

Electrical Properties of Polybithiophene–Polystyrene Composites

M. MORSLI,* A. BONNET, F. SAMIR, and S. LEFRANT†

Université de Nantes, Laboratoire de Physique des Matériaux pour l'Electronique, E.A. 1153, 2 rue de la Houssinière, 44072 Nantes cedex 03, France; and †Institut des Matériaux de Nantes, Laboratoire de Physique Cristalline, 2 rue de la Houssinière, 44072 Nantes cedex 03, France

SYNOPSIS

Conducting composites consisting of polybithiophene and based on porous crosslinked polystyrene as host polymer have been synthesized in the vicinity and above the percolation threshold by oxidative polymerization with FeCl_3 . Electrical conductivity and thermoelectric power measurements for different degrees of doping have been carried out in the temperature range 80–300 K. The electrical conductivity variations are weakly thermally activated while the thermoelectric power has metallic magnitude with positive sign and increases with temperature. Conduction mechanisms are interpreted on the basis of an hopping model involving bipolaronic clusters. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Among the electrically conducting polyheterocycles, polythiophene (PTh) exhibits several interesting properties, among which are ease of preparation procedure and relative conducting stability to atmospheric exposure.^{1,2} PTh has been prepared by both electrochemical polymerization³ and chemical polymerization,^{4,5} but the highly conducting PTh's have been obtained by the first synthesis method with conductivities in the range 10–100 S cm^{-1} . In order to improve these mechanic features such as processability and atmospheric stability, a number of methods⁶ have been suggested by combining strong insulating materials with conducting polyheterocycles.

In this article we discuss about the electrical properties of conducting polybithiophene–polystyrene (PBTh–PSt) composites chemically prepared.

EXPERIMENTAL RESULTS AND DISCUSSION

Conducting polymer composites containing PBTh have been synthesized by action of FeCl_3 solution

on porous crosslinked PSt as host polymer initially charged with 2-2'-bithiophene.⁷ The composites which are prepared according to this procedure are environmentally rather stable and reach conductivities as high as 2 S/cm at room temperature. The electrical conductivity was measured on thin sheets of lightly and heavily doped PBTh–PSt composites. The experimental dependence of the conductivity versus the reciprocal temperature was tested in temperature range 80–300 K with special care in order to ensure good temperature stability for each experimental point. The detailed description of the thermoelectric power (TEP) measurement technique was published elsewhere.⁸

The effect of the FeCl_3 /bithiophene molar ratio (y) on the conductivity of the composites (σ) is shown in Figure 1. The conductivity variations reveal the formation of an electrical network of polythiophene inside the composite and exhibit features characteristic of percolation systems. Below the percolation threshold which is found at about $y \approx 0.3$, the low conductivities must be attributed to the low connectivities among the deposited polythiophene domains. At high molar ratios of the oxidant concentration to monomer concentration, the formation of an electrical network of PTh inside the composite explain the high conductivity values.

* To whom correspondence should be addressed.

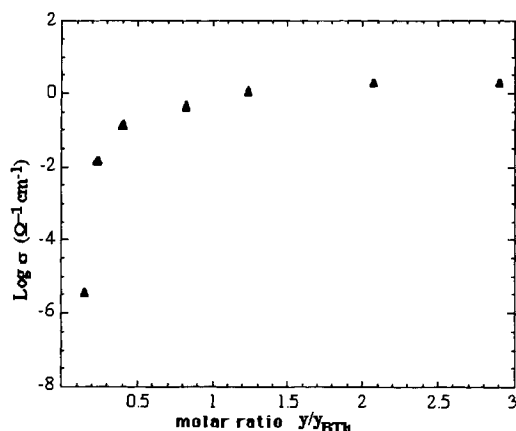


Figure 1 Experimental variations of $\log \sigma$ vs. $\text{FeCl}_3/\text{bithiophene}$ molar ratio. The percolation threshold is reached for $y_c \approx 0.36$.

The temperature dependence of the conductivity was investigated for compounds with PTh content in the vicinity and above the percolation threshold ($y = 2.08, 1.25, 0.83, 0.42, 0.25$). The experimental variations of $\log \sigma$ versus T^{-1} are presented in Figure 2. The room-temperature conductivity for all samples studied depends strongly on the doping rate and decreases from 2 S/cm for the highest polymerized sample ($y = 2.08$) to $14.5 \cdot 10^{-3}$ S/cm for the lowest polymerized sample ($y = 0.25$). The experimental variations are weakly thermally activated for all compounds. The activation energy decreases as the molar ratio y increases (nearly equal to 63 meV for the less doped composite and 17 meV for the highly doped one).

With regard to interpreting the transport properties obtained on conducting polymers, it is well known that the experimental results are often fitted in the frame of a hopping mechanism which obeys the law $\sigma = \sigma_0 \exp[-(T_0/T)^{1/\alpha}]$ where the power coefficient α may be 1, 2, 3, or 4.⁹ In this work, all experimental results have been interpreted on the basis of the model which has been developed by Bussac and Zuppiroli.^{10,11} This model involves transverse bipolarons within polaronic clusters and is based on the existence of an optimized T -dependent size d of the polaronic cluster for easy hopping. The electrical conductivity obeys a $T^{-1/2}$ law: $\sigma \sim \exp[-(T_0/T)^{1/2}]$. This model has been confirmed by electrical conductivity and magnetoresistance measurements carried out on polypyrrole doped with the sulfonate centers of a polyelectrolyte polymer. The term $K_B(T_0T)^{1/2}$ where K_B designates the Boltzmann constant is the hopping energy between clusters. T_0 reaches high value when the doping level decreases and is written as

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

where U is the repulsion energy of two electrons sitting at a distance a equal to the size of the monomer. The term δ is the average distance between dopants within clusters and $\bar{\delta}$ is the average distance between dopants in the sample when a uniform distribution without clusters is assumed.

The theoretical results obtained on PBTh-PSt composites can be summarized as follows:

1. For the highest doped samples ($y = 2.08$ and 1.25), a careful exam of the $\log \sigma$ versus T^{-1} dependence displays a quasi-linear dependence in the high temperature range limit (respectively 140–300 K and 160–300 K), whereas in the low temperature range (respectively 80–135 K and 80–140 K), experimental variations can be well fitted by a $T^{-1/2}$ dependence. This behavior can be explained in the frame of the Zuppiroli model. When the temperature increases, the optimized size d/a of polaronic cluster for easy hopping reaches at T_1 a value $(d/a)_1$ which corresponds to the minimal average size of the clusters and remains constant at higher temperatures. So, the jump rate $W(d)$ ¹¹ depends only on $1/T$ above T_1 . Consequently, in the low temperature range limit, σ , is written as $\sigma = \sigma_0 \exp - (T_0/T)^{1/2}$, whereas $\sigma = \sigma_1 \exp - (T_1/T)$ above T_1 where $K_B T_1$ is the hopping energy between clusters. The terms $T_0, \sigma_0, T_1, \sigma_1$ are found to be nearly equal to 507 K, 6.27 S/cm, 198.8 K, 3.74 S/cm and 255 K, 2.29 S/cm, 174.4 K, 2.02 S/cm

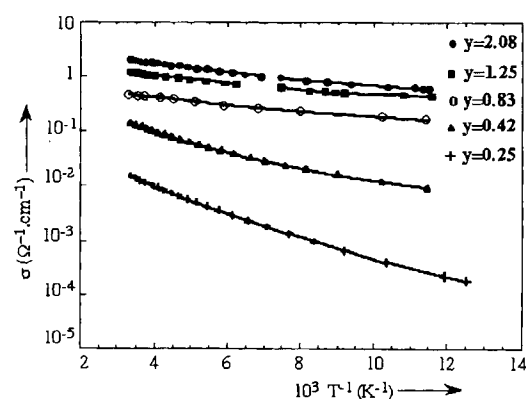


Figure 2 The log of the electrical conductivity vs. T^{-1} plots obtained on conducting PBTh-PSt composites with different dopant concentrations. The theoretical variations are drawn in full line.

Table I Physical Parameters Deduced by the Fit for the Two Less-Doped PBTh-PSt Composites

	$\sigma_s \exp\left(-\frac{T'_1}{T + T'_2}\right)$			$\sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^{1/2}\right]$	
	σ_s (S cm ⁻¹)	T'_1 (K)	T'_2 (K)	σ_0 (S cm ⁻¹)	T_0 (K)
$y = 0.42$	0.19	420	47	18	8570
$y = 0.25$	0.011	447	8.2	2.1	7880

cm, respectively for $y = 2.08$ and $y = 1.25$, whereas the minimum clusters size ratio $(d/a)_l$ is found to be nearly equal to 12.5 and 12.1. The limit temperature T_l is found in the vicinity of 140 and 150 K, respectively, for $y = 2.08$ and $y = 1.25$.

- In the case of the medium compound ($y = 0.83$), the data are well fitted with $\alpha = 2$ in the all temperature range investigated. The limit temperature T_l exists but its value is higher than the temperature reached in this work. T_0 and σ_0 are found to be nearly equal to 503.8 K and 1.64 S/cm, respectively.
- A slight discrepancy from the $T^{-1/2}$ law is found for the lower polythiophene contents ($y = 0.42$ and 0.25). In fact, it must be taken into account the composite nature of the material studied. Two predominant conduction mechanisms are assumed to be present: hopping between polaronic clusters in conducting polymer domains and hopping between conducting polymer domains separated by thin insulating polystyrene barriers. So, two types of conducting paths must be considered in the bulk

of the material:

The first ones result from an electrical network of polythiophene which connects one end of the sample to the other and leads to a $T^{-1/2}$ law.

For the second type paths, the conduction is mainly limited by the existence of thin insulating polystyrene barriers. The electrical conductivity results from fluctuation-induced tunneling.¹² It is written as $\sigma = \sigma_s \exp[-(T'_1/T + T'_2)]$ according to the parabolic barrier approximation where the parameters T'_1 and T'_2 depend upon the shape of the barrier in the presence of an electric field, the electric field which cancels the maximum value of the potential, the tunneling constant, and the tunnel junction volume.¹³

Consequently, the overall conductance is on the average made up of a sum of two conductances in parallel which exhibit a different temperature dependence. So, the experimental variations observed on the lowest doped compounds are well fitted on the whole temperature range investigated with σ given by $\sigma_0 \exp[-(T_0/T)^{1/2}] + \sigma_s \exp[-(T'_1/T + T'_2)]$. It should be emphasized that σ_0 and σ_s include a geometrical factor and, consequently, the two terms are only proportional to the electrical conductivities. The values of the physical parameters which give the best fit to the experimental curves have been collected in Table I.

Thermoelectric power measurements show that the TEP is positive, very low, and varies quasi-linearly with temperature (Fig. 3). At room temperature, the TEP decreases from 32.5 $\mu\text{V}/\text{K}$ to 10.7 $\mu\text{V}/\text{K}$, respectively for the less doped ($y = 0.25$) and the highest doped sample ($y = 2.08$).

There is a strong contrast between the behavior of thermoelectric power which is similar to a metallic behavior and the characteristically nonmetallic behavior of the electrical conductivity. This apparently conflicting behavior has also been seen in highly

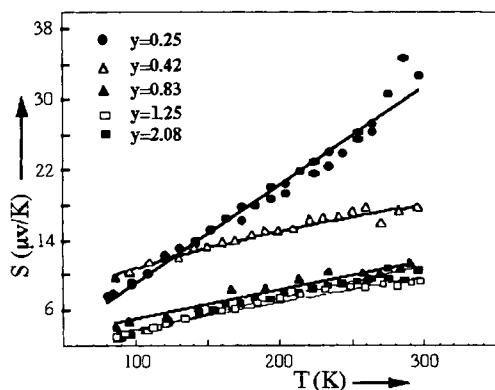


Figure 3 Thermoelectric power variations vs. temperature obtained on conducting PBTh-PSt composites with different dopant concentrations. The theoretical variations are drawn in full line.

Table II Parameters Deduced by the Fit on the Basis of an $AT + B$ Law for Thermoelectric Power Variations

Samples	$S = AT + B$	
	A ($\mu\text{V K}^{-2}$)	B ($\mu\text{V K}^{-1}$)
$y = 2.08$	0.037	1.39
$y = 1.25$	0.032	1.71
$y = 0.83$	0.033	2.97
$y = 0.42$	0.037	8.49
$y = 0.25$	0.108	0.09

doped polyacetylene¹⁴ and in polyvinyl alcohol-poly pyrrole composites,¹⁵ with resistivity being dominated by insulating barriers and thermopower by metallic regions between the barriers.

The experimental curves have been fitted on the basis of an $AT + B$ law where the "polaronic" constant B term¹⁶ is associated to hopping mechanisms between conducting clusters and to tunneling between conducting domains. The AT term is related to the "metallic" conduction within the clusters. It is found to be predominant because thermopower is determined by the thermal gradient rather than the electric potential gradient and, consequently, is less affected by thin electrical barriers.

The parameters which have been deduced by the fit are given in Table II.

CONCLUSION

It has been shown that the transport properties in conducting PSt-PBTh composites chemically polymerized are governed by hopping mechanisms. A model involving transverse bipolarons within polaronic clusters is considered for which hopping between bipolaronic clusters is the dominantly contributing mechanism to the electrical conductivity. The contribution of fluctuation-induced tunneling through thin insulating polystyrene barriers is required in order to fit the less doped

composites. The thermoelectric power of the PSt-PBTh- FeCl_3 composite remains generally similar to that in metals, with a tendency to increase in magnitude when the molar ratio y decreases. It is assumed that the TEP results essentially reflect the "metallic" conduction mechanisms within the clusters.

REFERENCES

1. G. Tourillon and F. Garnier, *J. Electroanal. Chem.*, **135**, 173 (1982).
2. J. E. Österholm, P. Passiniemi, H. Isotalo, and H. Stubb, *Synth. Met.*, **18**, 213 (1987).
3. Proc. Int. Conf. Physics and Chemistry Low Dimensional Synth. Met., Abano Terme, Italy, *Mol. Cryst. Liq. Cryst.*, **118**, 227 (1985).
4. M. B. Inoue, E. F. Velazquez, and M. Inoue, *Synth. Met.*, **24**, 223 (1988).
5. K. Kobayashi, J. Chen, T.-C. Chung, F. Moraes, A. J. Heeger, and F. Wudl, *Synthetic Metals*, **9**, 77 (1984).
6. J. S. Park and E. Ruckenstein, *J. Electronic Mater.*, **21**, 205 (1992).
7. F. Samir, M. Morsli, A. Bonnet, A. Conan, and S. Lefrant, *J. Phys. IV, C7*, **3**, 1565 (1993).
8. A. Bonnet, P. Said, and A. Conan, *Rev. Phys. Appl.*, **17**, 701 (1982).
9. A. L. Efros and B. I. Schklovskij, in *Electron Interaction in Disordered Systems*, A. L. Efros and M. Pollak, Eds., Elsevier Science Publishers, New York, 1985.
10. M. N. Bussac and L. Zuppiroli, *Phys. Rev. B*, **47**, 5493 (1993).
11. L. Zuppiroli, M. N. Bussac, S. Paschen, O. Chauvet, and L. Forros, *Phys. Rev. B.*, **50**, 5196 (1994).
12. P. Sheng, B. Abeles, and Y. Arie, *Phys. Rev. Lett.*, **31**, 44 (1973).
13. P. Sheng, *Phys. Rev. B*, **21**, 2180 (1980).
14. A. B. Kaiser, *Synth. Met.*, **45**, 183 (1991).
15. M. Makhlouki, M. Morsli, A. Bonnet, A. Conan, A. Pron, and S. Lefrant, *J. Appl. Polym. Sci.*, **99**, (3) 443 (1992).
16. N. F. Mott and E. J. A. Davis, *Electronic Processes in Non Crystalline Materials*, 2nd Edition Clarendon Press, Oxford, 1979.

Received August 3, 1995

Accepted November 19, 1995