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Electrical Conductivity of Sodium Doped Poly(4-Vinylpyridine)

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Poly(4-Vinylpyridine) was synthesized by free radicalic polymerization. Solution doping process with metallic sodium was carried out. A conductivity value around 10^{-6} S/cm was obtained. Relative change in the coductivity with dopant concentration, temperature dependence of conductivity, conductivity behavior in atmospheric conditions for the samples were analyzed. SEM and EDX techniques were also used for the characterization of the polymer.

Introduction

Vinyl pyridines are an important class of polymers exhibiting interesting properties due to the presence of a nitrogen atom in the aromatic ring. The weakly basic nitrogen atom makes a variety of reactions possible on pyridine polymers, e.g., reaction with acids, quaternization, and complexation with metals. Vinylpyridine polymers are particularly important as electrolytes, polymeric reagents, and in electrical applications[1].

Among the conjugated side chain polymers, vinylpyridine polymers (PVP) have been considered attractive in the formation of semiconductor because of the doping facilities with iodine [2–5] or electronic acceptors [6,7]. The conducting complexes of PVP, both P4VP and P2VP, were prepared for the first time by Mainthia et al. [3]. Depending on the method of preparation, their resistivities were found to be in the range of 10^4-10^7 $\Omega\cdot$ cm at room temperature.

$LiClO_4$ and TCNQ was also introduced as the dopants to the P4VP structure in literature [8,9]. In these studies, 10^{-3} - 10^{-4} $S.cm^{-1}$ conductivities were obtained.

In this article, we propose a relatively simple technique to obtain conducting P4VP by solution doping with metallic sodium which shows a conductivity around 10^{-6} $S\cdot cm^{-1}$.

Experimental

4-Vinylpyridine was supplied by Merck Co. and used after purification under vacuum. The pure monomer, azobisisobutyronitrile as initiator and toluene as the solvent were degassed. After 3 hours polymerization at 80°C, the product was collected by filtration and dried under vacuum. 88.9 % yield was calculated for the polymerization. 1% polymer solutions were prepared by using methanol as the solvent and sodium metal was introduced into these solutions. Thus, five samples having the same polymer quantities and different sodium concentrations were prepared. 30 ml of these solutions were poured onto the Teflon moldings and conductivity measurements were carried out after obtaining films by the evaporating of the solvent. Conductivity measurements were carried out using standard two probe and/or four probe techniques.

Results and Discussion

Different concentrations of sodium present in the solutions yield conductivities in the range of 10^{-5}-10^{-8} $S \cdot cm^{-1}$. Conductivity of the films arise from the doping of the P4VP with sodium methoxied that was produced by the reaction of metallic sodium with methanol. However, as it can be seen in Figure 1, conductivity values are not directly proportional with the concentration of the sodium present in the solutions. Undoped P4VP is practically insulating. Conductivity increases to 10^{-6} S/cm with 0.1 g Na per 0.34 g polymer and remains constant even after ten times increase in the dopant concentration. When the amount of sodium exceeds 1g per 0.34 g of polymer, conductivity decreases again. This may be due to the phenomenon of supersaturation of the polymer with the dopant[10]. Conductivity behavior of P4VP was analyzed under ambient conditions and it was observed that it decreases from 10^{-5} to 10^{-8} S/cm in about 18 days. (Figure 2). This can be explained by the interaction of the sodium doped P4VP films with the atmospheric moisture. Under atmospheric conditions, sodium mexhoxide is rapidly transformed to sodium hydroxide which decreases the dopant concentration in the polymer structure. However, when the conductivity measurements were carried out under vacuum conditions it remained almost constant (Figure 3).

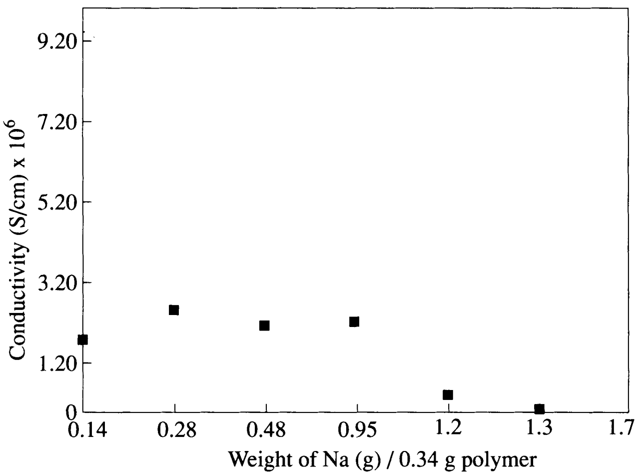

Figure 1. Change is conductivity with different contcentrations of metallic sodium

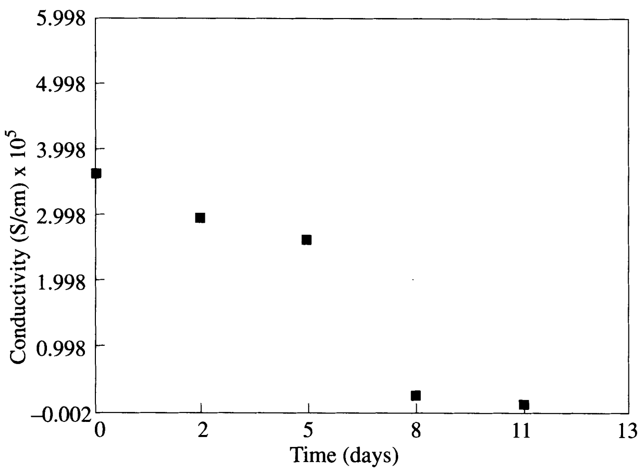

Figure 2. Conductivity behavior of doped P4VP under ambient conditions

The scanning electron micrograph (SEM) of the conducting P4VP sample was given in Figure 4. A cauliflower-like appearance, which is generally observed in many conducting polymer structures like polypyrrole, can also be detected in our case[11].

Energy Dispersive X-ray spectra (EDX) in Figure 5 shows the formation of sodium hydroxide in the surface. As shown in Figure 5a, sodium and the oxygen quantities on the surface of the film were nearly the same. However, in the inner side of the film, sodium quantity is higher on the surface.

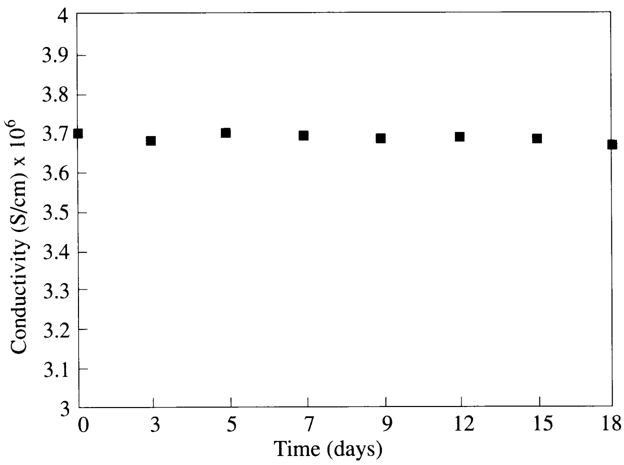

Figure 3. Conductivity behavior of doped P4VP under ambient conditions.

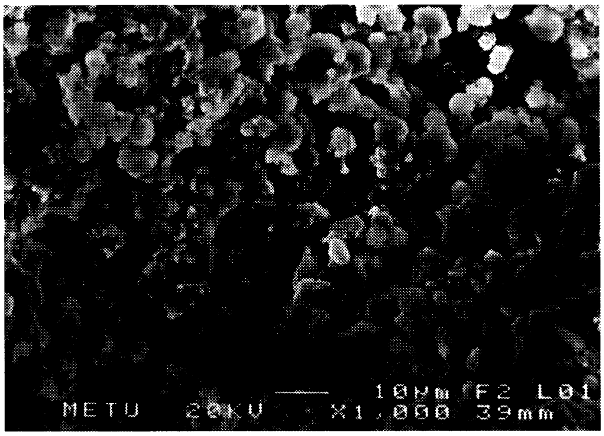

Figure 4. SEM of conducting P4VP sample.

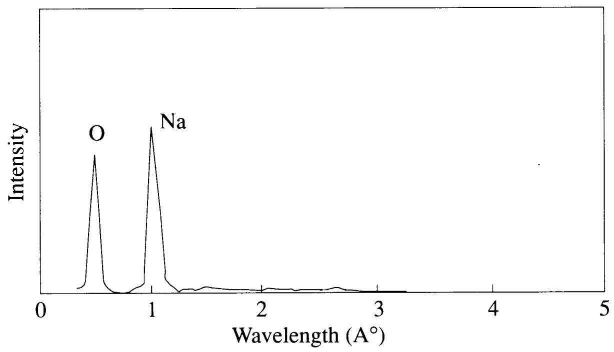

Figure 5a. EDX spectrum taken from the surface of the doped P4VP film.

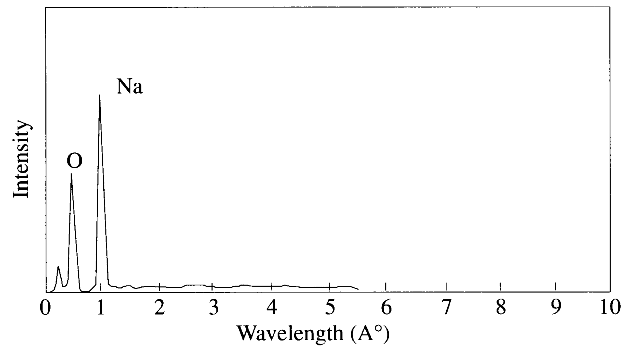

Figure 5b. EDX spectrum taken from the cross-section of the doped P4VP film.

In Figures 6a and 6b, temperature dependence of conductivity was examined according to two basic existing theories. In Figure 6a, an Arrhenius plot of conductivity versus temperature is shown according to following relation[12]:

$$\sigma = \sigma_0 exp[-Ea(c,T)/kT], \tag{1}$$

where σ_0 is the conductivity at infinite temperature and Ea is concentration and temperature dependent activation energy. Results indicate that conductivity increases with temperature, due to the increase in the number of charge carriers having enough activation energy. Also, their mobility increases with the temperature.

Mott variable range hopping (VRH) theory [13] predicts the following behavior:

$$\sigma(T) = (\sigma_0/T^{1/2})exp[-(T_0/T)^{1/4}], \tag{2}$$

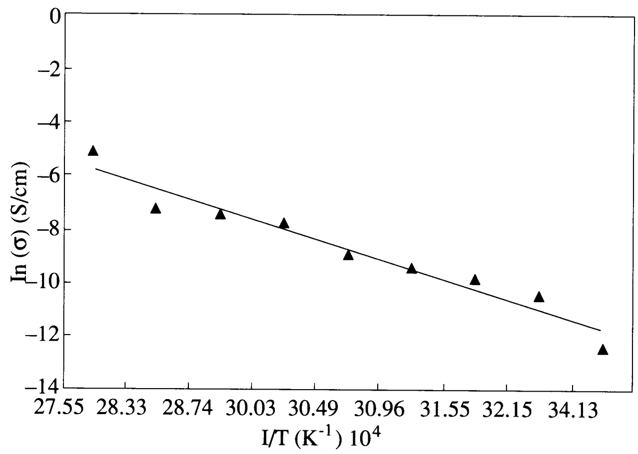

Figure 6a. Temperature dependence of conductivity plotted according to Arrhenius relation

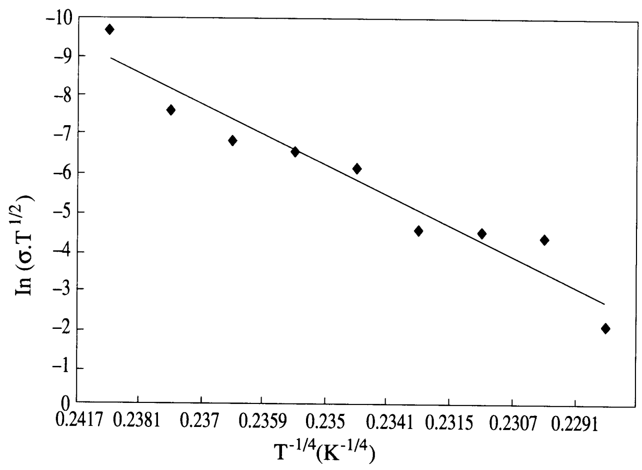

Figure 6b. Temperature dependence of conductivity plotted according to VRH Theory.

where σ_0 is the conductivity at infinite temperature and T_0 is the characteristic temperature. This leads to the establishment of the temperature dependence of conductivity in the form of $ln\sigma$ vs. $T^{-1/4}$. Since there si no restriction regarding the type of charge carrier in the VRH theory, it can also be applied to the P4VP.

Our results indicate that both theories are applicable to the variation of conductivity with temperature for doped P4VP samples

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