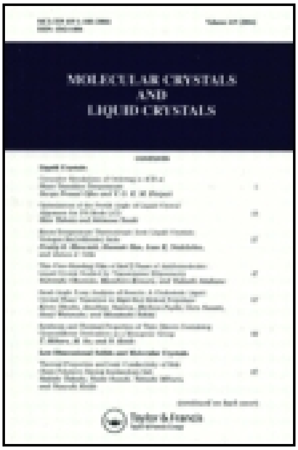

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CONDUCTIVITY MEASUREMENTS ON POLYPYRROLE AND SUBSTITUTED POLY-PYRROLES

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Abstract The temperature dependence of the conductivity has been measured on a large variety of oxydized polypyrroles and substituted polypyrroles (PPy). In all the compounds, the conductivity follows the typical law $\sigma \alpha \exp[-(T_0/T)^{1/4}]$. The experimental results are analyzed in the framework of Mott's model. Although qualitatively good, this model does not provide a satisfactory quantitative description of conductivity in these materials.

INTRODUCTION

Beside the well-known polyacetylene, polypyrrole is one of the most studied conducting polymers. Easy to prepare by electropolymerization[1], rather stable in air[2], oxydized PPy has interesting transport and magnetic properties. A spinless conduction model involving bipolarons has been proposed to account for the experimental results[3]. Some recent in situ ESR measurements during electrochemical doping have provided new arguments in favour of the existence of spinless bipolarons[4]. As concerns the conductivity, the observed temperature dependence is the type $\sigma \alpha \exp(-T^{-1/4})$ generally attributed to a variable range hopping (VRH) process[1-3-5]. But, very little has been studied on the quantitative relevance of VRH models. Here, we present a quantitative analysis of the conductivity temperature dependence of 9 different PPy samples in the framework of Mott's model[6].

EXPERIMENTAL

TABLE I Polypyrrole sample preparation parameters

Sample	Synthesis	Solvent	Monomer	Electrolyte	Sample form
1	E(Electro-chemical)	THF	Pyr	$LiClO_4$	film
2	E	CH_3CN	Pyr	$N(Et)_4BF_4$	film
3	E	CH_3CN	Pyr	$N(Et)_4BF_4+HBF_4$	film
4	E	CH_3CN	Pyr	$NHBu_3^+\phi SO_3^-$	film
5	C(Chemical)	CH_3CN	Pyr	$Fe(ClO_4)_3$	powder pellet
6	Autopoly-merization	Pentane	βBr-Pyr	-	powder pellet
7	E	CH_3CN	βBr-Pyr	$LiClO_4$	film
8	C	CH_3CN	ββ'DiMethyl-Pyr	$Fe(ClO_4)_3$	powder pellet
9	E	DMSO	Pyr + N-$(CH_2)_3$-SO_3^- K^+		film

The main parameters of the 9 sample preparations are listed in table I. All the samples have been prepared in a dry box, washed in soxlet and dried under vacuum. They were mounted on the four probes measurement system inside the dry box, and transferred into the variable temperature cryostat using an air-tight chamber. Contacts between samples and the four gold wires were made by mechanical tightening in order to avoid any contamination. Measurements have been performed between 4 and 300 K.

RESULTS

In figure 1, the conductivity (σ) of the different samples is plotted in a logarithmic scale versus $T^{-1/4}$ where T is the temperature. All the data fit rather well with straight lines in this type of plot, which indicates that σ follows the typical law $\sigma(T) \propto \exp(-T^{-1/4})$. One can make some qualitative remarks. First, the conductivity of non-substituted PPy is practically independent of the nature of both the counter-ion and the solvent, and of the polymerization technique -electrochemical or chemical- (see samples 1.2.3.5). In sample 4 the counter-ion could be involved in the

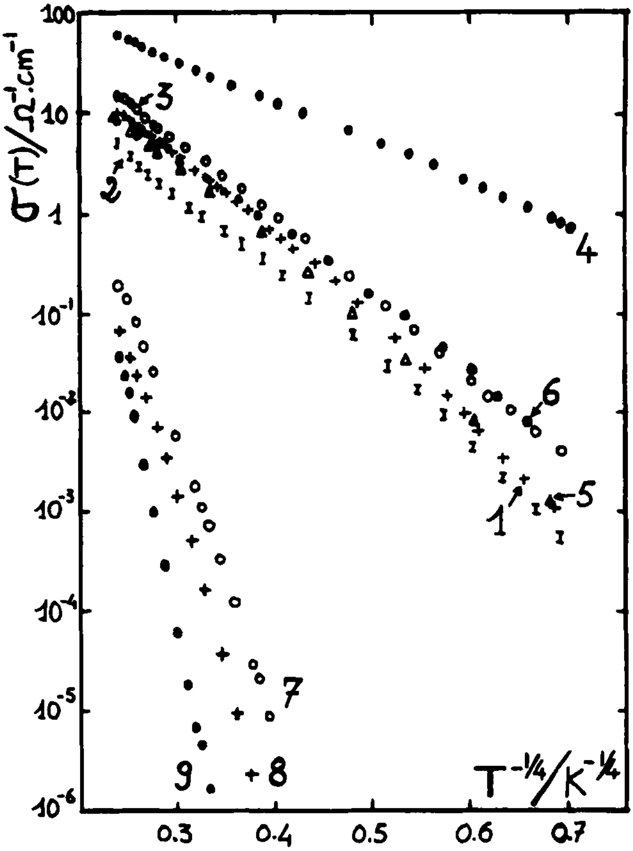

FIGURE 1 - Log conductivity vs $T^{-1/4}$ for different PPy samples

TABLE II - Physical parameters derived from Mott's model in different PPy samples - "st" denotes "states"

Sample	1	2	3	4	5	6	7	8	9
T_0 (10^5 K)	2.9	3.4	2.7	0.38	3.6	2.0	260	550	2000
K_0 (10^4)	4.6	2.5	5.5	2.6	5.3	2.2	10^4	2×10^5	2×10^8
α^{-1} (Å)	3.0	5.0	2.6	15.0	2.3	7.7	1×10^{-4}	6×10^{-6}	3×10^{-9}
$N(E_F)$(st/eV Pyr)	1.6	0.3	2.7	0.10	2.8	0.14	2×10^{11}	10^{15}	10^{24}

polymerization. Second, all the substituted PPy have lower conductivities than the non-substituted ones. Then, the conductivity behaviour of sample 6 -obtained from βBromo-Pyrrole monomer- appears paradoxal compared with previous remarks. This supports the model of the autopolymerization mechanism which leads to a non-substituted PPy with Br^- as the counter-ion[7].

The data have been fitted by least mean squares with Mott's law[6] :

$$\sigma(T) = K_0 . T^{-1/2} \exp\left[-(T_0/T)^{1/4}\right]$$

where T_0 and K_0 are related to α^{-1} -the electronic state localization length- to $N(E_F)$ -the density of states at Fermi level- and to ν_{ph} -a phonon frequency- by the following expressions

$$T_0 = 16 \frac{\alpha^3}{kN(E_F)} \text{ and } K_0 = A \frac{N(E_F)}{\alpha} \nu_{ph}$$

The experimental values of T_0 and K_0 are given in table II. In order to extract the physical parameters α^{-1} and $N(E_F)$ we have made te following assumptions : i) ν_{ph} is independant of the sample, ii) to get an estimate of ν_{ph}, we have supposed that α^{-1} is about the pyrrole monomer dimension (~ 3 Å) in one of the more conducting samples. From sample 1, we have obtained $\nu_{ph} = 6 \times 10^{13}\ s^{-1}$. By means of this value, α^{-1} and $N(E_F)$ have been derived for all the samples. They are presented in table II. Although somewhat dispersed, α^{-1} and $N(E_F)$ take reasonable values for samples 1 to 6. On the other hand, Mott's model leads to completely unrealistic values for both $N(E_F)$ and α^{-1} in samples 7,8 and 9.

CONCLUSION

Mott's model, a conventional model of VRH process, gives the right qualitative behaviour of the conductivity. Nevertheless, it is unsuccessful for providing a good description of the transport properties in polypyrrole.

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