Transport Properties in Polypyrrole Powders and in PPy–PVA Composites: Evidence for Bipolaronic Clusters

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ABSTRACT: Experimental results on electrical conductivity of both doped polypyrrole (PPy) powder and conducting poly(vinyl alcohol)(PVA)–PPy composite are presented. In each case, $FeCl_3$ has been used as the oxidizing–polymerizing agent. Results are interpreted on the basis of a model in which counter-ions act through their attractive potential by forming conducting ways between chains and allowing transverse conduction. In the case of PPy powder, the major contribution to conduction mechanisms is hopping between polaronic clusters. In the case of the composite, an additional contribution results from fluctuation-induced tunneling through thin insulating PVA barriers. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 709–713, 1998

Key words: conducting polymers; polymer composites; transport phenomena; polypyrrole

INTRODUCTION

Polypyrrole (PPy) is one of the most extensively studied conducting polymers. PPy has received considerable interest because, on one hand, it can be prepared relatively easily by electrochemical or chemical oxidation of pyrrole and, on the other hand, it exhibits high conductivity and good environmental stability in the conducting oxidized form, as compared with the majority of conducting polymers. However, PPy is insoluble in any solvent and is infusible up to the decomposition temperature. Thus PPy is extremely difficult to process which, in turn, limits its technological applications. Nevertheless, several attempts have been made to prepare composites or blends of PPy with classical polymers in order to improve their processability while retaining high conductivity. In this context, a simple method of preparing PPy–poly(vinyl alcohol) (PPy–PVA) composites has been proposed[1–3] based on the oxidation of pyrrole by PVA–transition metal salt complexes.

In this article we focus on the possibility of comparing the conduction mechanisms in PPy powder prepared by chemical oxidation of pyrrole with $FeCl_3$ and in a PPy–PVA composite obtained by polymerization of pyrrole within the PVA matrix in which the oxidant ($FeCl_3$) was molecularly dispersed through the formation of chelate-type complexes with the polymeric matrix. To achieve this goal, electrical conductivity versus temperature has been studied over a wide range. Transport properties of PPy powders are explained with the help of a hopping model involving transverse bipolarons within polaronic clusters.[4] For the PVA–PPy composite, it has been found necessary to introduce an extra contribution to the conduction mechanisms by considering thermal fluctuation-assisted tunneling between conducting PPy domains through thin PVA barriers.
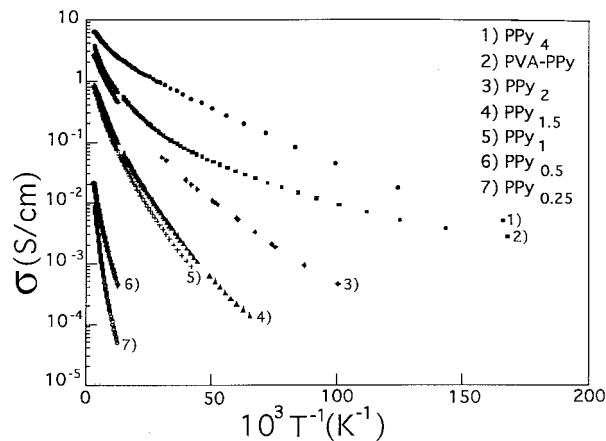
Figure 1 Experimental variations of log σ versus $10^3/T$ obtained on conducting PPy powder and PVA–PPy composite.

EXPERIMENTAL

The PPy powder was synthesized by mixing solutions of pyrrole and $FeCl_3$. Polymerization was allowed to proceed for about 1 h. Longer polymerization times did not result in an increase of the polymerization yield. Water was used as solvent. PPy was formed[5-7] as a black precipitate which was collected by filtration and finally rinsed with water and dried for 24 h at 300 K in vacuum. In general, oxidation of pyrrole with $FeCl_3$ leads to Cl^- doped PPy.[8] However, in addition to Cl^- counterion, small amounts of $FeCl_4^-$ could be detected in the product,[9] indicating that PPy is presumably partly doped with $FeCl_4^-$ according to the following reaction:

$$ny\,C_4H_5N + (2y + 2)n\,FeCl_3$$
$$\rightarrow [(C_4H_3N)_y^+ FeCl_4^-]_n + (2y + 1)_n FeCl_2$$
$$+ 2yn\,HCl$$
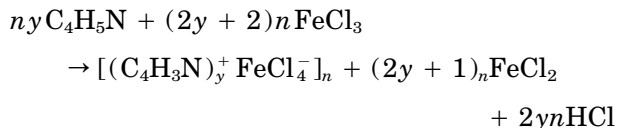
Series of PPy samples polymerized at various $FeCl_3$ concentrations have been prepared which present different chemical characteristics and also different physical properties. The initial concentration of Fe^{3+} varied from 4 to $0.25M$ while that of pyrrole was kept constant at $0.04M$. In our discussion, the polymer samples are identified by the notation PPy_x, where x is the initial concentration of Fe^{3+} used in the polymerization solution. The samples studied here are PPy_4, PPy_2, $PPy_{1.5}$, PPy_1, $PPy_{0.5}$, and $PPy_{0.25}$.

The conducting composite films of polypyrrole PVA–PPy have been synthesized according to the technique previously described.[10,11] The PPy/PVA molar ratio (y) of the composite studied here is 0.09. The PPy content in this case is much higher than the one obtained at the percolation threshold $(y_c = 0.012)$.[12]

The electrical conductivity was measured by a four-probe technique. Samples were pressed into pellets and gold wires stuck with "electrodag" organic glue were used as contacts. An alternative current resistance measurement method was used at 80 Hz with an AC 700 susceptometer system. A connector placed at the tip of the stick allowed establishment of electrical connections to the sample. The temperature dependence of the electrical conductivity was studied over a wide range (4–300 K) at ambient pressure.

The room-temperature (T) conductivity of the various PPy_x samples strongly depends on the

Table I   Parameters of $\sigma = \sigma_o \exp\left[-\left(\dfrac{T_o}{T}\right)^{1/n}\right]$

PPy_x	$n = 2$			$n = 4$		
	σ_o (S/cm)	T_o (K)	e (%)	σ_o (S/cm)	T_o (K)	e (%)
$x = 4$	18	316	3.2	82	12126	5.2
$x = 2$	17	1047	1.2	184	93112	4.1
$x = 1.5$	11	1671	0.6	100	143964	3.7
$x = 1$	14	2289	0.5	445	453886	4.5
$x = 0.5$	1.3	4984	1.5	157	1874450	5.8
$x = 0.25$	5.4	11372	1.7	7535	9571734	5.3
PVA–PPy	25	1088	0.3	327.95	119640	0.5

Equation obtained via best-fitting procedure for PPy powders and PVA–PPy composite.
e denotes the average quadratic deviation of the experimental data from the best adjusted curves.
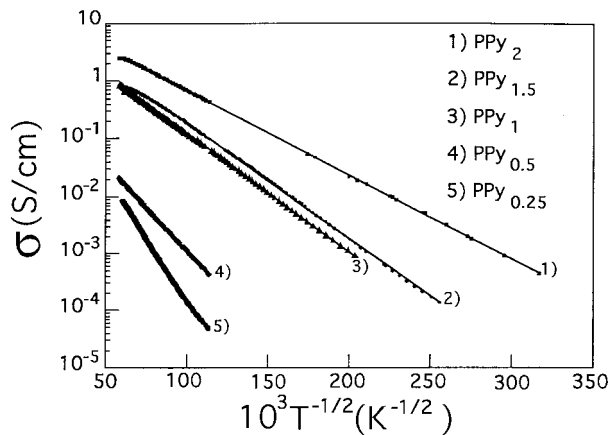
Figure 2 Log of the conductivity plotted versus $T^{-1/2}$ over a large temperature range. We present a model explaining this exponent value ($\alpha = \frac{1}{2}$). Numbers refer to samples.

doping level and decreases from 6 S/cm for the sample polymerized at highest reactant concentration ($x = 4$) to 10^{-4} S/cm for the sample polymerized at the lowest reactant concentration ($x = 0.1$). It must be noticed that the dependence of σ versus the molar ratio Fe^{3+}/Py in the reaction mixture is not characteristic of a percolation system, as in the case of composites.[12] These results show that the polymers obtained with the largest excess of $FeCl_3$ are the most conducting. The experimental dependence of σ versus $10^3/T$ is shown in Figure 1 for samples PPy_4, PPy_2, $PPy_{1.5}$, PPy_1, $PPy_{0.5}$, and $PPy_{0.25}$. The general shape of all the curves is almost the same and is independent of the samples. Measurements of $PPy_{0.5}$ and $PPy_{0.25}$ were performed up to 70 K because these samples are strongly resistive with strong fluctuation of the signal phase. In the high temperature limit, these compounds have a weak activation energy which diminishes with the increase of the amount of the oxidant used (11, 21, 25, 40, 45, and 57 meV for PPy_4, PPy_2, $PPy_{1.5}$, PPy_1, $PPy_{0.5}$, and $PPy_{0.25}$, respectively).

The experimental variations of the electrical conductivity σ of the conducting PVA–PPy composite film versus reciprocal temperature are shown in Figure 1. They are weakly activated in the high temperature limit (about 25 meV), and σ ranges from 0.003 S/cm at the lower temperature to 5 S/cm at room temperature.

RESULTS AND DISCUSSION

PPy generally exhibits some structural disorder due to polymerization defects, such as a–b cou-

plings, groups breaking the conjugation, or others.[13] As a consequence, the charge carriers do not move as in a crystalline lattice. Therefore, the dominant transport mechanism in the PPy compounds is hopping between localized states. In the case of the composite, an additional disorder comes from the distribution of conducting domains of PPy within the PVA matrix. The electrical conductivity σ is limited mainly by macroscopic hopping between conducting domains.

In this respect we tried to fit the experimental conductivity curves, taking into account dominant hopping between localized states, obeying the law

$$\sigma = \sigma_0 \exp - \left[\frac{T_0}{T} \right]^{1/n},$$ in which the power coeffi-

cient n may be 1, 2, 3, or 4.[14–16] The appropriate value which gives the best fit is considered to provide information about the conduction mechanisms.

All data obtained from the fits are collected in Table I. The results of this analysis can be summarized as follows:

1. In the case of PPy_x samples with $0.25 \leq x \leq 2$, the best fit is achieved with $n = 2$ over the whole investigated temperature range (Fig. 2).
2. For PPy_4, there is no agreement between experimental and calculated curves, either for $n = 2$ or $n = 4$.
3. For the composite PVA–PPy, a good fit is obtained for $n = 4$.

Over the whole temperature range investigated, in the case of PPy_x samples with $0.25 \leq x \leq 2$, results are in good agreement with the hop-
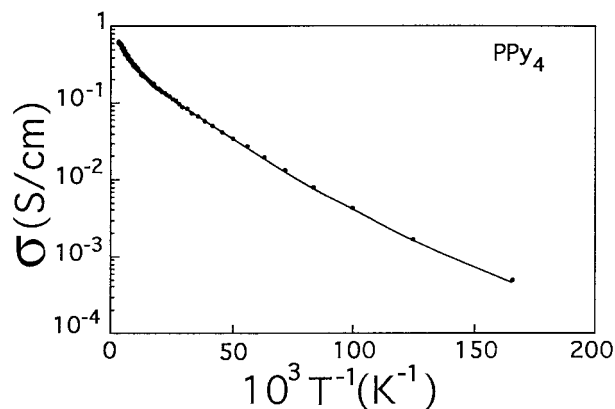

Figure 3 Experimental variations of log σ versus $10^3/T$ obtained PPy_4. The theoretical variations are drawn in full line.
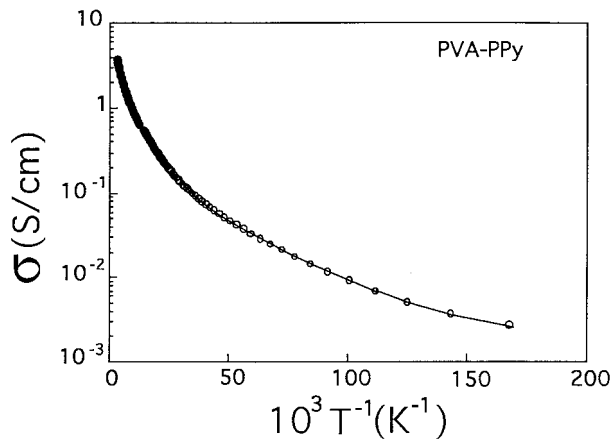
Figure 4 Experimental variations of σ versus $10^3/T$ obtained PVA–PPy. The theoretical variations are drawn in full line.

ping model which has been developed recently by Zuppiroli and colleagues.[17] This model involves transverse bipolarons within polaronic clusters and is based on the existence of an optimized T-dependent size of the polaronic cluster for easy hopping. The electrical conductivity obeys a $T^{-1/2}$ law:

$$\sigma \approx \exp\left[\frac{T_0}{T}\right]^{1/2}$$

The validity of this model has been confirmed in PPy doped with sulfonated polyelectrolyte counterions.[17] T_0 reaches high values when the doping level decreases. According to Zuppiroli and associates,[17] T_0 can be expressed as follows:

$$T_0 = 8U/K_B(\overline{\delta}/\delta - 1)^2/(\overline{\delta}/\delta - \tfrac{1}{2})$$

where U is the repulsion energy of two electrons sitting at the distance "a" equal to the size of the monomer, and K_B designates the Boltzman constant. The term δ is the average distance between dopants within clusters and $\overline{\delta}$ is the average distance between dopants when a uniform distribution without clusters is assumed.

According to Zuppiroli and coworkers,[17] the diameter of the polaronic clusters d and the inter-cluster distance s are independent. The existence of clusters is related to dopant-density fluctuations. Assuming that the mean distance d does not depend on δ, the radius $s/2$ of the cluster is related to δ by: $\overline{\delta}/\delta = (d + s)/d$. Taking for U the value 2 eV ($\varepsilon_r \sim 2$), as has been sug-

gested,[17] the $\overline{\delta}/\delta$ ratios for the PPy$_x$ samples have been calculated from the T_0 relation and are found to be equal to 1.056, 1.072, 1.085, 1.130, and 1.208 for PPy$_2$, PPy$_{1.5}$, PPy$_1$, PPy$_{0.5}$, and PPy$_{0.25}$, respectively. These values match those of Zuppiroli and colleagues.[17] The quantity δ being independent of d, the ratio $\overline{\delta}/\delta$ decreases when the dopant concentration increases; as a consequence, it is found that the most-doped polymers exhibit weak $\overline{\delta}/\delta$ ratios.

A careful examination of the σ-versus-T^{-1} dependence for the highest-doped compound PPy$_4$ shows a quasi-linear dependence in the high temperature range limit (135–300 K), whereas in the low temperature range (6–90 K), experimental variations can be well fitted by a $T^{-1/2}$ law. This behavior can also be explained in the frame of the Zuppiroli model.[17] When the temperature increases, the optimized polaronic cluster size d/a for easy hopping reaches at T_l a value $(d/a)_l$ which corresponds to the minimal average size of the clusters and remains constant at higher temperatures. So the jump rate $W(d)$[17] depends only on $1/T$ above T_l. Consequently, in the low temperature range limit, σ is written as

$$\sigma = \sigma_0 \exp\left[\frac{T_0}{T}\right]^{1/2}$$

whereas, above T_l,

$$\sigma = \sigma_1 \exp\left[-\left[\frac{T_1}{T}\right]\right]$$

(Fig. 3). T_0, σ_0, T_1, and σ_1 are found to be nearly equal to 281 K, 16 S/cm, 129 K, and 10 S/cm, respectively, and T_l is about 130 K. The minimum cluster size d_l deduced from T_0 value is nearly equal to 90 Å, with $a = 7.134$ Å.

In order to explain the slight discrepancy from the $T^{-1/2}$ law found for the highly doped PVA–PPy composite, the composite nature of this compound has been invoked. In fact, the conduction in this material is limited by hopping between conducting PPy domains through thin PVA insulating barriers. Consequently, two types of conducting paths which connect the two ends of the sample have to be considered to describe the PVA–PPy experimental σ variations:

First, conduction (type 1 PPy paths) results from hopping between bipolaronic clusters and leads to a $T^{-1/2}$ law.

Second, conduction (type 2 paths) is limited mainly by fluctuation-induced tunneling through small insulating PVA barriers; in the case of the parabolic barrier approximation,[18] the electrical conductivity is written as

$$\sigma = \sigma_S \exp\left[-\left(\frac{T_1}{T + T_2}\right)\right].$$

Consequently, the overall conductance is, on average, made up of a sum of two conductances in parallel which exhibit a different temperature dependence. So the experimental variations observed on PVA–PPy are well fitted over the whole temperature range investigated with σ given by

$$\sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^{1/2}\right] + \sigma_s \exp\left[-\left(\frac{T_1}{T + T_2}\right)\right].$$

It should be emphasized that σ_0 and σ_s include a geometric factor and, consequently, σ_1 and σ_2 are only proportional to the electrical conductivities. The values of the physical parameters which give the best fit to the experimental curves have been found to be equal to 8.3 S.cm^{-1}, 607.8 K, 12.9 S.cm^{-1}, 777.7 K, and 88.8 K for σ_0, T_0, σ_s, T_1, and T_2, respectively. The results are presented in Figure 4 (log σ versus $10^3/T$).

It must be noted that the contribution of the intrinsic conduction within the bipolaronic clusters is weak, whereas those of hopping between clusters and between conducting PPy domains are of the same order of magnitude. Taking into account the geometric factors, this means that type 2 paths are likely predominant in the composite studied here.

CONCLUSIONS

To summarize, the electrical properties of differently oxidized PPy powders and a PVA–PPy composite prepared by chemical oxidation have been studied over a large temperature range. The obtained results have been interpreted on the basis of a model recently developed[17] which allows us to draw the following conclusions:

1. Measurements obtained on PPy obey a "$T^{-1/2}$" law suggested by Zuppiroli and associates[17] over the whole temperature range investigated. However, for the most-doped sample, a "T^{-1}" dependence is found in the high temperature range which can be related to the minimal average size of the clusters.

2. In the case of the composite, a relevant contribution of thermal fluctuation-assisted tunneling through isolating PVA regions has to be considered.

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