitrogen. To this end, we focus on the homogeneous chemical synthesis and the investigation of d.c. conductivity of poly-2-vinylpyridine (P2VP) after doping with a number of metal salts such as NaI, KI, NaSCN and KSCN.

P2VP structure is thermally stable due to strong carbon-carbon and carbon-nitrogen covalent bond. We are of the opinion that doping of P2VP with salts will engage nitrogen atom of the pyridine ring to give environmental stability. Furthermore, it is expected that the conductivity of P2VP should increase on doping with metal salts either due to intrachain coupling through π-π orbital overlap of the anion and the pyridine ring or due to formation of ion dipole interaction between metal ion and nitrogen of the ring. The introduction of the metal ion or an anion into the polymer matrix increases the conductivity in them due to (i) improved intermolecular orbital overlap of bare π-orbitals of anions, and (ii) extension of the intermolecular conduction path by delocalization of lone pair on nitrogen through metal atom.

Results and Discussion

Conductivities for P2VP and its composites are calculated by the formula $\sigma = L/RA$, (where L is average thickness of the sample, R is resistance of the sample and A is the effective area of the circular electrode) and are presented in Table-2. Conductivities are enhanced on complexation with alkali metal salts. This augmentation in conductivities is by a factor of three, six, seven and eight for KI, KSCN, NaSCN and NaI, respectively.

A plot of lnI versus lnV at various temperatures for P2VP and its composites is shown in Fig. 3 (a-e). The gradient for P2VP and B_2 at all tempera-

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Table-1: Melting points of salts and composites

Salt	m.p.	Composite	Tg.
		P2VP	100-110 °C
NaSCN	287 °C	A₁	170-200 °C
KSCN	172.3 °C	A₂	130-150 °C
NaI	651 °C	B₁	160-190 °C
KI	723 °C	B₂	120-140 °C

B_1 shows V^3 dependence approaching space-charge limited conduction as we move from lower to higher temperature. A more rapid increase in current is noted in case of A_1 and A_2 exhibiting V^4 and V^2 dependence at lower and higher temperatures, respectively. Square law dependence can be explained on

Table-2: Values of charge density n, carrier mobility μ, conductivity σ and activation energy E_a

| Sample | Dopant | at 233K at 50 volts | | | at 285K at 50 volts | | | at 310K at 50 volts | | | |
		n (cm⁻³)	μ (cm²V⁻¹s⁻¹)	σ (Scm⁻¹)	n (cm⁻³)	μ (cm²V⁻¹s⁻¹)	σ (Scm⁻¹)	n (cm⁻³)	μ (cm²V⁻¹s⁻¹)	σ (Scm⁻¹)	E_a(eV)
P2VP	-------							6.37E+00	2.98E+04	3.05E-14	1.511
A₁	NaSCN	4.67E-12	9.57E+17	7.16E-13	2.96E-05	5.29E-07	5.11E-07	8.66E-03	1.73E+15	2.41E-06	1.687
		198E+11	2.25E-05		9.35E+13	3.41E-02		8.79E+14	1.71E-02		0.643
B₁	NaI	1.45E-03	5.71E+12	1.33E-09	2.60E-02	1.30E+15	5.42E-06	1.65E+03	5.40E+10	6.24E-06	1.362
		6.04E+18	1.37E-09		1.22E+20	2.75E-07		3.71E+20	1.05E-07		0.297
A₂	KSCN	8.15E-02	7.81E+07	1.02E-12	1.30E+07	5.79E+03	1.21E-08	4.38E+08	9.90E+02	6.95E-08	1.029
		6.40E+09	9.96E-04		5.65E+12	1.33E-02		6.66E+13	6.51E-03		0.711
B₂	KI	1.22E+16	5.43E-08	1.06E-10	7.69E+17	1.25E-07	1.54E-08	3.50E+18	2.12E-07	1.19E-07	0422
		1.69E+09	3.92E-01		1.90E+12	5.05E-02		2.45E+13	3.03E-02		0.738

the basis of space-charge limited current, as the slope for this type of mechanism is around 2 [12], whereas higher values of slope indicate the tunneling effect [13]. Furthermore, the current-voltage linear relationship confirms the dominance of Poole-Frenkel effect [14].

Conductivity of the base material and its composites increases with temperature (Table-2). This characterizes semiconductor-like conduction in these materials. In addition, the conductivity follows the well-known exponential law which is true for crystalline semiconductors. The corresponding rise in conductivity with temperature is described by Equation 1
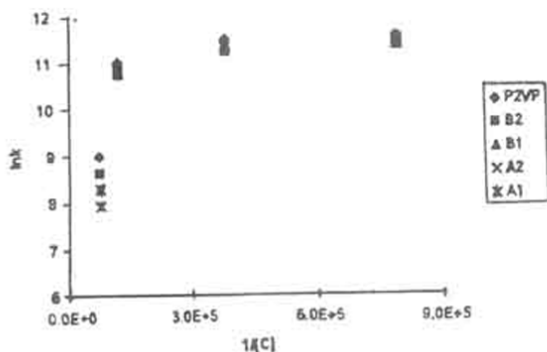

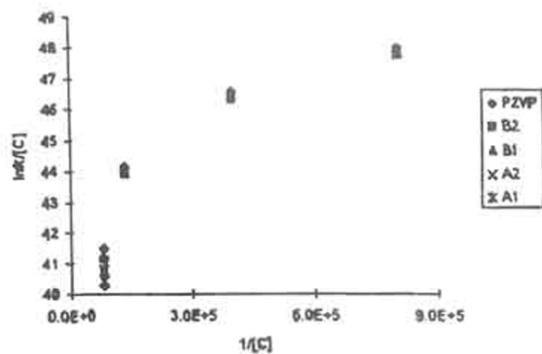Fig. 1:   Plot of lnk/[C] versus 1/[C] for P2VP and its composites.

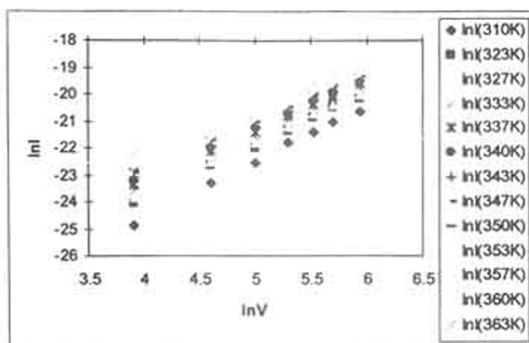Fig. 2:   Plot of lnk/[C] versus 1/[C] for P2VP and its composites.

$$\sigma = \sigma_0 \exp(-E_a/k_B T) \qquad 1$$

The plots of $\ln\sigma$ versus $1/k_B T$ in Fig.4 (a-e) show a kink for composites A_1, A_2, B_1 and B_2, which is a clear indication of a temperature dependent phase transition, which seems to shift with increasing voltage allowing the shallow traps to be filled at high voltage. The dependence of current on voltage at higher voltage values, indicate a non-uniform density of hole trap. It is possible to suggest that the trap distribution is not uniform but consists of discrete levels Then, the rise of current with voltage may be interpreted as trap-filled limit voltage [15]. These composites have been found to be thermally stable for the temperature range in which the electrical conductivity measurements are carried out. This may be attributed to a transition from band to tunneling conduction facilitated due to the crystalline to amorphous phase transition of the samples.
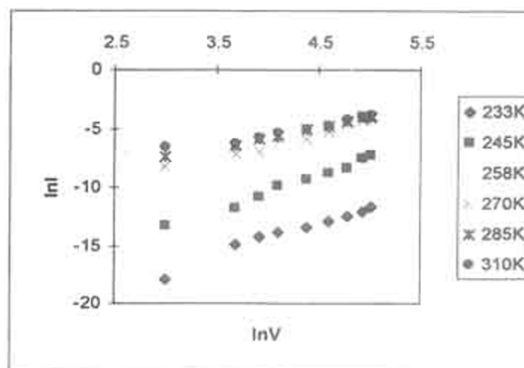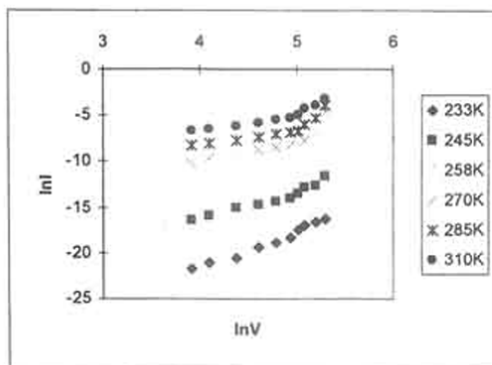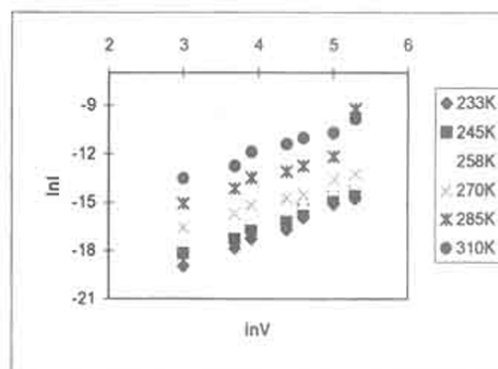
tures under investigation is about 2 showing square-law dependence upon voltage. However, composite

Fig. 3(a): Plot of lnI versus lnV for P2VP.

Fig. 3(b): Plot of lnI versus lnV for composite A_1.
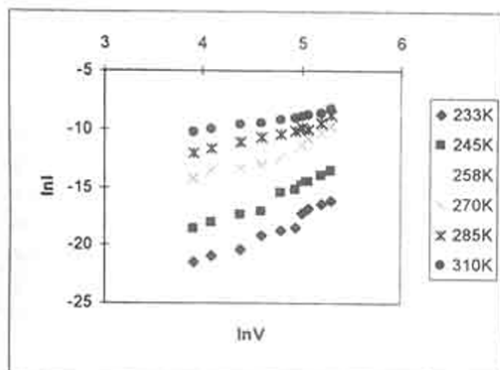
Fig. 3(c): Plot of lnI versus lnV for composite A_2.

The electrical conductivity σ (= $qn\mu$, where n is the concentration per volume of the charge-carriers, μ is the carrier mobility and q is the electronic charge) due to drift of free charge carriers like electrons and holes, and the value of carrier concentration which is determined through the relation,

$$n = 2(2\pi m k_B T/h^2)^{3/2} \exp(-E_a/k_B T)$$

Fig. 3(d): Plot of lnI versus lnV for composite B_1.

Fig. 3(e): Plot of lnI versus lnV for composite B_2

(where m is the effective mass of the charge carriers, which is assumed to be the rest mass of an electron, h is the Plank's constant, k_B is the Boltzmann's constant, T is the absolute temperature and E_a is activation energy). Activation energy is calculated from Equation 1. For typical parameters, charge carriers concentration (n), carrier mobility (μ) and energy of activation (E_a) are depicted in the Table-2. The values of energy of activation reflects the dynamic equilibrium of electron and hole concentrations by continual thermal generation and recombination centers [13], which may be attributed to shallow levels in some cases and deep levels in other cases [16].

The effect of temperature on the concentration of charge carriers of the composites is also investigated. It appears from Table-2 that the concen-tration of carriers (n) increases with increasing temperature, which means that the activation process can be attributed to the electron transfer from the valence to the conduction band by thermal activation, and increase in electrical conductivity of P2VP compo-
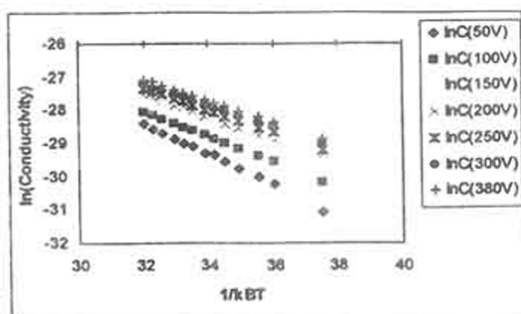
Fig. 4(a): Plot of lnσ versus $1/k_BT$ for P2VP.
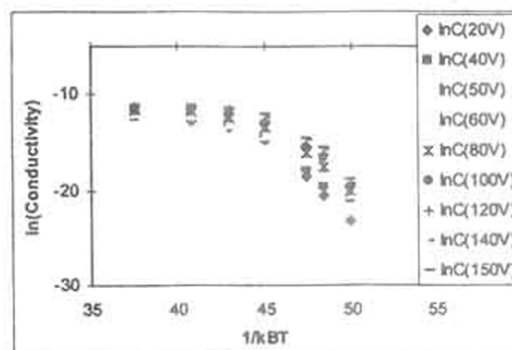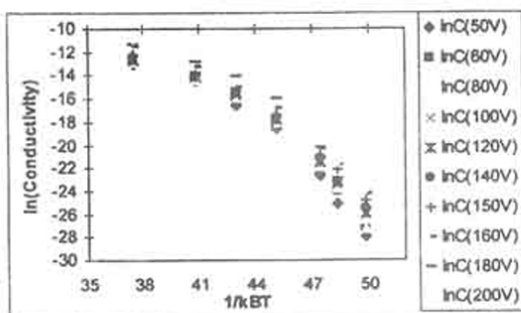
Fig. 4(b): Plot of lnσ versus $1/k_BT$ for composite A_1.
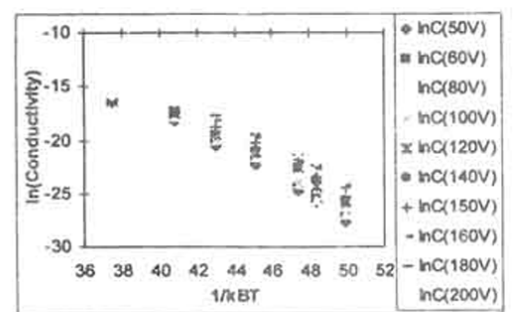
Fig. 4(c): Plot of lnσ versus $1/k_BT$ for composite A_2.

Fig. 4(d): Plot of lnσ versus $1/k_BT$ for composite B_1.
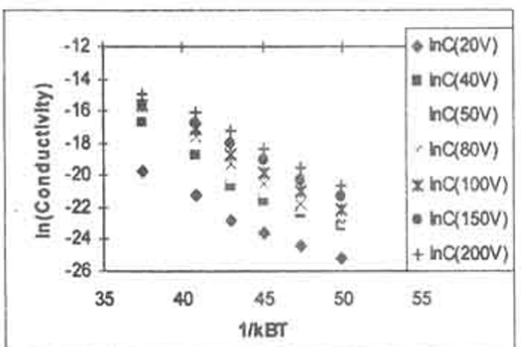
Fig. 4(e): Plot of lnσ versus $1/k_BT$ for composite B_2

sites may be ascribed to the production of carriers in the conduction band. In most semicon-ductors, a rise of temperature (from 233 to 310K) increases the current carriers concentration and narrower the forbidden gap, the sharper will be this increase. This may be due to the strengthening tunneling process taking place in the samples at higher temperature. The carriers mobility decreases with increase of temperature i.e., from 233K to 310K. This again is in agreement with the semiconductor like behavior in the samples. The manifold increase in conductivity enhances the tunneling effect in the samples which is a characteristic of semi conducting material which further increases on doping.

A plot of lnσ as a function of $T^{-0.25}$ is given in Fig.5 (a-e). Deviation of conductivity data from straight line fits [17] for the composites in compari-son to base material (Fig. 5(a)) confirms the tempera-ture dependent crystalline to amorphous structural phase transition in the materials, showing thiocya-nates (Fig. 5 b, d) being more amorphous than iodides (Fig. 5 c, e). It also suggests that more than one conduction mechanisms are operative with domi-nance of conduction through tunneling at the elevated temperatures.

Experimental

50 ml 2-vinylpyridine (97 %) obtained from Aldrich Chemical Company was dried over anhy-drous sodium carbonate for 48 hours and distilled under vacuum at 60 ^{0}C. Tetrahydrofuran (THF) used as solvent for polymerization and composite forma-tion was dried over sodium benzophenoate and distilled immediately before use. All other chemicals were of A.R. grade.
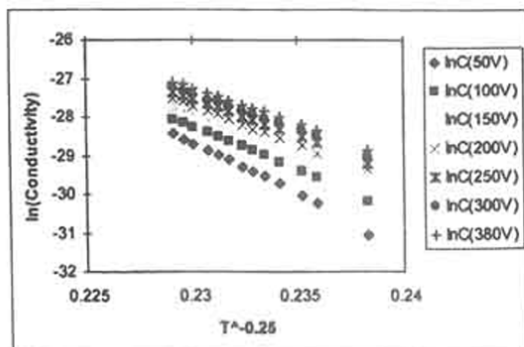
Fig. 5(a): Plot of lnσ versus T^-0.25 for P2VP.
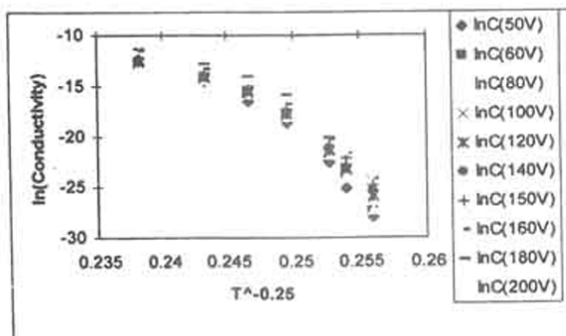
Fig. 5(b): Plot of lnσ versus T^-0.25 for composite A_1.
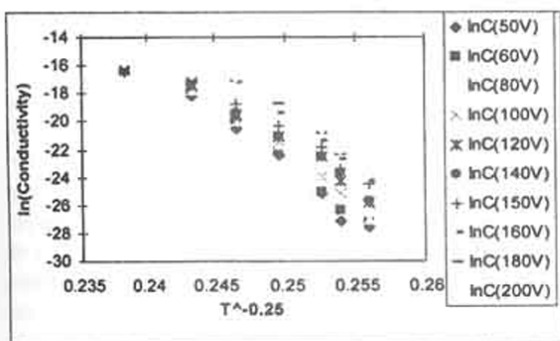
Fig. 5(c): Plot of lnσ versus T^-0.25 for composite A_2.
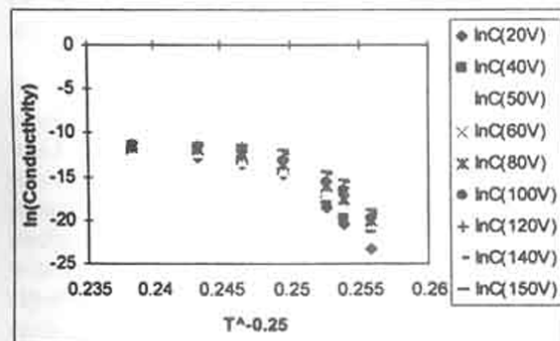
Fig. 5(d): Plot of lnσ versus T^-0.25 for composite B_1.
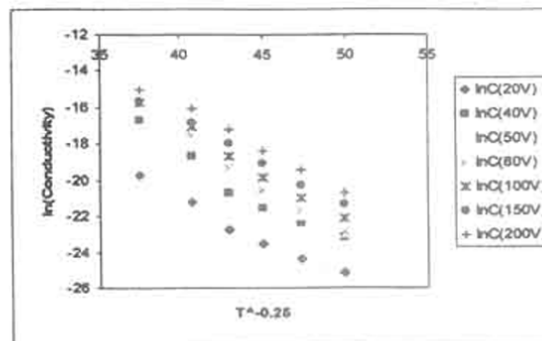
Fig. 5(e): Plot of lnσ versus T^-0.25 for composite B_2

Polymerization of 2-Vinylpyridine

40 ml (0.36 mol) of distilled 2-vinylpyridine was stirred with azoisobutyronitrile (AIBN) (0.1-2 wt. % / vol) in a round bottom flask fitted with water condenser and hot- plate at 60 ^{0}C for 10 hours under inert atmosphere of helium gas. Poly-2-vinylpyridine obtained was purified by dissolving in THF and precipitating with dry n-hexane. The polymer was dried under vacuum for several hours.

Preparation of Semiconducting Polymeric Composites

The following general procedure was adopted for the preparation of semiconducting composites.

0.526 g of poly-2 vinylpyridine was dissolved in 20 ml of dry THF in a 3-necked round bottom flask fitted with a magnetic stirrer and cold water condenser under inert atmosphere. 0.25 g of salt was dissolved in 20 ml of THF and added drop by drop to the stirring solution of P2VP over a period of two hours. The solvent was removed by rotary evaporation followed by vacuum drying for several hours. In all the preparations 1:3 stoichiometry of salt to monomer was assumed as prescribed by Armand [9], Hibma [10] and Okamura & Chatani [11].

Characterization

The molecular weight of P2VP as determined by vapour pressure osmometric method was 9755 with an error margin of ± 5 %. Glass transition temperature (Tg) of the P2VP and its composites was determined on NETZSCH Simultaneous Thermal Analyzer STA 429 using the ambient of argon and are shown in Table-1. Addition of potassium and sodium-thiocynates as dopant have stabilizing effect on P2VP whereas potassium and sodium iodides facilitates thermal decomposition making it relatively

unstable. Glass transition temperature of the composite is influenced by nature of the salt as reported earlier in polypropylene oxide salts. We observed that the larger the size of the anion of the dopant higher the Tg of composite and has no relationship with the melting temperature of the pure dopent.

Electrical Conductivity Measurement

For the electrical conductivity studies, the chemically synthesized polymer and its composites were pressed to pellets with dimensions of 0.18 cm in thickness and 1.76 cm^2 in area with a Beckmann Dye Model No. KB-0112 under a pressure of 60 KN for 2 minutes. Electrical conductivity of the polymer samples was determined by two probe method using a Keithley 610 Electrometer and a regulated power supply which can provide maximum voltage of 380 volts. The measured resistance was converted to conductivity from the sample dimensions.

Conclusions

The following conclusions may be drawn:

1.   The method adopted to synthesize P2VP and its composites provides a convenient and efficient method of preparation which excludes the possibility of getting impurities or moisture into it.

2.   Conductivity of P2VP is greatly enhanced on its complexation with alkali metal salts. It shows that tunneling is the conduction pathway through metal-nitrogen overlap at elevated temperatures.

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