

## Charge carrier properties below and above the metal–insulator transition in conjugated polymers – recent results

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The strong doping dependence of the dc conductivity in conjugated polymers below the metal–insulator transition (MIT), illustrated for PPV, is argued to be due to an increase in the density of states *and* the growth in size of the regions, in which the charge is delocalized. Obviously in the metallic states these regions have to overlap. Phase sensitive dielectric spectroscopy data show that when this overlap is achieved less than 1% of the donated charges (at least in polypyrrole) participates in metallic transport. The data up to the MIT allow a tentative picture of the density of states.

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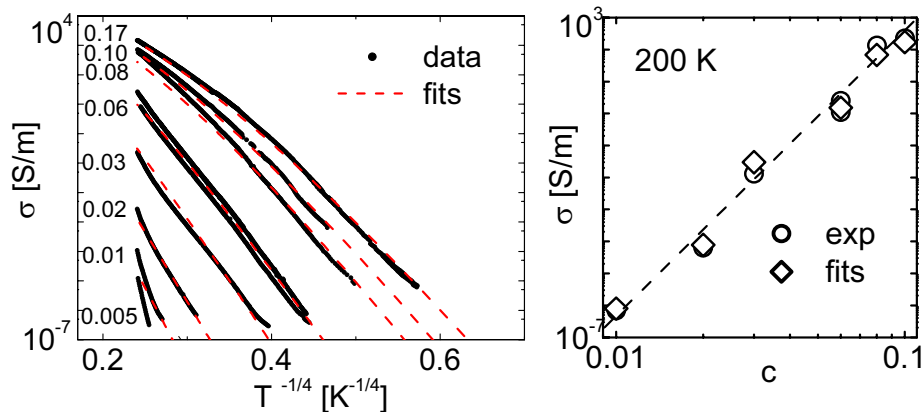
**1 Introduction** Chemical doping of conjugated polymers, like polyacetylene, polypyrrole (PPy) and poly(*p*-phenylene vinylene) (PPV) makes them conducting and even let them pass through a metal–insulator transition (MIT) to become metallic. Often the conduction processes below the metal–insulator transition are described by (variable range) hopping and above the MIT as Drude-like. Here we show that if one has to explain the strong doping-concentration dependence of the dc conductance below the MIT, the variable-range hopping-mechanism between point-like sites has to be modified to allow for the growing size of the localized regions and indicate how such a modification can be justified theoretically [1]. For a characterization of the metallic state close to the MIT we use dielectric data on PPy from  $10^{-4}$  to 4 eV down to 4.2 K [2], to argue that only 1% of the carriers are delocalized. The subtle metallic features and the anomalies in carrier dynamics are modelled by coherent and incoherent transport between short conjugated segments. The data up to the MIT can be reconciled to a Gaussian density of states.

**2 Experimental** (OC<sub>1</sub>C<sub>10</sub>-PPV) has been doped in solution with FeCl<sub>3</sub> [1]. The doping of polypyrrole with PF<sub>6</sub> is done electrochemically [2, 3]. The dc-data are always taken in the ohmic regime. The dielectric scans up to 1 THz (4 meV) were made in transmission with phase sensitive equipment. Between 1 THz and the UV the samples were measured in reflectance [2].

**3 Results and discussion** Figure 1 shows the characteristic temperature (*T*) and concentration (*c*) dependence of the dc conductivity of FeCl<sub>3</sub> doped PPV. The conductivity ( $\sigma$ ) has the familiar exponential dependence on  $T^{-1/4}$  at low temperatures, characteristic for Mott variable range hopping [4] and at fixed *T* an 8 orders of magnitude increase with one order in concentration. To gain insight into the physics behind these features, we made the choice to stay within the framework of variable range hopping, while

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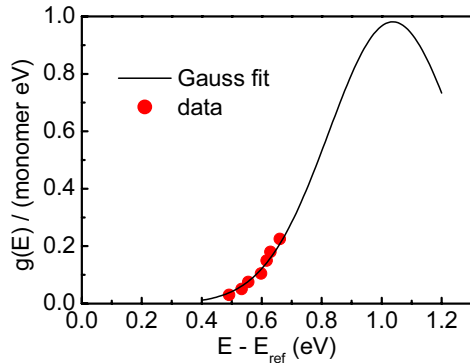
allowing for a finite ( $c$ -dependent) volume  $V_0$  of the transport sites (i.e. delocalized regions), and an energy dependence of the density of states  $g(E)$ . The squared wave function outside  $V_0$  decays within a (localization) length  $1/\alpha$ . For a carrier at the Fermi level  $E_F$  the hopping probability depends exponentially on the hopping distance  $R$  between the delocalized regions and the activation energy ( $E - E_F$ ). The density of final sites  $N$ , which can be reached with activation energy less than  $E - E_F$ , is given by  $N(E, E_F) = \int g(E') dE'$ , where the integration is made from  $E_F$  to  $E$ . Mott's criterion states that the conductivity is governed by those hops for which  $E$  and  $R$  are such that about one state lies within a volume  $V$ , defined by  $VN \approx 1$ , which makes  $R$  a unique function of  $V$  and the radius  $A$  of  $V_0$  (for simplicity  $V_0$  will be assumed to be spherical). The conductivity can now be written as  $\sigma = \sigma_0 \exp[-\alpha R - \beta(E - E_F)]$  with  $\beta = 1/k_B T$  and  $\sigma_0$  a prefactor. By performing some mathematics [1] an explicit expression for the  $c$  dependence of the conductivity can be derived, which at sufficiently low temperatures can be simplified to  $\sigma = \sigma_0 \exp[\alpha A(c)] \exp[-(T_0(c)/T)^{1/4}]$ , Mott's variable-range-hopping formula with the important addition of the factor  $\exp[\alpha A(c)]$ . The density of states can be calculated from the value of  $k_B T_0 \propto 1/g$  [5] or from numerical fits (see Fig. 1) based on the equations obtained with the model. The values for  $g(E)$  agree closely and are shown in Fig. 2. At a given temperature the growth of the delocalized regions (the radius  $A$  increases by a factor 4 in the measured concentration range) and the increase in the density of states appear to be equally important for the increase in conductivity.



**Fig. 1** DC-conductivity ( $\sigma$ ) versus  $T^{-1/4}$  (left) for various  $c$  and  $c$ -dependence of  $\sigma$  at 200 K (right) in  $\text{FeCl}_3$  doped PPV. The concentration levels are expressed per monomer. The fits shown by the dashed lines (left) and diamonds (right) are made with the model discussed in the text. The dashed line in the right figure corresponds to  $\sigma \propto c^8$  [1].

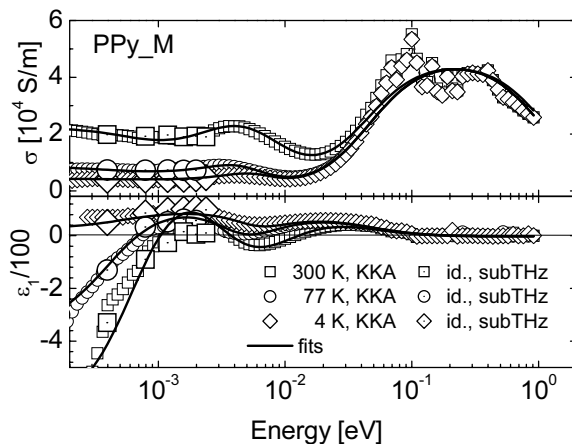
Theoretically [6, 7] and experimentally [8] arguments have been given for the density of states to be Gaussian. Although the data are consistent with such a profile, see Fig. 2, the range is clearly insufficient. At present we are studying PPV in an electrochemically gated transistor [9], where by changing the gate voltage the doping level could be varied by two orders of magnitude, and the density of states is directly obtained as function of energy. Preliminary results [10] confirm the Gaussian fit presented in Fig. 2 (in view of these new results, the previous published values of  $g(E)$  [2] have been adjusted by a factor of 3).

By further increasing the doping level the delocalized regions will begin to overlap and we expect to reach the metal–insulator transition. We leave aside the interesting questions around such a quantum phase transition [11] and concentrate on the number of charges, which are really delocalized in the metallic state. For an answer we investigated the metallic state of polypyrrole by reflectance measurements up to 4 eV. As an extension of previous studies of other groups [12–15] phase sensitive transmission



**Fig. 2** Reconstructed density of states per monomer as function of energy. The Gaussian fit is mainly inspired by new (preliminary) data obtained in an electrochemically-gated transistor [10].

measurements (below 4 meV) complemented these data and appeared to be essential in the Kramers-Kronig analysis. The new data show convincingly that more than 99% of the charges remain localized (responsible for the features above 0.1 eV). The remaining (1% or less) charges contribute to the transport by hopping and tunnelling, see Fig. 3, which leads to the low energy structure and the negative dielectric constant. The optical data are well described by a model that includes both coherent tunnelling and incoherent hopping between delocalized regions. The unusually long values of the scattering time found previously [16] and low density of delocalized charges stem from the small coherent tunnel rate [2].



**Fig. 3** Dielectric data on the most metallic polypyrrole sample (PPy\_M). The subTHz (below 4 meV) phase sensitive measurements, shown here for three temperatures, have been performed down to 4.2 K [2]. The reflection data above 0.01 eV are temperature independent [12] (data shown are taken at room temperature; KKA stands for Kramers-Kronig analysis).

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## References

- [1] H. C. F. Martens, I. N. Hulea, I. Romijn, H. B. Brom, W. F. Pasveer, and M. A. J. Michels, *Phys. Rev. B* **67**, 121203(R) (2003).
- [2] I. G. Romijn, H. J. Hupkes, H. C. F. Martens, H. B. Brom, A. K. Mukherjee, and R. Menon, *Phys. Rev. Lett.* **90**, 176602 (2003).
- [3] C. O. Yoon et al., *Phys. Rev. B* **49**, 10851 (1994).
- [4] N. F. Mott, *Philos. Mag.* **19**, 835 (1969).
- [5] H. Böttger and V. V. Bryksin, *Hopping Conduction in Solids* (Akademie Verlag, Berlin, 1993).
- [6] H. Bässler, *phys. stat. sol. (b)* **175**, 15 (1993).
- [7] S. D. Baranovskii, H. Cordes, F. Hensel, and G. Leising, *Phys. Rev. B* **62**, 7934 (2000).
- [8] H. C. F. Martens, P. W. M. Blom, and H. F. M. Schoo, *Phys. Rev. B* **61**, 7489 (2000).
- [9] E. A. Meulenkaamp, *J. Phys. Chem. B* **103**, 7831 (1999); A. J. Roest, J. J. Kelly, D. Vanmaekelbergh, and E. A. Meulenkaamp, *Phys. Rev. Lett.* **89**, 036801 (2002).
- [10] I. N. Hulea et al., unpublished.
- [11] S. Sachdev, *Quantum Phase Transitions* (Cambridge University Press, Cambridge 1999).
- [12] R. S. Kohlman et al., *Phys. Rev. Lett.* **74**, 773 (1995); **77**, 2766 (1996); **78**, 3915 (1997).
- [13] K. Lee et al., *Phys. Rev. B* **52**, 4779 (1995), *Adv. Mater.* **10**, 456 (1998).
- [14] A. B. Kaiser, *Adv. Mater.* **13**, 927 (2001), *Rep. Prog. Phys.* **64**, 1 (2001).
- [15] V. N. Prigodin and A. J. Epstein, *Synth. Met.* **125**, 43 (2002).
- [16] H. C. F. Martens et al., *Phys. Rev. B* **63**, 073203 (2001); **64** R201102 (2001); **65**, 079901 (2002).