

The routes towards three-dimensional conducting polymers: 2. Transport properties of fully conjugated gels of poly(3-*n*-octylthiophene)

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The conductivity and the thermoelectric power of fully conjugated networks of poly(3-*n*-octylthiophene) have been measured as a function of the temperature between 15 and 300 K. Despite the interchain conjugated reticulation the conduction process is still governed by hopping. The data are in good agreement with a model of inter-cluster hopping conduction. The cluster size is discussed as a function of the reticulation ratio. It is pointed out that the presence of the reticulation points gives rise to specific properties, in particular the intrinsic intra-cluster conductivity is enhanced as compared to that of poly(3-*n*-octylthiophene). © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

We have previously reported the preparation of four series of conducting networks (or 'gels') obtained by reticulating (with different reticulation ratios) poly(3-*n*-octylthiophene) (POT) chains¹, respectively with four different fully conjugated reticulation points (also prepared and characterized^{2,3}). The present paper deals with the transport properties of one series of these gels.

Transport properties of conducting polymers, which are commonly one-dimensional, have been extensively studied. The macroscopic conductivity (σ) is generally assumed to result from hopping processes except in special structures, such as oriented polyacetylene and polyaniline^{4–7}. The very nature of the hopping conduction depends on the structure of the material. It should be noted that various parameters are important in determining the conduction process, including the preparation method.

Several hopping models have been investigated in the literature, leading generally to the same temperature dependence, expressed as:

$$\sigma = \sigma_0 \exp[-(T_0/T)^\alpha] \quad (1)$$

where exponent α is model dependent. Various values for α have been found in the literature: $1/2^{8–12}$, $3/7^{13}$, $1/3^{14}$, $1/4^{15}$, 0.35^{16} , 0.69^{17} or 1^{18} . It is noteworthy that a same α value may be obtained by different models, i.e. by different microscopic pictures of the transport behaviour. To be able to discriminate between

different possible models complementary transport and structural studies may be necessary. Whatever the conduction process, it is a general rule that the conductivity is enhanced by three-dimensional ordering transport properties has been given by MacCullough *et al.*¹⁹ with poly(3-*n*-alkylthiophenes). These authors prepared regioregular structures, which present much higher conductivities than their non-regioregular analogues. For example non-regioregular, and regioregular polys-(dodecylthiophene) exhibited conductivity of 20 and 1000 S cm⁻¹, respectively. Such an increase of conductivity cannot be explained only by a larger delocalization length along the main chains (because of the minimization of the steric hindrance between lateral alkyl groups), but also by a self-ordered three-dimensional structure resulting from the regular disposition of the alkyl groups. It seems clear that not only the local but also the three-dimensional structure have to be controlled in conducting polymers.

In preparing three-dimensional networks of fully conjugated structures the basic idea was to explore possible new routes for conduction at the nanoscopic level, such as anomalous diffusion expected for a fractal network, and which gives rise to a specific frequency dependence of the conductivity²⁰. Note that the conductivity of gels has been theoretically studied by de Gennes in the framework of a very specific model²¹.

EXPERIMENTAL

Selected compound and doping

The selected compound was obtained by reticulation of poly(3-*n*-octylthiophene) chains with

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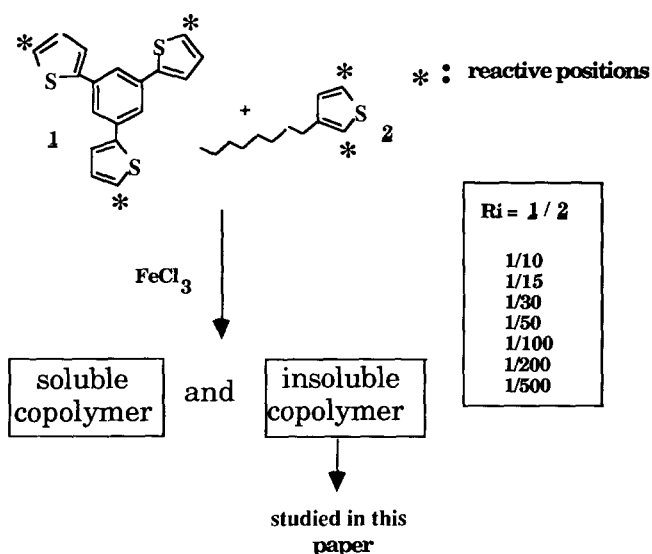


Figure 1 The studied series of copolymer networks

different trithienylbenzenes. We have prepared four series of non-regioregular networks which have been compared with the non-regioregular POT¹. In the present paper we report results obtained with one of the series of insoluble networks obtained by oxidative copolymerization of tri(2'-thienyl)-1,3,5-benzene used as reticulation points, with 3-*n*-octylthiophene (Figure 1). Different initial molar ratios, R_i , have been used, with $R_i = [\text{tri}(2'\text{-thienyl})\text{-}1,3,5\text{-benzene}]_1 / [3\text{-}n\text{-octylthiophene}]_2$.

Two methods were used for doping.

Low doping level. A total of 6 ml of a 3.4×10^{-3} M solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in nitromethane was added to 40 mg of copolymer or POT, respectively, swelled or dissolved (as far as POT is concerned) in 8 ml of chloroform. The sample was kept at room temperature without stirring for 60 h. The doped samples were then washed with nitromethane, dried under vacuum at room temperature and reweighed in order to determine the dopant uptake. Because of the uncertainty arising from the different operations we can only say that the molar doping levels were around 10%.

High doping level. The doping route was the same as the previous one, with the changes as follows: (1) the solution of FeCl_3 was 1 M instead of 3.4×10^{-3} M; (2) only 2 ml of chloroform were used for swelling, instead of 8 ml; and (3) the doped samples were washed with acetonitrile. The molar doping levels were approximately equal to 20%.

D.c. room temperature conductivity measurements

Doped polymers were pressed as pellets, 7 mm diameter and ≈ 0.5 mm thick. The room temperature conductivity was measured by the collinear four-point probe method²².

Variable (low) temperature d.c. conductivity measurements

Each doped polymer pellet was cut in order to get a sample of typical size $8 \times 5 \times 0.5$ mm³ which was mechanically pressed on four parallel gold wires. The

d.c. current was supplied by a Keithley 220 current source and two Keithley 617 programmed electrometers (with an input impedance of 10^{14} Ω) were used to measure the voltage drop between the inner contacts. The measured conductivity remained constant as the current density was varied over several decades. Possible thermoelectric effects were avoided by permuting the current polarities.

The low temperature measurements were performed in a Cryostat (Oxford Instruments) in the range 15–300 K. The measuring cell was placed into a closed chamber filled with a low pressure of He as exchange gas. The temperature of the cryostat was controlled and regulated using a computer-driven Oxford temperature controller. The sample temperature was measured using a calibrated platinum resistor within the range 300–40 K or a calibrated Carbon Glass resistor in the range 40–15 K.

Thermoelectric power

The thermoelectric power (S) measurements were performed as a function of temperature T using a slowly varying alternating temperature gradient ΔT (method first described by Chaikin and Kwak²³) between 35 K and 300 K. The temperature gradient ΔT was created between two electrically isolated copper blocks (placed upon a copper heat sink) between which the sample was held. The temperature gradient was measured with a Constantan/Cu thermocouple. It never exceeded 0.5 K in order to get a linear response of the sample/Cu thermocouple as a function of the Constantan/Cu voltage. The average temperature T was measured with a carbon-glass, or platinum (depending on the temperature range), resistance sensor, mounted in the heat sink. The temperature being constant, the slope of the linear evolution of the voltage of the sample/Cu thermocouple as a function of the one of the Constantan/Cu thermocouple was equal to the ratio

$$\frac{S(T) - S_{\text{Cu}}(T)}{S_{\text{constantan}}(T) - S_{\text{Cu}}(T)}$$

From the difference $S_{\text{constantan}} - S_{\text{Cu}}$ given in the literature, we could obtain the thermoelectric power of the sample $S(T)$ assuming a linear variation of $S_{\text{Cu}}(T)$ (room temperature value of $1.6 \mu\text{VK}^{-1}$ and $S_{\text{Cu}}(0) = 0 \mu\text{VK}^{-1}$).

RESULTS AND DISCUSSION

Room temperature d.c. conductivity

The room temperature conductivities, σ_{RT} , of the gels are not very different from those found for POT doped in the same way. Figures 2a and b present σ_{RT} versus the initial reticulation ratio R_i for low and high doping levels, respectively. We have performed different measurements on the same pellet, varying the current density in so far as no heating effects were observed and measurements on different pellets corresponding to the same initial ratio R_i . The data thus obtained show that the relative uncertainty on the conductivity values is never higher than 5%. In both cases, σ_{RT} presents a maximum for $R_i = 1/100$. It is noteworthy that $\sigma_{\text{RT}}(R_i = 1/100)$ is higher than σ_{RT} measured in POT ($R_i = 0$) prepared and doped in the same way. We stress the fact that the other series of networks related to other

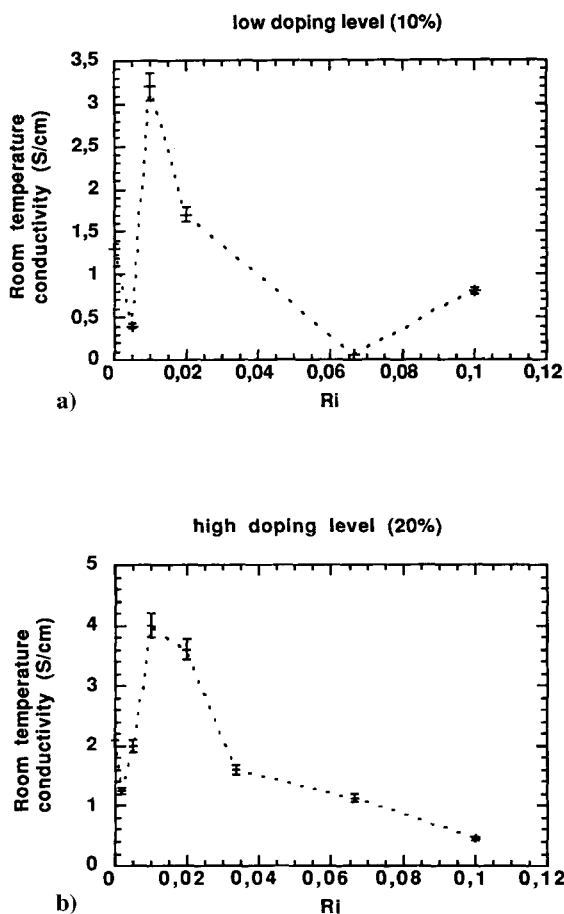


Figure 2 Room temperature d.c. conductivity as a function of the initial reticulation ratio R_i with (a) a low molar doping level (10%); (b) a high molar doping level (20%). The estimated relative uncertainty on the conductivity values is equal to 5%

reticulation points display similar maximum in the data of σ_{RT} versus R_i .

Conductivity as a function of temperature

Experimental results. We observe that the conductivity is an increasing function of temperature (within the range 15–300 K) which is not compatible with a metallic behaviour. Taking into account the experimental uncertainty on the conductivity values (lower than 5%), none of the plots of $\ln(\sigma/\sigma_{RT})$ as a function of $1/T^\alpha$ with α equal to the common values reported in the literature and summarized in the Introduction can be fitted linearly except those corresponding to $\alpha = 1/2$ and $\alpha = 3/7$. We shall see in the section dealing with the discrimination between the different models that the one related to $\alpha = 3/7$ has to be ruled out in our case. Therefore, we report the experimental data (in reduced units) for the other compounds in Figures 3a and b and Figure 4 for low and high doping level respectively plotting $\ln(\sigma/\sigma_{RT})$ as a function of $1/\sqrt{T}$. The linear evolution in each case shows that:

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

As suggested by Yoon *et al.*²⁴, an alternative way to determine the exponent α of the hopping law (equation (1)) consists in calculating the reduced activation energy:

$$W(T) = T \frac{d \ln(\sigma(T))}{dT}$$

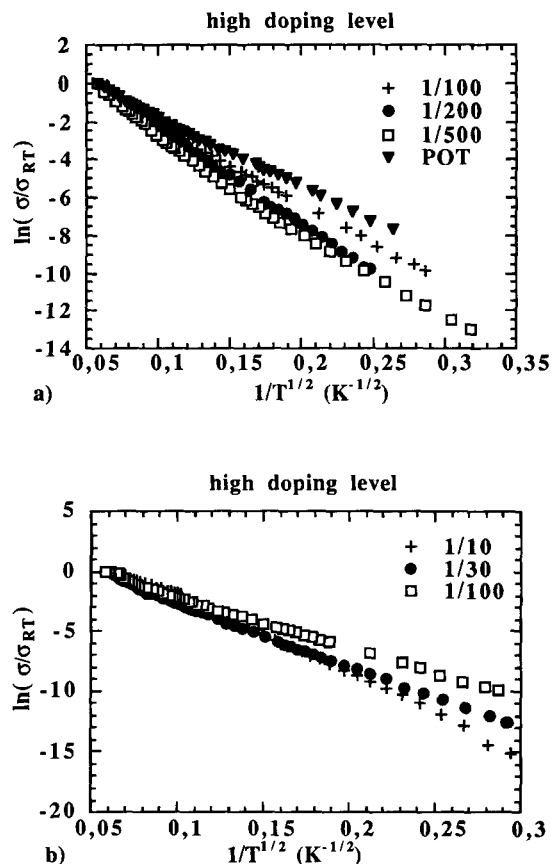


Figure 3 Logarithm of the ratio of the conductivity at temperature T , σ , to the conductivity σ_{RT} at room temperature, versus $1/\sqrt{T}$ (a) for POT and for the networks with R_i equal to, respectively, 1/500, 1/200 and 1/100 (high doping level (20%)); (b) for the networks with R_i equal to, respectively, 1/100, 1/30 and 1/10 (high doping level (20%)). The estimated relative uncertainty on the conductivity values is equal to 5%

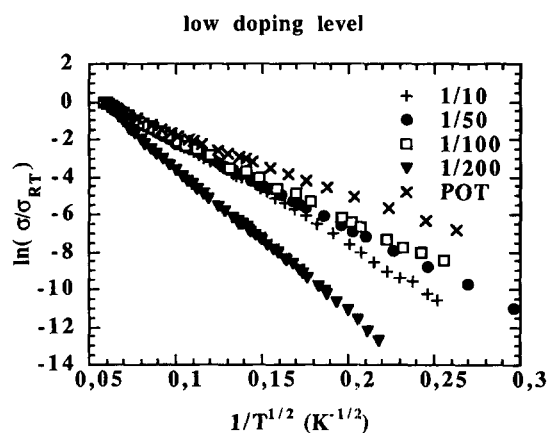


Figure 4 Logarithm of the ratio of the conductivity at temperature T , σ , to the conductivity σ_{RT} at room temperature, versus $1/\sqrt{T}$, for POT and for the networks with R_i respectively equal to 1/200, 1/100, 1/50, 1/10 (low doping level, 10%)

From equation (1), we obtain:

$$\ln W(T) = A - \alpha \ln T$$

where $A = \alpha \ln(T_0) + \ln(\alpha)$. For example, Figure 5 reports the variation of $\ln(W)$ versus $\ln(T)$ for the network with the initial reticulation ratio $R_i = 1/200$.

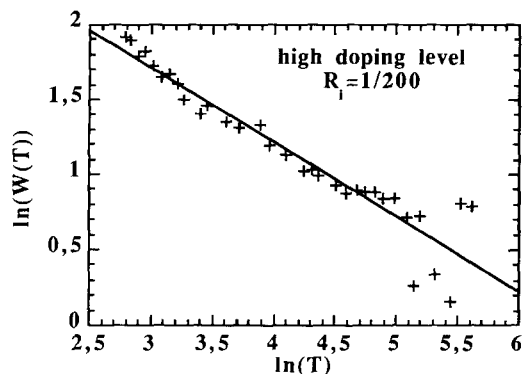


Figure 5 Logarithm of the reduced activation energy W versus $\ln(T)$ for the network with the initial reticulation ratio $R_i = 1/200$

This variation is linear and the best fit leads to an estimated value for α of 0.48 ± 0.05 . Despite the dispersion observed above 250 K, the only valid fits related to the exponents reported in the literature are obtained with $\alpha = 1/2$ and $3/7$. The dispersion can be accounted for by a larger sampling interval above 250 K or (and) by the fact that the former hopping law (equation (1)) is based on the Miller and Abrahams one phonon transition rate which is valid in the low temperature region. Multiphonon processes are expected for high temperatures²⁵.

The parameter T_0 has been determined as a function of the initial reticulation ratio R_i . The data are presented in Figures 6a and b for high (20%) and low (10%) doping levels, respectively. The absolute uncertainty on the fitting parameter $T_0(\Delta T_0)$ has been estimated in each case and never exceeds $\Delta T_0 \approx \pm 100$ K. It turns out that a maximum occurs for $R_i = 1/100$, whatever the doping level. We note that the room temperature d.c. conductivity also presents a maximum for the same value of R_i . The T_0 values are in the ranges 1880–6040 K at low doping level and 1730–3340 K at high doping level. These values are similar to those reported in the literature^{9,26}.

Discussion: discrimination between various models. The observed temperature dependence of the conductivity (equation (2)) is suggestive of a hopping process. To our knowledge, the four models listed below lead to such a temperature dependence.

Model 1: quasi one-dimensional variable range hopping (homogeneous material). In the quasi one-dimensional variable range hopping model of Nakmedov *et al.*⁸, the polymer is regarded as homogeneous and made up of weakly coupled parallel chains. The one-dimensional feature of the structure is expected to prevail on the disorder and to determine the macroscopic properties. The intrachain diffusion rate is much higher than the interchain diffusion rate. This model is not applicable to a system exhibiting strong polaronic features and neglects Coulomb interactions. Wang *et al.*⁸ have used such an approach to explain their conductivity and thermopower data in polyaniline (PANI) and poly(*o*-toluidine) (POTol). They found that the higher localization in POTol was due to a weaker interchain coupling resulting from greater interchain disorder and from larger interchain separation because of the presence of the methyl groups.

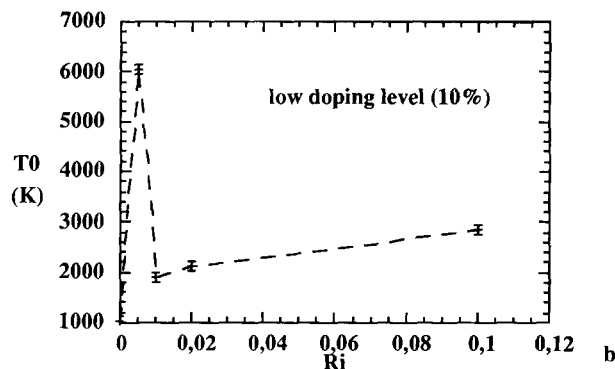
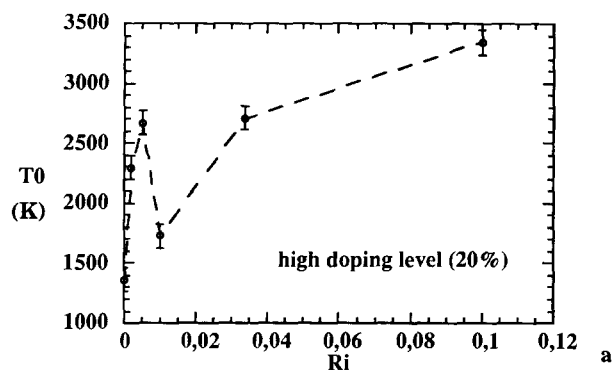


Figure 6 Variation of the parameter T_0 with the reticulation ratio R_i (a) for the high doping level (20%); (b) for the low doping level (10%). The estimated uncertainty on the T_0 values never exceeds ± 100 K

Within the framework of this model, the parameter T_0 is given by:

$$T_0 = \frac{8\gamma}{g(E_f)k}$$

where γ is the inverse of the longitudinal localization length, $g(E_f)$ the density of states at the Fermi level and k is the Boltzmann constant. We have seen that T_0 varies by one order of magnitude for the studied networks. If we assume that the density of states at the Fermi level $g(E_f)$ is constant for the gels with a given doping level, that implies that γ should have varied by nearly one order of magnitude. Such a variation seems unlikely. For this reason we rule out model 1.

Model 2: Coulomb interactions controlled hoppings (homogeneous material). The value $1/2$ of the exponent α is also expected when the conduction mechanism is controlled by Coulomb interactions as shown by Efros and Shklovskii¹². The Coulomb interactions create a gap in the density of states that tends towards zero in the same way as the square of the energy E (the Fermi level being taken as the reference). This model is relevant only at very low temperatures and the conductivity is expected to exhibit a smooth crossover to the Mott behaviour at higher temperatures ($\alpha = 1/4$)^{24,27}. For our networks, the temperature dependence of the conductivity was well fitted with $\alpha = 1/2$ from 15 K up to the room temperature. Moreover, within the framework of the Efros–Shklovskii model, the localization length is proportional to $1/T_0$ and it should therefore vary by nearly one order of magnitude. Such a variation

seems to us unlikely, and we also rule out the Efros–Shklovskii model.

Model 3: hoppings restricted to a fractal sublattice (homogeneous material). For systems not too far from the percolation threshold, variable range hopping models with motion restricted to a fractal sublattice lead to $\alpha = 3/7$, a value which is difficult to distinguish experimentally from $1/2^{28}$. These models are based on the superlocalization property of the wave function and they neglect Coulomb interactions. We believe that in conducting polymers electron–electron interactions cannot be neglected. Moreover, the classical Mott's exponent $1/4$ should be recovered in the low temperature range. In our data no crossover to an exponent $1/4$ is observed. Thus we do not retain this model.

Model 4: conducting islands (heterogeneous material). The model proposed by Zuppiroli *et al.*¹⁰ seems appropriate to account for the data. It is inspired by the work of Sheng *et al.*¹¹ on granular metals and extended to the case where the grains are not metallic. It takes into account the disorder present in the polymer rather than the quasi one-dimensional structure. Conduction is supposed to proceed by tunnelling between small conducting clusters separated by insulating barriers. The conducting clusters are assumed to be highly doped polaronic islands generated by heterogeneities in the doping distribution. They may also be regarded as more ordered and crystalline grains or regions where the interchain transfer is easier. The prefactor σ_0 is considered as temperature independent in a first approximation. The parameter T_0 is given by:

$$T_0 = \frac{8U}{k} \times \frac{s^2}{d^2} \times \frac{1}{1/2 + s/d} \quad (3)$$

where d is the average diameter of the clusters, s the average distance between them, and U the on-site Coulomb repulsion of a few eV (estimated from electron spin resonance (e.s.r.) observation). The electronic transport through the sample is characterized by the charging energy E_c between the conducting clusters, that is, the electrostatic energy required to create a positive–negative charged pair of grains. It is expressed as follows:

$$E_c = \frac{2Ua}{d(1 + d/2s)} \quad (4)$$

where a is the monomer size. In the following we have taken $a = 5 \text{ \AA}$. The model applies to cluster sizes that are small enough to allow E_c to be significant with regard to kT . In order to obtain the average diameter of the conducting islands from T_0 , we have assumed that $U = 0.5 \text{ eV}$ and that $s + d$ was constant and equal to the mean diameter of the crystalline islands obtained from X-ray diffraction studies on doped samples (we have observed 50 \AA). Actually, our interpretation is only based on the evolution of T_0 with R_i and the variation of the diameter d of the conducting clusters with R_i (see Figure 7) is, in fact, only another illustration of this experimental result. This variation displays a maximum for the specific reticulation ratio $R_i = 1/100$ for both doping levels.

Transport properties: copolymer networks versus POT. It has been observed that, at a constant doping level,

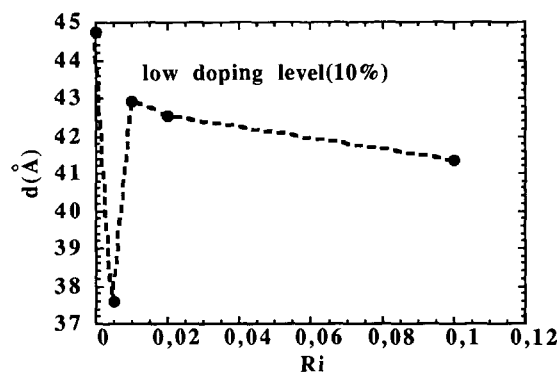


Figure 7 Variation of the conducting cluster diameter deduced from equation (3) (with the assumption that $s + d = 50 \text{ \AA}$ and $U = 0.5 \text{ eV}$) as a function of R_i (low doping levels (10%))

whatever its value, the d.c. conductivity of some polymers is higher than that of POT. Conversely, the T_0 value for POT is always higher than for the copolymers. This implies that the copolymer prefactor σ_0 is higher than the POT σ_0 (at least for the copolymers in which the room temperature d.c. conductivity is higher than that of POT). This result could be explained in two ways:

1. The prefactor σ_0 arises from the pre-exponential factor of the Miller and Abrahams transition rate^{29,30}. It is related to the electron–phonon coupling constant and therefore higher σ_0 values in some networks could result from weaker electron–phonon coupling and thus from higher delocalization volume, that means a larger conducting cluster size^{10–25} compared with the one of POT. However, we have shown that the conducting cluster size was always smaller in the networks than in POT.
2. σ_0 reflects the intrinsic conductivity within the conducting cluster. Therefore, a higher value of σ_0 for some of the networks could be explained in terms of better intracluster conductivity in the copolymers than in POT.

Thermopower

Experimental results. The thermopower temperature dependences of POT and of the copolymer networks with an initial reticulation ratio respectively equal to $R_i = 1/15$, $1/100$, $1/500$ and with a high doping level (20%) are shown in Figures 8a and b. The room temperature thermopower values are of the order of $50 \mu\text{V K}^{-1}$.

For the copolymer networks the data are well described in the whole temperature range (35–300 K) with a linear fit $S(T) = AT$. Let us now consider the variation of the slope A with R_i : we observe a minimum ($A = 0.145 \pm 0.005$) for the specific initial reticulation ratio $R_i = 1/100$, which is also related to the maximum in the room temperature conductivity. For the other reticulation ratios, $R_i = 1/500$ and $R_i = 1/15$, this slope is significantly higher than for $R_i = 1/100$ ($A = 0.154 \pm 0.005$ and $A = 0.169 \pm 0.005$ respectively). Such a decrease of the slope A of the thermopower with increasing the conductivity has already been observed^{31,32}.

A linear dependence of S versus T is also observed for POT. However, the slope in the case of POT is higher than for the copolymer networks.

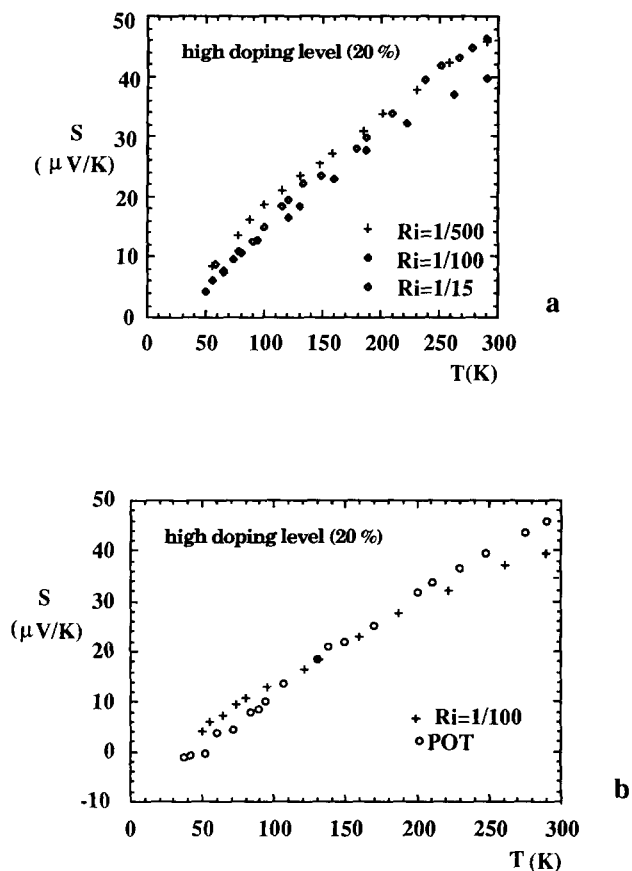


Figure 8 Temperature dependence of the thermoelectric power of the networks (high doping level (20%)) with (a) $R_i = 1/500$, $1/100$ and $1/15$; (b) $R_i = 1/100$ and $R_i = 0$ (POT)

Copolymer network results. The linear dependence of the thermopower with temperature could be attributed to a disordered homogeneous system with a finite density of states at the Fermi energy and tunnelling between states at the Fermi energy, as proposed for highly conducting polyacetylene^{33,34}. In this case, the following formula would apply³⁵:

$$S = -\frac{k^2 \pi^2}{3q} T \left| \frac{d \ln \sigma(E)}{dE} \right|_{E_f} \quad (5)$$

where q is the charge of the carrier. However, such a model would imply a metallic behaviour, which is not consistent with the observed activated temperature dependence of the conductivity. So, the thermopower data have to be interpreted in terms of a hopping model. Consistent with the conductivity data, the conducting island model should be considered.

Although there are no exact calculations of the thermopower in the case of conducting islands, the variation of S as a function of T can be predicted by using the Kaiser's work³¹. The total thermopower can be considered as the superimposition of two contributions corresponding to (1) the conducting grains and to (2) the insulating barriers. In the very simple case where the two types of regions are in series along the thermal gradient, the thermopower can be expressed as the sum of two parts:

$$S = \frac{\Delta T_c}{\Delta T} S_c + \frac{\Delta T_b}{\Delta T} S_b \quad (6)$$

where S_c and S_b are, respectively, the thermopower of

the conducting cluster and of the intercluster insulating barrier. ΔT_c and ΔT_b are the temperature gradients in the conducting regions and in the insulating barriers, respectively.

Let us assume that the conducting clusters exhibit a metallic-like behaviour. Their thermopower would follow equation (5). If the conducting grains are the regions where the largest temperature gradient occurs that is to say $\Delta T_b \ll \Delta T_c$, then the observed total thermoelectric power (equation (6)) would be free of the contribution of the insulating barriers and would also exhibit a metallic-like behaviour (equation (7)):

$$S \approx \frac{\Delta T_c}{\Delta T} S_c \approx S_c \approx AT \quad (7)$$

while the conductivity would still be limited by hopping phenomena.

Within this model, the evolution of A with R_i would reflect a microscopic modification within the cluster, which would induce a change of the thermopower via the alteration of

$$\left| \frac{d \ln \sigma(E)}{dE} \right|_{E_f}$$

The slope of the curve $S(T)$ exhibits a minimum for $R_i = 1/100$. This could be attributed to a better intrinsic conduction inside the conducting grains related to this particular value of the initial reticulation ratio.

Transport properties: copolymer networks versus POT. We have observed that the resulting slope A of the curve $S(T)$ was higher for POT ($A = 0.193 \pm 0.005$) than for all copolymer networks. Within the framework of model 4, this result shows that the intrinsic conductivity within the conducting clusters is higher in the copolymers (with a maximum for $R_i = 1/100$) than in POT. We stress that this result could not be deduced from the conductivity study which only allowed us to conclude that some of the gels displayed better conductivity within the conducting islands.

The original of the negative thermopower values at low T for POT is currently not well understood. The negative thermopower values were not observed for the copolymers in the temperature range of measurement. Nevertheless, they could exist at lower temperatures.

CONCLUSION

The transport data we have obtained on well-defined fully conjugated gels of poly(3-*n*-octylthiophene) have been interpreted in terms of an inter-conducting cluster hopping process. Furthermore, the conductivity data are suggestive that the intrinsic conductivity within the conducting clusters can be higher in some networks than in POT. This result has been further confirmed by thermopower study, which has shown that this conclusion is valid for all the gels. The gels of POT exhibit specific transport properties compared with POT.

REFERENCES

- 1 Rebourt, E., Pépin-Donat, B., Dinh, E. and Nechtschein, M. *Synth. Met.* 1995, **69**, 293

- 2 Pépin-Donat, B., Rebourt, E. and Dinh, E. *Synth. Met.*, 1995, **69**, 291
- 3 Rebourt, E., Pépin-Donat, B. and Dinh, E. *Polymer* 1995, **36** (2), 399
- 4 Ishiguro, T., Kaneko, H., Nogami, Y., Ishimoto, H., Nishiyama, H., Tsukamoto, J., Takahashi, A., Yamaura, M., Hagiwara, T. and Sato, K. *Phys Rev. Lett.* 1992, **69**, 660
- 5 Ishiguro, T., Kaneko, H., Pouget, J. P. and Tsukamoto, J. *Synth. Met.* 1995, **69**, 37
- 6 Reghu, M., Yoon, C. O., Moses, D., Heeger, A. J. and Cao, Y. *Phys. Rev. B* 1993, **48**, 17685
- 7 Yoon, C. O., Reghu, M., Moses, D. and Heeger, A. J. *Phys. Rev. B* 1994, **49**, 10851
- 8 Wang, Z. H., Ray, A., MacDiarmid, A. G. and Epstein, A. *Phys. Rev. B* 1991, **43** (5), 4373
- 9 Nakhmedov, E. P., Prigodin, V. N. and Samukhin, A. N. *Sov. Phys. Solid State* 1989, **31**, 368
- 10 Zuppiroli, L., Bussac, M. N., Paschen, S., Chauvet, O. and Forro, L. *Phys. Rev.* 1994, **50** (8), 5196
- 11 Sheng, P., Abeles, B. and Arie, Y. *Phys. Rev. Lett.* 1973, **31**, 44
- 12 Efros, A. L. and Shklovskii, B. I. *J. Phys. C: Solid State Phys.* 1975, **8**, L49
- 13 Deutscher, G., Levy, Y. and Souillard, B. *Europhys. Lett.* 1987, **4** (5), 577
- 14 Baughman, R. H. and Shacklette, L. W. *Phys. Rev. B* 1989, **39**, 5872
- 15 Ambegaokar, V., Halperin, B. I. and Langer, J. S. *Phys. Rev. B* 1971, **4** (8), 2612
- 16 Harris, A. B. and Aharony, A. *Europhys. Lett.* 1987, **4**, 1355
- 17 van der Putten, D., Moonen, J. T., Brom, H. B., Brokken-Zijp, J. C. M. and Michels, M. A. *J. Phys. Rev. Lett.* 1992, **69**, 494
- 18 Shklovskii, B. I. and Efros, A. L. 'Electronic Properties of Doped Semiconductors', Springer, Heidelberg, 1984
- 19 MacCullough, R. D., Tristram-Nagle, S., Williams, S. P., Lowe, R. D. and Jayaraman, M. *J. Am. Chem. Soc.* 1993, **115**, 4910
- 20 Devreux, F. and Lecavellier, H. *Phys. Rev. Lett.* 1987, **59**, 2586
- 21 De Gennes, P. G. *C. R. Acad. Sc. Paris Série 2* 1986, 302, **1**, 1
- 22 Weider, H. H. 'Laboratory Notes on Electrical and Galvanometric Measurements, Materials Science Monographs', Vol. 2, Elsevier, New York, 1979
- 23 Chaikin, P. M. and Kwak, J. F. *Rev. Sci. Instrum.* 1975, **46**, 218
- 24 Yoon, C. O., Reghu, M., Moses, D., Heeger, A. J. and Cao, Y. *Synth. Met.* 1994, **63**, 47
- 25 Emin, D. in 'Handbook of Conducting Polymers' (Ed. T. A. Skotheim), Marcel Dekker Inc., New York, 1986
- 26 Zuo, F., Angelopoulos, M., MacDiarmid, A. G. and Epstein, A. J. *Phys. Rev. B* 1987, **37**, 3475
- 27 Aharony, A., Zhang, Y. and Sarachik, M. P. *Phys. Rev. Lett.* 1992, **26**, 38000
- 28 Deutscher, G., Levy, Y. and Souillard, B. *Europhys. Lett.* 1987, **4**, 577
- 29 Emin, D. *Phys. Rev. Lett.* 1974, **32**, 303
- 30 Miller, A. and Abrahams, B. *Phys. Rev.* 1960, **120**, 745
- 31 Kaiser, A. B. *Phys. Rev. B* 1989, **40**, 2806
- 32 Nogami, Y., Kaneko, H. and Ishiguro, T. *Solid State Commun.* 1993, **76**, 583
- 33 Park, Y. W., Han, W. K., Choi, C. H. and Shirakawa, H. *Phys. Rev. B* 1984, **30**, 5847
- 34 Javadi, H. H., Chakraborty, A., Li, C., Theophilou, N., Swanson, D. B., MacDiarmid, A. G. and Epstein, A. J. *Phys. Rev. B* 1991, **43**, 2183
- 35 Mott, N. F. and Davis, E. A. 'Electronic Processes in Non-crystalline Materials', 2nd Edn, Clarendon Press, Oxford, 1979