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## DC AND MICROWAVE CONDUCTIVITY OF FeCl<sub>3</sub>-DOPED POLYPARAPHENYLENE (p-C<sub>6</sub>H<sub>4</sub>)<sub>x</sub>

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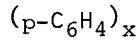
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DC AND MICROWAVE CONDUCTIVITY OF  $\text{FeCl}_3$ -DOPED POLYPARAPHENYLENE

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**Résumé** - Nous présentons des mesures de conductivité continue et microonde et de constante diélectrique sur des échantillons de  $(\text{C}_6\text{H}_4)_x$  dopés avec  $\text{FeCl}_3$ . Nous montrons que pour les systèmes faiblement dopés le modèle de conduction par saut entre soliton de Kivelson, modifié et appliqué aux polarons et bipolarons décrit bien l'expérience. Pour les forts dopages la conduction par saut semble dominer et des valeurs raisonnables des paramètres de Mott sont déduites.

**Abstract** - D.c. and microwave conductivity and dielectric constant measurements on  $\text{FeCl}_3$ -doped  $(\text{C}_6\text{H}_4)_x$  are reported. It is shown that in lightly doped samples Kivelson's intersoliton hopping conduction model as modified and applied to polaron and bipolaron states fits well. In heavily doped samples variable range hopping seems to dominate and reasonable values for Mott's parameters are found.

Many physical properties of doped poly(p-phenylene) (PPP) are very similar to those of polyacetylene (PA) which is the most studied electrically conducting polymer. Especially the very low Pauli susceptibility in well conducting materials as well as the strong doping dependence of the conductivity are common features in both polymers. Many unusual optical, magnetic and electrical properties of PA have been accounted for by the presence of soliton defects. For instance the T-, pressure and frequency dependence of the conductivity in lightly doped trans-PA have been nicely explained by Kivelson's intersoliton hopping model /1,2/. PPP does not possess a degenerate ground state and is therefore not expected to accommodate single solitons. Bredas et al. /3/ have shown, however, that soliton-antisoliton pairs could be stable in doped PPP and this could be one of the reasons for the similarity between the properties of PA and PPP.

The electrical transport properties of heavily doped PPP have previously been studied by several investigators /4/. In this paper we present the results of dc and microwave conductivity ( $\sigma_{dc}$ ,  $\sigma_{mw}$ ) measurements in lightly and heavily  $\text{FeCl}_3$ -doped PPP and test the applicability of various models for the electrical transport.

#### I - EXPERIMENTAL PROCEDURE AND RESULTS

Powder of PPP was polymerized from benzene using the method of Kovacic et al. /5/. The powder was doped with  $\text{FeCl}_3$  as described by Prón et al. /6/ and then pressed into pellets.  $\sigma_{dc}$  measurements were made using the ordinary four point method except for at sample resistances  $>10 \Omega$  where a two point method was utilized. The evaporated gold contacts were ohmic in the temperature range studied.  $\sigma_{mw}$  and the dielectric permeability  $\epsilon_r$  were measured at 24 GHz (K-band) using the cavity perturbation technique /7/.

The doping levels,  $\sigma_{dc}$  and its activation energy  $\Delta$  at 300K, concentration  $N_s$  of Curie law spins and  $\epsilon_r$  at 24 GHz are listed in Table I for the studied samples.

TABLE I. Samples studied in the conductivity measurements

| Sample | Doping (mol %) | $\sigma_{dc}$ (300K) ( $\Omega^{-1} \text{cm}^{-1}$ ) | $\Delta$ (300K) (eV) | $N_s$ ( $\text{g}^{-1}$ ) | $\epsilon_r$ |
|--------|----------------|---|----------------------|---------------------------|--------------|
| 1      | 0              | $< 10^{-10}$  | -                    | $1.6 \times 10^{17}$      | 2.9          |
| 2      | 0.12           | $2 \times 10^{-7}$                                    | 0.36                 | $1 \times 10^{18}$        | 4.4          |
| 3      | 1              | $5 \times 10^{-4}$                                    | 0.28                 | $2 \times 10^{16}$        | 4.8          |
| 4      | 26             | 1   | 0.068                | $< 10^{15}$               | -            |
| 5      | 22             | 7   | 0.052                | $< 10^{15}$               | -            |

The T-dependence of  $\sigma_{dc}$  is shown in Fig.1. A linear behaviour on the scale  $\lg(\sqrt{T}\sigma_{dc})$  vs.  $(1/T)^{1/4}$  is found, especially in the highest conductivity samples. The strong frequency dependence of  $\sigma$  is shown in Fig. 2 for the lightly doped samples 2 and 3. In highly conducting samples the cavity perturbation method could not be used due to the small skin depth.

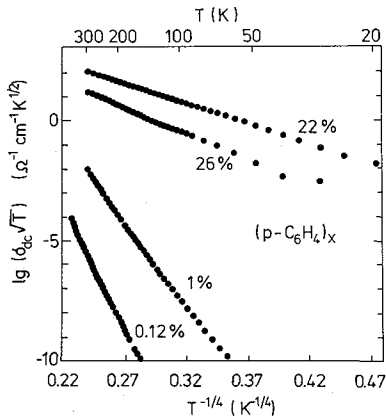


Fig.1  $\lg(\sigma_{dc}\sqrt{T})$  vs.  $(1/T)^{1/4}$  in samples 2,3,4 and 5.

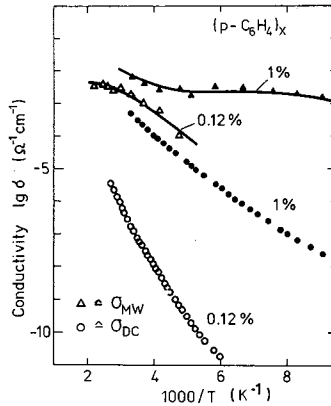


Fig. 2 - Dc( $\circ$ ) and mw ( $\Delta$ ) -conductivities vs.  $1/T$  in samples 2 and 3.

II - DISCUSSION

II.1 Heavily doped PPP

As shown in Fig. 1 the law  $\sigma_{dc}(T) = \sigma_0 \exp[-(T/T_0)^{1/4}]$  for the variable range hopping (VRH) is well obeyed in heavily doped samples. Mott's parameter  $T_0 = 2.2 \times 10^5$  ( $3.9 \times 10^5$ ) K and  $\sigma_0 \sqrt{T} = 1.6 \times 10^5$  ( $4.4 \times 10^5$ )  $\sqrt{\text{K}} \Omega^{-1} \text{cm}^{-1}$  can be estimated for sample 5 (4). Further one gets the density of localized states  $N(E_f)$  at the Fermi level  $E_f$  and the wavefunction decay  $\alpha^{-1}/8$ .

$$N(E_f) = (1.996 \times 10^{48} / v_0^3) [(\sigma_0 \sqrt{T})^3 \sqrt{T_0}] \text{cm}^{-3} \text{eV}^{-1} \tag{1}$$

$$\alpha = (2.122 \times 10^{16} / v_0) (\sigma_0 \sqrt{T} \sqrt{T_0}) \text{m}^{-1} \tag{2}$$

These equations give reasonable values  $N(E_f) = 10^{21-22} \text{cm}^{-3} \text{eV}^{-1}$  and  $\alpha^{-1} = 3-5 \text{ \AA}$  in samples 4 and 5 using a jump rate prefactor  $v_0 = 10^{16} \text{ s}^{-1}$  typical of disordered semiconductors /9/. The origin of the localized states where the hopping conduction occurs

remains open. VRH in a bipolaron band or between metallic islands due to inhomogeneous doping are both possible. However, from optical reflectivity measurements we have got some evidence for highly conducting regions separated by thin potential barriers in our heavily doped samples. The optical conductivity is more than two orders of magnitude larger than  $\sigma_{dc}$  (300K). Further evidence for the barriers in sample 6 is obtained at low temperatures from Fig. 3. Sheng's tunneling model /10/ with barrier modulation by thermal fluctuations,  $\sigma_{dc} = \sigma_0 \exp[-T_1 / (T+T_0)]$ , is fitted with parameters  $T_0 = 24.2$  K and  $T_1 = 330$  K.

II.2 Lightly doped PPP

When the values  $T_0$  and  $\sigma_0 \sqrt{T}$  obtained from Fig. 1 are inserted into eqs. (1) and (2) one gets for the lightly doped samples 2 and 3 quite unreasonable values for  $N(E_f)$  and/or  $\alpha^{-1}$  for any value of  $v$ . Hence we have applied Kivelson's intersoliton hopping model /1/ slightly modified to polaron and bipolaron states in doped PPP. Further indications for these states we have obtained from IR-measurements i.e. a possible quinoid mode at  $1280 \text{ cm}^{-1}$  was found in  $\text{FeCl}_3$ -doped samples but not in undoped ones. In Fig. 4  $\lg \sigma$  vs.  $\lg T$  is plotted and the law  $\sigma \sim T^n$  predicted by Kivelson's model/1/

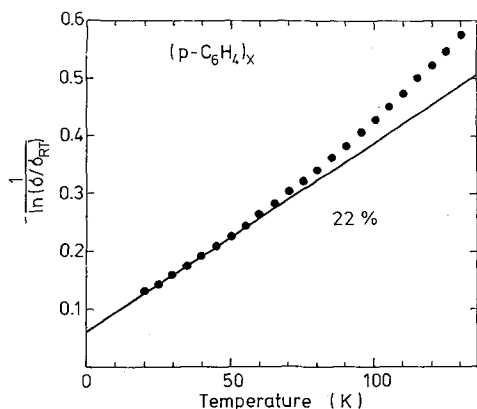


Fig. 3 - Low temperature conductivity  $-\ln(\sigma/\sigma_{RT})^{-1}$  vs. T in sample 5.

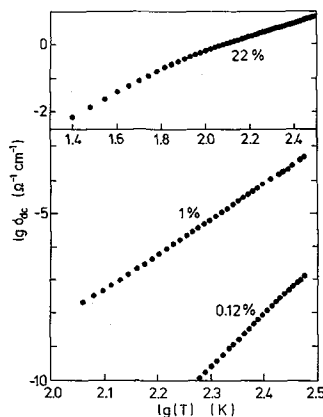


Fig. 4 - dc conductivity  $\lg \sigma$  vs.  $\lg T$  in samples 2,3 and 5.

is well obeyed in the lightly doped samples 2 and 3 with  $n=13.8$  and  $11$  respectively. The modified expressions for  $\sigma_{ac}$  and  $\sigma_{dc}$ , read (having dropped out the factor  $1/N$ , which in PA gives the probability for a neutral soliton being close to a charged impurity, since in PPP both polarons and bipolarons are charged and thus bound to dopant molecules):

$$\sigma_{dc}(T) = \frac{Ae^2 \gamma(T)}{k_B T} \left[ \frac{\xi}{R_0^2} \right] \frac{y_p y_{bp}}{(y_p + y_{bp})^2} e^{-2BR_0/\xi} \tag{3}$$

$$\sigma_{ac}(\omega, T) = \sigma_{dc}(T) + \frac{e^2}{h384} \frac{c_{imp}^2}{k_B T} \frac{y_p y_{bp}}{(y_p + y_{bp})^2} \xi_{||}^3 \xi_{\perp}^2 h\omega \left[ \ln \left( \frac{2\omega}{\Gamma_0} \right) \right]^4 \tag{4}$$

Here  $A=0.45$ ,  $B=1.39$ ,  $y_p$  and  $y_{bp}$  are the concentrations of polarons and bipolarons, respectively,  $R_0 = (39/4 \pi c_{imp})^{1/3}$  is the typical separation between impurities whose concentration is  $c_{imp}$ ,  $\xi = (\xi_{||} \xi_{\perp})$  is the average decay length of a polaron (or bipolaron),  $\xi_{||}$  and  $\xi_{\perp}$  being the decay lengths parallel and perpendicular to the polymer chain direction, respectively, and  $\Gamma_0 = y_p y_{bp} / (y_p + y_{bp})^2 \gamma(T)$ , where  $\gamma(T) = \gamma_0 (T/300 \text{ K})^{n+1}$  is the transition rate of a charge carrier between polaron and bipolaron states.

Eqs. (3) and (4) are fitted to the measured  $\sigma_{dc}$  and  $\sigma_{mw}$  of sample 2 in Fig. 5. The pre-factor  $\gamma_0 = 7.6 \times 10^{17} \text{ s}^{-1}$  was determined from the  $T$ -dependence of  $\sigma_{mw}(T)$  and the order of magnitude of  $\sigma_{dc}$  and  $\sigma_{mw}$  were fitted with  $c_{imp}$ . The other parameters were  $\xi_{11} = 17 \text{ \AA}$  (4 phenyl rings /3/,  $\xi_{\perp} = b/2$  where  $b = 5.2 \text{ \AA}$  is the interchain distance in PPP,  $y_b =$  spin density (Table I) and  $y_{bp} = c_{imp}$ . The values of  $c_{imp}$  found in the fitting were  $c_{imp}^{dc} = 0.26 \times 10^{-3}$  and  $c_{imp}^{mw} = 1.2 \times 10^{-3}$ . As an interesting feature, the model accounts well for the rather strong  $T$ -dependence of  $\sigma_{mw}$ . The ratio  $\sigma_{mw}/\sigma_{dc}$  is shown in Fig. 6. The decrease in  $\sigma_{mw}/\sigma_{dc}$  with increasing doping excludes the metallic island model in lightly doped PPP since the model predicts the opposite behaviour /11/.

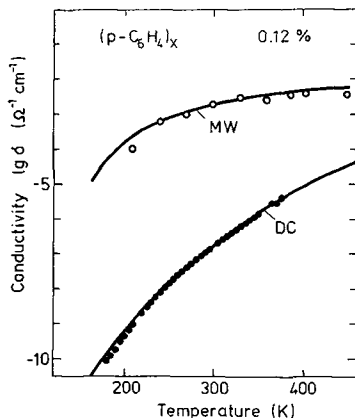


Fig. 5 - Dc and mw conductivities vs.  $T$  in sample 2.

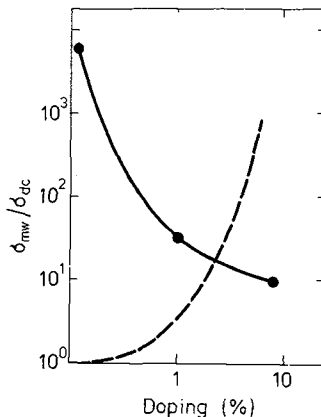


Fig. 6 - Ratio  $\sigma_{mw}/\sigma_{dc}$  vs. doping concentration. The dashed line shows the ratio as predicted by the metallic island model /10/.

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