

Comparative study of electrical properties of polyaniline films and polyaniline-polystyrene blends

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Received: 20 April 1998 / Revised and Accepted: 21 December 1998

Abstract. In this paper, a simple model classically used to describe electrical behavior in conducting polymers can take into account transport properties in polyaniline doped with two different counter-ions and in polyaniline-polystyrene blends. Conduction is mainly limited by hopping or tunneling between polaronic conducting clusters. When the structural disorder is less pronounced, a metallic contribution can occur near room temperature in series with the hopping/tunneling one. This heterogeneous picture used for unblended polyaniline can be applied to explain electrical blend properties above the percolation threshold when conduction occurs among completely connected polyaniline paths. Below the percolation threshold, the model has to take into account an additional contribution due to a hopping mechanism between large disconnected segments of polyaniline. It is shown that thermoelectric power reflects essentially the metallic behavior of the conducting clusters.

PACS. 72.80.Le Polymers; organic compounds (including organic semiconductors)

1 Introduction

For several years, conducting polymers have received considerable interest for numerous researchers because they present a real interest for use in the electronic area (electronic devices [1], EMI shielding [2], power electronic protection [3], ...). Among all conducting polymers, polyaniline (PANI) seems to be the most promising material because it associates a good processability, a high electrical conductivity ($\sigma > 300$ S/cm) and a good environmental stability. Indeed, polyaniline can be solubilized in its conducting form in common solvents using an appropriate counter-ion [4,5]. Then, it is easy to fabricate conducting PANI films by casting a doped polyaniline solution onto an appropriate substrate. Furthermore, in order to ameliorate mechanical properties of these films, it is possible to blend PANI with classical polymers (polystyrene, PMMA, ...) [4,6]. Lots of materials with various properties can be synthesized using a simple process.

The transport properties can differ from one sample to another depending on preparation method, counter-ion used, sample morphology... In strongly disordered systems, the temperature dependence of electrical conductivity is generally described using a classical hopping law $\sigma = \sigma_0 \exp[-(T_0/T)^\gamma]$. For $\gamma = 1/4$, the conduction mechanism is the three dimensional variable range hopping (VRH) described by Mott [7]. For the case $\gamma = 1/2$, several models can be invoked: quasi-one-dimensional variable range hopping [8], hopping through a coulomb gap

[9], granular models [10,11]. Sometimes, a metallic behavior near room temperature (*i.e.* showing a positive temperature coefficient resistivity) is observed in rather ordered conducting polymers (like polyaniline protonated with camphor sulfonic acid) [12,13]. An heterogeneous picture is used considering "metallic islands" separated by poorly conducting barriers [13]. Another possible explanation has been proposed by some authors assuming polyaniline as a disordered metal near the metal-insulator boundary [12].

The aim of this work is mainly to compare electrical properties of doped polyaniline with different counter-ions and those of polyaniline-polystyrene (PANI-PSt) blends above the percolation threshold. All the experimental results (electrical conductivity and thermoelectric power measurements between 80 K and 300 K) can be interpreted in the frame of an heterogeneous picture of conducting polyaniline involving a dominant hopping/tunneling contribution between polaronic conducting clusters eventually in series with a quasi-one-dimensional metallic conduction contribution for blends with high weight fraction of polyaniline.

2 Experimental

Polyaniline base (PANI) has been prepared by chemical oxidation of aniline using ammonium persulfate in the presence of hydrochloric acid [14]. This partially protonated polymer was then deprotonated in an ammonia solution. Protonation of polyaniline was achieved in a

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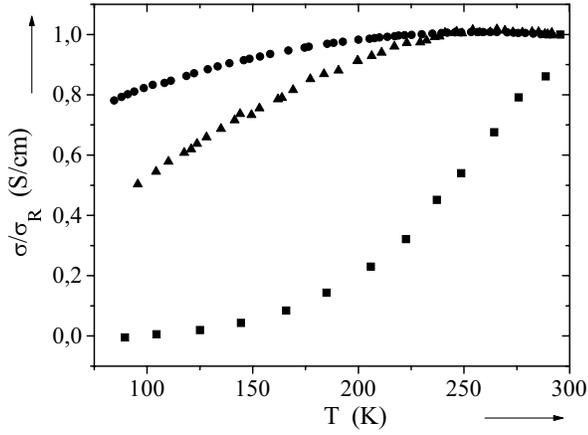


Fig. 1. Temperature dependence of the normalized electrical conductivity of unblended PANI (● PANI-CSA, ▲ PANI-DiOHP, ■ PANI-HCl).

m-cresol solution. Different counter-ions were used to simultaneously protonate and induce solubility of PANI in the solvent: the bis (2-ethyl-hexyl) hydrogen phosphate (DiOHP) and the camphor sulfonic acid (CSA). Polyaniline-polystyrene (PANI-PSt) blends were prepared by mixing a PANI-counter-ion solution with polystyrene in *m*-cresol. This mixture was casted onto a glass substrate before dried at 60 °C in neutral atmosphere for several hours. Then, the film could be peeled off from the substrate to give high quality free standing samples with thickness near 100 μm .

The experimental variations of the electrical conductivity σ was measured in the temperature range 80–300 K following the standard four probe method. The linearity of the $I(V)$ characteristic was systematically checked on a three order of magnitude current range and possible thermoelectric effects were excluded by inverting the polarity current. The thermoelectric power (TEP) was measured by using the four wire method in the temperature range 80–300 K. The samples were placed between two microheaters made of constantan wires wrapped around an aluminium oxide tube. The thermal *emfs* between the two cooper and the two constantan wires were measured simultaneously using two digital nanovoltmeters and all measurements were computer controlled [15].

3 Results and discussion

3.1 Pure doped polyaniline

The thermal variations of normalized electrical conductivity $\sigma(T)/\sigma_R$ (where σ_R is the room temperature electrical conductivity) are shown in Figure 1 for pure doped polyaniline. The positive temperature coefficient of the resistivity observed above 250 K on PANI-DiOHP and PANI-CSA samples, reveals a “metallic” character. On the contrary, PANI-HCl powder prepared by protonation of polyaniline base in aqueous 1 M HCl does not exhibit this “metallic” behavior which is in agreement with a higher

structural disorder in this material. A model based on an heterogeneous picture has been used to describe the conduction mechanisms in this type of conducting polymers [11–17].

(i) At low temperature, the thermal variations of conductivity follow the law $\sigma = \sigma_0 \exp[-(T_0/T)^{1/2}]$.

This expression has been proposed by Sheng *et al.* [18] to take into account the properties of granular metals in which conduction is limited by tunneling between small conducting grains separated by insulating barriers. It is not surprising that the electrical conductivity of conducting polymers follows the same law as several authors describe conducting polymers like “metallic” regions (sometimes crystalline) separated by amorphous or less doped regions [10–19].

Furthermore, Zuppiroli *et al.* [11] assumed that dopant counter-ions play a very active role in the formation of these conducting clusters by acting as tunneling bridges between neighboring chains and stabilizing the conducting regions. In this model, the temperature T_0 is a crucial parameter which is directly related to the clusters size d and the inter cluster width s :

$$T_0 = \frac{8U s^2}{k_B d^2} \frac{1}{1/2 + s/d}$$

where U is the repulsion energy of two electrons sitting at the distance a (monomer size). It appears that T_0 is a decreasing function of the conducting clusters size.

The charging energy E_c can be expressed as

$$E_c = 2U \frac{a}{d \left(1 + \frac{d}{2s}\right)}$$

However, if the grain size is large, the energy E_c required to remove an electron from a neutral grain and placed on a neighboring neutral grain is negligible against the thermal energy. In this case, a charge transfer by tunneling effect assisted by thermal voltage fluctuation can occur between insulating barriers and the model of fluctuation induced tunneling (FIT) described by Sheng [20] can be used. The temperature dependence of the electrical conductivity is written as

$$\sigma = \sigma'_0 \exp \left[- \left(\frac{T'_0}{T_1 + T} \right) \right]$$

T'_0 depends upon the average potential parabolic barrier height and T_1 represents the temperature for which the thermal fluctuations produce a significant contribution to the tunneling current. This relationship ($kT > E_c$) is always verified for PANI-CSA films. In this case, the structure consists of large conducting clusters with thin insulating barriers.

(ii) However, at high temperature, an additional mechanism is necessary to interpret the positive temperature coefficient resistivity. A possible mechanism which can take into account the experimental results observed on some conducting polymers is the quasi-one-dimensional

conduction along the polymer chains described by Kivelson *et al.* [21]. In this model, only the $2k_F$ component of the scattering potential is relevant for the scattering process and the conductivity expression is:

$$\sigma = \sigma_m \exp\left(\frac{T_m}{T}\right)$$

with T_m corresponding to the energy of the $2k_F$ wavevector.

To describe the thermal variations of electrical conductivity on the whole temperature range investigated, Kaiser [22] introduced a resistivity term representing highly-anisotropic metallic conduction in series with a hopping/tunneling term. The conductivity expression can be written:

$$\rho = \rho_1 \exp\left(-\frac{T_m}{T}\right) + \rho_2 \exp\left(\frac{T_0}{T_1 + T}\right)^\gamma.$$

Then, the temperature dependence of the d.c. electrical conductivity for each doped polyaniline (unblended) can be described using this expression with $\gamma = 1/2$ and $T_1 = 0$ for hopping between conducting clusters with $kT < E_c$ and $\gamma = 1$ and $T_1 \neq 0$ for fluctuation induced tunneling.

No maximum in the electrical conductivity variations is observed in PANI doped HCl ($\sigma_R \approx 3$ S/cm). The metallic term is always masked by the hopping contribution between conducting clusters and the best fit is obtained using the Zuppiroli model ($\gamma = 1/2$). This result reveals some disorder in polyaniline doped with HCl ($T_0 > 15000$ K) and is in good agreement with other experiments [8–10].

For PANI-DiOHP films, the best fit is obtained by adding the quasi-unidimensional metallic contribution to that of a hopping mechanism between conducting clusters ($\gamma = 1/2$, $T_1 = 0$ and $\rho_m \neq 0$). At low temperature, the use of the FIT model can also take into account the experimental results, the fit being slightly less good. In fact, it is difficult to discriminate between the two types of quasi exponential laws since measurements have been carried out in a narrow temperature range.

It is interesting to note that a metallic character is observed in this sample with electrical conductivity of about 16 S/cm at room temperature which is an order of magnitude lower than the minimum metallic criterion proposed by Holland *et al.* [13].

For PANI-CSA films ($\sigma_R \approx 250$ S/cm), it is also difficult to discriminate between the CELT model ($\gamma = 1/2$, $T_1 = 0$) and the FIT model ($\gamma = 1$ and $T_1 \neq 0$) at low temperature. However, the low characteristic temperature T_0 found using the CELT model ($T_{0(\text{CELT})} \approx 35$ K) plead rather for the FIT model. Large value of T_0 can be associated with large conducting clusters and thin insulating barriers between them. In this case, the charging energy is negligible against the thermal energy and the conduction process (below 250 K) is dominated by tunneling induced by thermal fluctuations. Near room temperature, the quasi-1D metallic contribution have to be take into account.

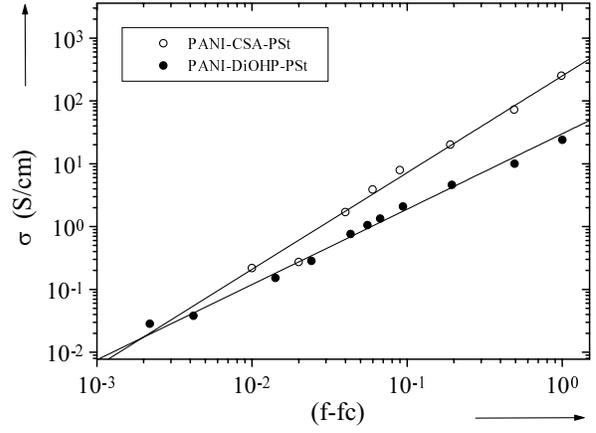


Fig. 2. Experimental variations of σ vs. $(f - f_c)$ at room temperature (log₁₀-log₁₀ plot). Solid line corresponds to $\sigma = \sigma_T |f - f_c|^t$ (f_c is the percolation threshold).

Table 1. Physical constants deduced on the basis of a $\exp[-(T_0/T)^{1/2}]$ law for the electrical conductivity variations at low temperature.

	s/d (%)	E_c (meV)
PANI-HCl (powder)	20	150
PANI-DiOHP	2.6	21
PANI-DiOHP-PSt 10%	3.1	25
PANI-DiOHP-PSt 3%	3.0	25

3.2 Polyaniline-polystyrene blends

In all studied families, the electrical conductivity is strongly dependent on the doped polyaniline content. At room temperature, the electrical conductivity systematically decreases with the decrease of the PANI weight fraction f of polyaniline in polystyrene. The experimental variations of the electrical conductivity (Fig. 2) are correctly described by the classical law of the percolation theory $\sigma = \sigma_T |f - f_c|^t$ [23]. In the case of films doped with DiOHP, the percolation threshold is near 0.6% [24], and it is less than 1% for PANI-CSA-PSt blends. These low values of the percolation threshold have already been observed in blends based on polyaniline and it has been associated to the formation of a self-assembled interfibrillar conducting network of polyaniline in the host polystyrene matrix [25].

Thermal variations of electrical conductivity of polyaniline-polystyrene blends with different weight fractions of PANI are shown in Figure 3 for films doped with DiOHP and in Figure 4 for films doped with CSA. The maximum of conductivity observed above about 250 K in pure doped polyaniline persists after dilution in the polystyrene matrix until very low weight fractions of PANI (Fig. 5) and it gradually disappears near and below the percolation threshold. Each curve can be well-fitted using the same expression as in pure doped polyaniline.

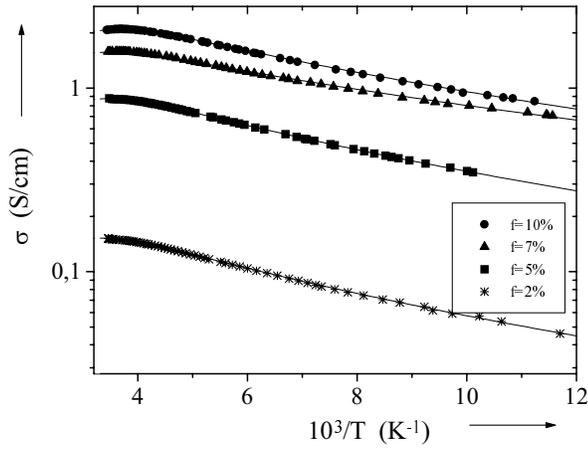


Fig. 3. Electrical conductivity *vs.* temperature on conducting PANI-DiOHP-PSt blends. The theoretical variations are drawn as solid lines.

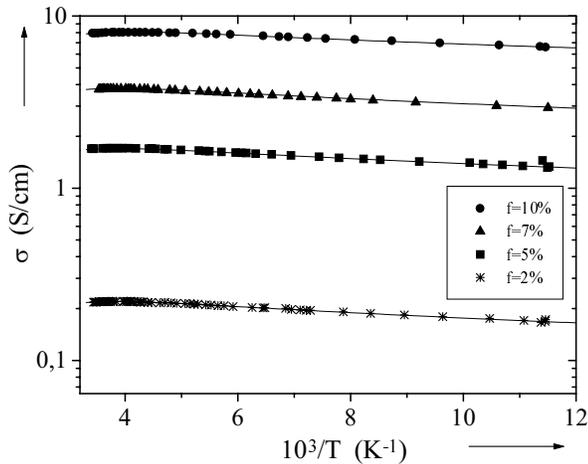


Fig. 4. Electrical conductivity *vs.* temperature on conducting PANI-CSA-PSt blends. The theoretical variations are drawn as solid lines.

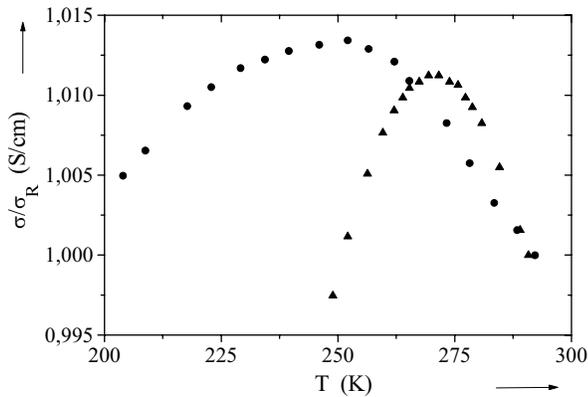


Fig. 5. Temperature dependence of the normalized electrical conductivity on PANI-PSt blends ($f = 10\%$) (● PANI-CSA-PSt, ▲ PANI-DiOHP-PSt).

3.2.1 Above the percolation threshold

For PANI-DiOHP-PSt blends, the best fit is obtained associating a quasi one dimensional metallic term with a hopping mechanism between conducting polaronic clusters ($\gamma = 1/2$). Like in unblended PANI-DiOHP, the use of the FIT model can also take into account the experimental results at low temperature and it is difficult to discriminate between the two types of quasi exponential laws since measurements have been carried out in a narrow temperature range. The CELT characteristic temperature T_0 is found to be nearly 500 K for all blends above the percolation threshold like in pure PANI-DiOHP. It must be recalled that this model has already been used to explain transport properties in PANI-DiOHP-PSt films presenting a metallic character less pronounced [24], the principal difference between the two types of samples being the method of preparation: in this work, solution concentrations and drying time have been optimized in order to increase the electrical conductivity value.

For PANI-CSA-PSt blends, it is also difficult to discriminate between the CELT model and the FIT model at low temperature. However, like in PANI-CSA, the use of the CELT model leads to weak characteristic temperature T_0 (35 K). In this case the charging energy is negligible against the thermal energy and it seems more correct to use the FIT model associated with the quasi-1D metallic model ($\gamma = 1$, $T_1 \neq 0$ and $\rho_m \neq 0$).

Table 1 summarizes some physical parameters (s/d and E_c) associated with the CELT model. The values of $s + d$, U and a have been assumed to be equal to 100 Å, 3 eV and 7 Å, respectively [19].

Near room temperature, the intrinsic metallic contribution of the conducting clusters is not negligible for all blends and it occurs in series with the hopping/tunneling contribution.

Finally, PANI blends can be described using the same heterogeneous picture as in pure doped polyaniline. Above the percolation threshold, a network of conducting paths exists which crosses over all the film. In films doped with DiOHP, the T_0 characteristic temperature seems to be few influenced by dilution. Then, in PANI blends, polyaniline fibrils are composed of many conducting clusters like in doped unblended polyaniline (Fig. 6a). The polystyrene matrix has little influence on the conduction which occurs essentially along these conducting paths.

3.2.2 Below the percolation threshold

Below the percolation threshold, the metallic contribution disappears and the use of the law

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

permits to describe the thermal variations of the electrical conductivity on all the temperature range in the two types of blend. Figure 7 shows that T_0 increases rapidly

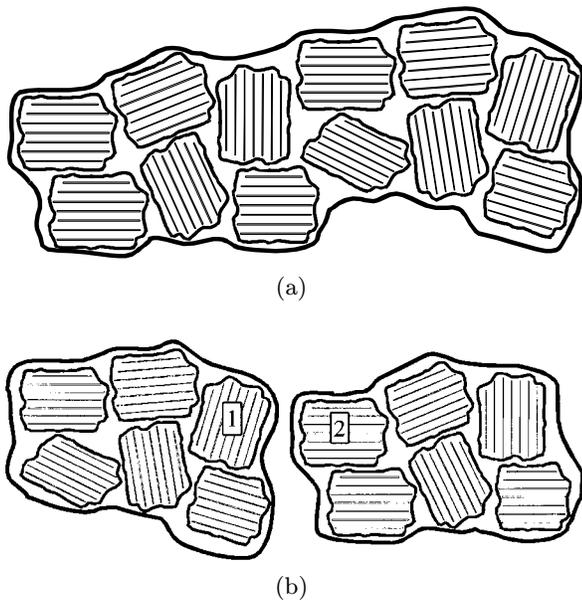


Fig. 6. Schematic view of: (a) conducting path with many polaronic clusters in polyaniline blend above the percolation threshold; (b) two conducting segments separated by a thin barrier of polystyrene in polyaniline blend below the percolation threshold. Hopping through cluster 1 and cluster 2 is the main limiting process.

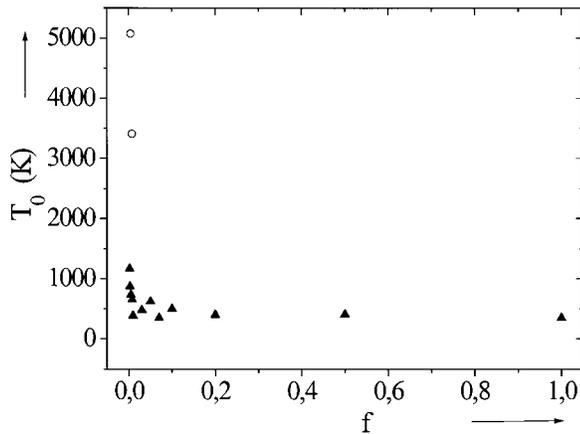
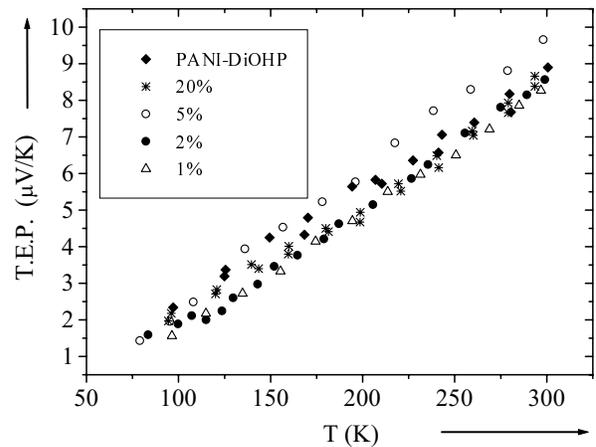
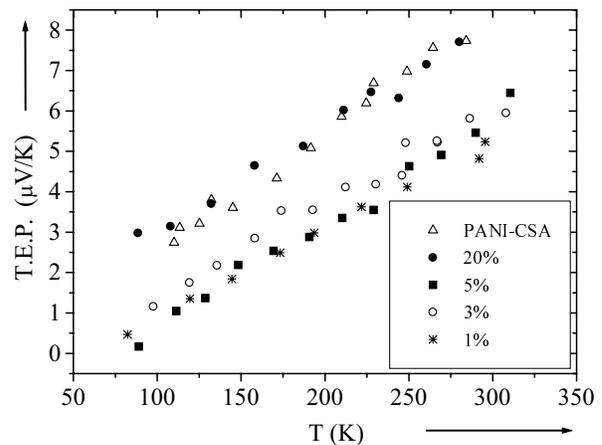


Fig. 7. T_0 variations *vs.* the weight fraction (f) of PANI-PSt blends, obtained with the CELT model (○: PANI-CSA-PSt, ▲: PANI-DiOHP-PSt).

with the decreasing of the weight fraction of polyaniline. This behavior reveals the change of geometry which occurs below the percolation threshold with the rupture of conducting paths (Fig. 6b). The high values of T_0 obtained for PANI-DiOHP-PSt and PANI-CSA-PSt blends below the percolation threshold implies high value of the charging energy and justify the use of the CELT model. Hopping/tunneling between conducting clusters in a segment of polyaniline is no longer the main limiting process: indeed, hopping between two conducting clusters through an insulating barrier of polystyrene is more difficult and



(a)



(b)

Fig. 8. Thermoelectric power S *vs.* T on: (a) conducting PANI-DiOHP films and PANI-DiOHP-PSt blends; (b) conducting PANI-CSA films and PANI-CSA-PSt blends.

mainly limits the electrical conductivity. Correlatively, the corresponding charging energy which depends upon the s/d ratio increases since the conducting cluster size d remains practically constant.

4 Thermoelectric power

Figure 8 shows thermoelectric power variations *versus* temperature between 80 K and 300 K for PANI-DiOHP films, PANI-CSA films and polyaniline-polystyrene blends above the percolation threshold. The TEP for all these samples is weak ($< 10 \mu\text{V/K}$) and positive. Experimental thermoelectric power variations are quasi linear which is usually attributed to a quasi metallic behavior. No change is observed near temperatures for which a maximum in the electrical conductivity variations versus temperature is obtained. These results can be interpreted in the framework of the heterogeneous model described previously. The thermoelectric power results from the contribution

Table 2. Parameters deduced by the fit of the thermoelectric power variations ($S = AT + B$).

	A ($\mu\text{V}/\text{K}^2$)	B ($\mu\text{V}/\text{K}$)
PANI-DiOHP	0.031	0.56
PANI-DiOHP-PSt 20%	0.031	-0.99
PANI-DiOHP-PSt 1%	0.033	-1.73
PANI-CSA	0.025	0.11
PANI-CSA-PSt 20%	0.025	0.55
PANI-CSA-PSt 1%	0.022	-1.24

of the conduction within polaronic clusters and that of hopping between these clusters. When two types of regions are connected in series, it has been shown that the thermoelectric power can be expressed as follows [26]:

$$S = \frac{\Delta T_1}{\Delta T} S_1 + \frac{\Delta T_2}{\Delta T} S_2$$

where ΔT represents the total temperature difference, ΔT_1 and ΔT_2 with $\Delta T = \Delta T_1 + \Delta T_2$ are the total temperature differences along the conducting regions and the insulating region, respectively and S_1 and S_2 represent the corresponding thermoelectric power.

According to the small value of s/d , the total temperature difference is developed essentially along the clusters ($\Delta T_1 \approx \Delta T \Rightarrow S \approx S_1$) [26,27]. Then, thermoelectric power reflects mainly the metallic behavior of conducting clusters.

In fact, a best fit is obtained using a $AT + B$ law. Table 2 shows typical values of A and B for different polyaniline films and polyaniline blends. The predominant AT term can be associated to the metallic type conduction within the conducting clusters and the correcting B term represent the small contribution of the insulating barriers.

5 Conclusion

In this paper, transport properties in polyaniline doped with different counter-ions and in polyaniline-polystyrene blends are described with the help of a simple model. The retained picture is based on a structure which results from doping heterogeneity and consists of conducting clusters separated by less doped insulating barriers. Then, conduction is limited by hopping or tunneling between these clusters depending on the cluster size. When disorder is less pronounced (in PANI-CSA for example), a metallic contribution emerges near room temperature and the quasi-one-dimensional conduction along polymer chains model fits the temperature dependence of the electrical conductivity.

Polyaniline-polystyrene blends synthesized using the codissolution method are characterized by low percolation threshold ($f_c < 1\%$). The electrical blends properties are not very influenced by the polystyrene matrix above the percolation threshold and the model used for unblended polyaniline can be applied. In this case, conduction occurs

along completely connected polyaniline paths. Below the percolation threshold, hopping conduction between large disconnected segments of PANI takes place. For all samples above the percolation threshold, the thermoelectric power reflects essentially the metallic behavior of conducting clusters and is not very affected by the hopping mechanisms.

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